Research Article

# Evaluation and Interpretation of Legacy Major-Ion Chemistry for the Niobrara River Watershed, Northwestern and Northcentral Nebraska, USA

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### Abstract
*The Niobrara River watershed (NRW) is home to a National Scenic River reach (122-km (76-mi) and to the unique and ancient Sand Hills, a National Natural Landmark. Examination of historical (1968–1991) aqueous geochemistry data [major cations and anions, pH, specific conductance, and total dissolved solids (TDS)] for 500 water samples contained in the Water Quality Portal maintained online by the US Environmental Protection Agency for the Niobrara River, and six tributary creeks, a reservoir, and two tributary rivers, located in northwestern and northcentral Nebraska, revealed that the mineralization (TDS) is relatively low. Calculated median TDS for the Niobrara River is 192 mg/L (n = 322); calculated median TDS for the tributary rivers and creeks is 129 mg/L (n = 181). Only a few sample analyses are not the Ca-HCO$_3$ hydrochemical facies. The mineralization level of Niobrara River water is essentially constant from upstream to downstream. This contrasts with several Nebraska rivers, e.g., the Elkhorn River immediately south of the NRW, where TDS increases significantly downstream. Hydrochemical equilibrium modeling of the NRW reveals that most samples occurred in an aqueous environment characterized by slight calcite and dolomite supersaturation and gypsum undersaturation; low supersaturation index values comprise a line of evidence for the thermodynamic equilibrium or near equilibrium of the NRW waters. Statistical analysis (one-way ANOVA) and graphical methods (e.g., Piper diagrams, scatter plots of chemicals) are used to characterize and interpret the hydrogeochemistry of the NRW. This statistical analysis reveals the impact of silicate minerals (e.g., feldspar) weathering on the aqueous geochemistry throughout the watershed. These ubiquitous feldspar minerals most likely originated along the eastern slope of the Front Range during the Laramide Orogeny of Late Cretaceous and Tertiary time.*

**Keywords:** Hydrogeochemistry, Surface-Water Quality, National Scenic River, Sand Hills, Nebraska

## 1. Introduction

From the late 1960s through approximately 1991, the Nebraska Dept. of Environment and Energy (NDEE) and its predecessors [Neb. Dept. of Environmental Quality (NDEQ) and Neb. Dept. of Environmental Control (NDEC)] sampled numerous rivers and streams throughout the state, typically monthly, and analyzed the grab samples for all major ions, TDS, pH, specific conductance (SC), and temperature. Major-ion analyses allow aqueous hydrogeochemical evaluation, encompassing hydrochemical facies determination and identification of probable parent material source(s) [1]. These legacy data were placed in the STOrage and RETrieval (STORET) warehouse maintained on the internet by the US Environmental Protection Agency [2]. This legacy warehouse was replaced in 2018 by the Water Quality Portal (WQP) which is maintained jointly by the USEPA and the US Geological Survey.

This study evaluates historical major-ion data collected by the NDEE for the NRW located in northwestern and northcentral Nebraska. Major-ion data for the NRW encompassing tributary rivers and creeks, collected during the period 1968–1991, 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 objective of this study was to comprehensively evaluate and interpret hydrogeochemically the extensive legacy surface-water STORET data in the WQP and to integrate pertinent aqueous chemistry, the geological framework, and hydrological information for the NRW in Nebraska. These comprehensive, integrated, major-ion data provide a hydrogeochemical baseline for this expansive Nebraska watershed.

## 1.1. Study area Description

The NRW occurs in the northwestern and northcentral parts of Nebraska (Fig. 1), includes parts of Sioux, Dawes, Box Butte, Sheridan, Cherry, Brown, Keya Paha, Rock, Holt, Boyd, and Knox counties, and covers approximately 4,130 km² (1,595 mi²). Almost all the NRW is located within the High Plains Section of the Great Plains physiographic province of the Interior Plains Division and borders Wyoming to the west and South Dakota to the north. The Niobrara River watershed encompasses seven surface-water subbasins collectively designated as hydrologic unit codes (HUCs) 10150001–10150007 [3, 4].
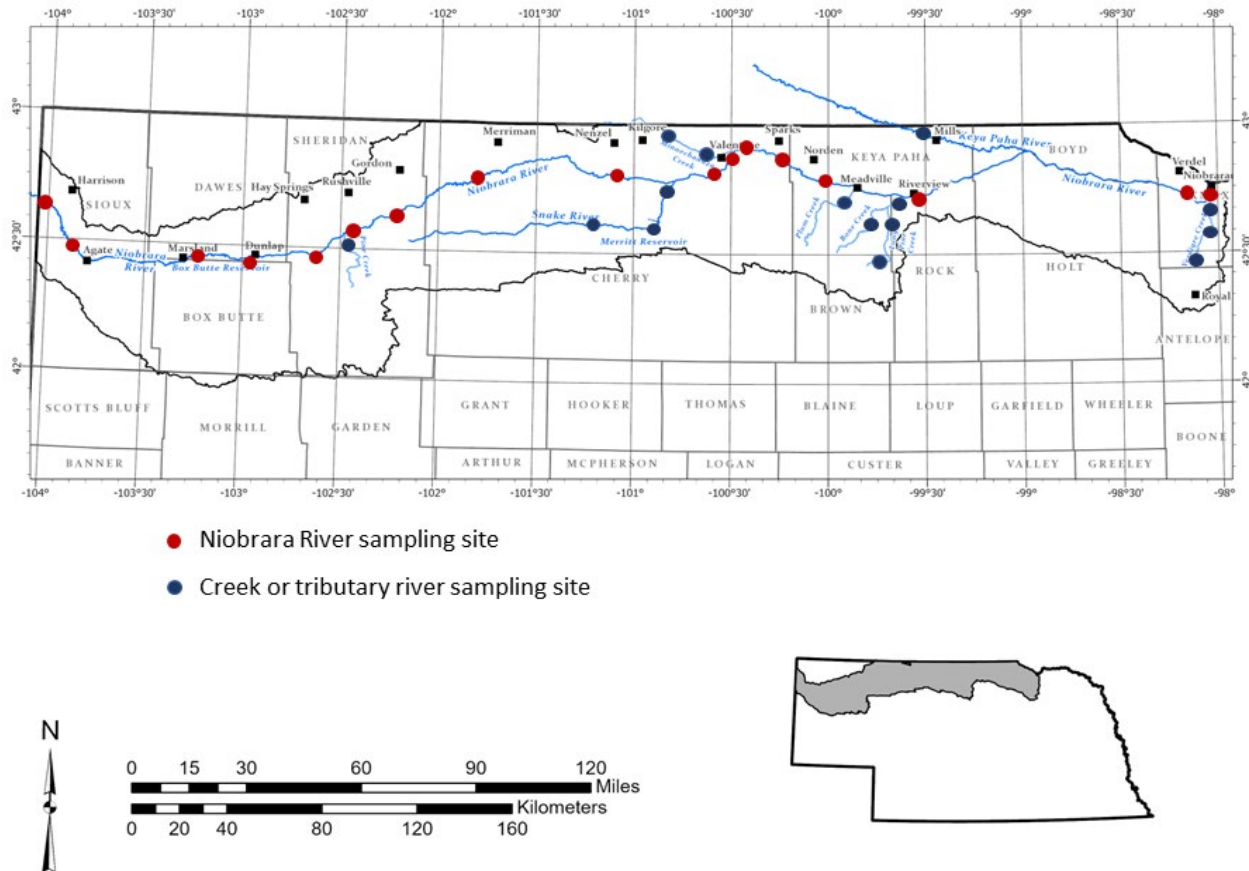


**Figure 1:** Niobrara River Watershed Showing the Niobrara River and Tributary Creek and River Sampling Sites.

## 1.2. Climate

The study area is subject to an extreme, continental climate characterized by year-to-year variability for both temperature and precipitation [5]. Annually, in the Valentine area (Cherry County) and beyond, the temperature typically varies from about −11°C–32°C (12°F–89°F) and is rarely below −22°C (−7°F) or above 38°C (100°F). The average annual precipitation is 51 cm (20.0 in.). The highest monthly average rainfall in the Valentine, Nebraska, area is about 8.9 cm (3.5 in.) in June, and the lowest mean monthly precipitation is 0.66 cm (0.26 in.) occurring in January. The growing season in the Valentine area and beyond typically lasts about five months from about May 1 through September [6]. The mean annual precipitation across the NRW varies from about 41 cm (16 in.) (western boundary) to about 61 cm (24 in.) (eastern boundary) [7].

Reported the pan evaporation at a western Nebraska location relatively near the study area, Mitchell, Nebraska (41°57' N, −103°41' W), about 80 km (50 mi) south-southwest of Box Butte Dam), as seasonally variable, with monthly averages ranging from 12.7–23 cm (5.0–9.08 in.), and an average total of 107 cm (42 in.) for the period May–October [8]. Reported an annual lake evaporation rate of approximately 119 cm (47 in.) for the relatively nearby Platte River basin in southcentral Nebraska [9]. Consequently, surface-water evaporation in the study area is significant.

## 1.3. Geology and Hydrogeology

The regional and uppermost geological units found in northwestern and northcentral Nebraska, in descending order, encompass: the Ogallala Group (or Formation), Arikaree Group, and the White River Group (Brule, Chadron, and Chamberlain Pass Formations) of Tertiary age and the Pierre Shale and the Niobrara Formation of Late Cretaceous age (Fig. 2).
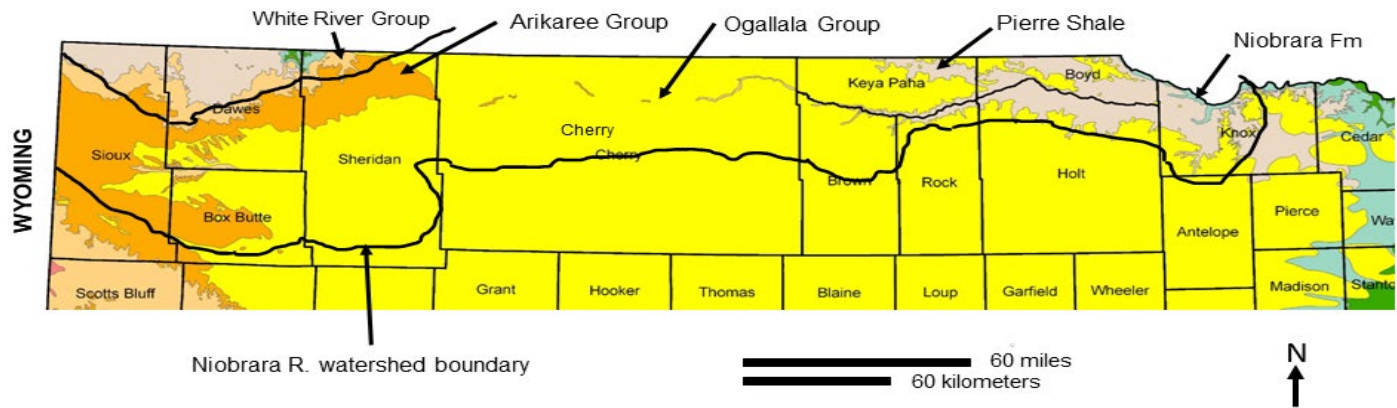
**Figure 2:** Uppermost Geologic units in the Niobrara River Watershed

The following is a brief discussion of the NRW stratigraphic units in ascending order.

The Niobrara Formation is the uppermost bedrock in a few small areas beneath the streambed of the Niobrara River near its confluence with the Missouri River (Fig. 2). It consists primarily of argillaceous chalk, limestone, and shale aggregating a thickness of about 30 m (100 ft) [10]. Thin layers of gypsum (calcium sulfate) commonly occur at the top of the unit [11].

The Pierre, a major Late Cretaceous bedrock unit in Nebraska, is the uppermost bedrock in the Niobrara River valley in Keya Paha, Boyd, Holt, and Knox Counties (Fig. 2). The Pierre Shale consists mostly of fissile clay shale. Locally, it contains thin seams of gypsum and sparse selenite crystals. This marine shale serves as a regional hydrologic confining unit within the study area [12, 13].

The White River Group consists of clay, some claystone, silt, and siltstone deposited in fluvial, eolian, and lacustrine environments. It is predominantly greenish gray and volcaniclastic but includes greenish gray to white and bentonitic variations [14]. This Tertiary age stratigraphic group represents the oldest deposition following the retreat of the Western Interior Seaway [15]. The White River Group is divided into the Chamberlain Pass Formation (CPF), the Chadron, and the Brule (youngest) [16, 17].

The CPF is the oldest Tertiary formation of record in the western portion of the NRW. It lies with marked unconformity on top of the Pierre Shale. The CPF is composed of fluvial subarkosic sandstones and conglomerates interbedded with light green bentonitic mudstones.

The upper part of the Eocene-age Chadron is claystone and mudstone that some places contain bentonitic shales that serve as a confining unit to separate the unconfined zones of the High Plains aquifer from the underlying confined aquifers. The total thickness of the Chadron can be more than 91 m (300 ft) in some paleovalleys.

The Brule Formation lies conformably on top of the Chadron Formation. It is made up almost entirely of buff to medium brown siltstones, with minor sand channels and mudstone. Thickness of the Brule in places in northwestern Nebraska exceeds 183 m (600 ft) [18].

Quaternary age terrace deposits (primarily occurring in Sioux, Dawes, and Keya Paha Counties) encompass clay to boulder-size clasts deposited as pediments, paleochannels, and terrace fills of former flood plains. Total thickness is up to 23 m (75 ft). Quaternary alluvial and colluvial materials are present in the study area ranging in depth from 0.2 to ~12 m (0.5–~40 ft). Alluvium consisting of unconsolidated silt, sand, and gravel of Quaternary age mantles the older rocks in many places throughout the study area, and, in measurable thickness, underlies the Niobrara River and major tributaries (e.g., Snake River, Long Pine Creek) [19].

The Laramide Orogeny (Late Cretaceous to Tertiary time) formed the Rocky Mountains of Colorado and surrounding mountainous areas [20]. Thousands of years of erosion resulted in fluvial transport of rock and mineral fragments and sediment down the east slope of the Front Range and into the Great Plains of northwestern Nebraska and continuing transport eastward.

### 1.4. Topography and Geography

The topography and physical geography of the NRW falls into five major regions: dissected plains, plains, valleys, bluffs-escarpments, and Sand Hills. In Sioux, Dawes, and Box Butte Counties, valleys, dissected plains, and plains are primary; in Sheridan County, Sand Hills, plains, and bluffs-escarpments predominate; in Cherry County, Sand Hills, bluffs-escarpments, and plains primarily occur; in Keya Paha, Brown, and Rock Counties, valleys, plains, bluffs-escarpments are predominant; in Boyd, Holt, and Knox Counties, valleys, bluff-escarpments, and dissected plains primarily occur [21]. By far, the Sand Hills is the most widespread topographic region in the NRW.

The unique and ancient Sand Hills region of Nebraska (a National Natural Landmark), formed during the Pleistocene Epoch (1.8M to about 10K years ago), encompasses the study area (55,000 km²) mostly south of the Niobrara River in Sheridan, Cherry, Brown, and Rock Counties [22]. These ancient sand dunes now are mostly stabilized by grassland vegetation. Unique grasses and plants largely comprise this vegetation [23].

### 1.5. Soils

The soils in Dawes County and much of the NRW formed under grass in a wide variety of materials. The parent materials are shale, siltstone, sandstone, loess, eolian sand, gravel, colluvium, and alluvium. The carbonate content is high in most of the soils because the parent materials commonly contain lime, and the semiarid climate has resulted in a minimum of leaching [24]. The Keith-Rosebud, and Anselmo associations cover large areas in Dawes and Sheridan Counties. Keith-Rosebud upland soils are typically silt loam with moderate permeability to water and air. The Anselmo association commonly is composed of sandy loam with moderately rapid permeability. Throughout the Sand Hills, most of the soils belong to the Valentine-Dunday association, possessing sand and loamy sand texture with rapid permeability. Thurman-Jansen association soils occur widely in Brown, Rock, and Holt Counties. These upland and terrace soils are characterized as loamy sand and sandy loam (Thurman) and loam and clay loam (Jansen) with rapid and moderate permeabilities, respectively [25].

### 1.6. Surface-Water Hydrology

The Niobrara River heads in Niobrara County, Wyoming, about 8 km (5 mi) west of Lusk, Wyoming, and flows generally eastward into Nebraska and across Sioux, Dawes/Box Butte, Sheridan, Cherry, Brown/Keya Paha, Rock, and Holt/Boyd Counties and discharges into the Missouri River in northwestern Knox County. Stream flow is a component of precipitation runoff, groundwater discharge, and groundwater and surface-water usage.

The Niobrara River enters Nebraska at about 1430 m (4690 ft) above mean sea level (amsl) and enters the Missouri River at approximately 369 m (1210 ft) amsl [26]. Topographic gradient varies from: (1) 1.2 m/km (6.4 ft/mi) in the approximate 68 km (42 mi) reach (550–618 km) (342–384 mi)] immediately upgradient of the Box Butte Dam, (southeastern Dawes County), and (2) 2.2 m/km (11.3 ft/mi) along the reach extending from about 373–407 km (232–253 mi) or about a 34 km (21 mi) reach downstream from the mouth of Antelope Creek (western Cherry County).

Based on the criteria of area drained and annual discharge, the Niobrara River and its tributaries rank second to the Platte River basin for rivers systems in Nebraska. Average historical discharge for the Niobrara River at Sparks was 20.5 m³/s (723 ft³/s) for 1964–1989; at Spencer 41 m³/s (1448 ft³/s) for 1964–1989; and at Verdel it was 44.9 m³/s (1584 ft³/s) for 1941–1989. This average discharge near the mouth of the river is approximately $1.414 \times 10^9$ m³/year ($1.15 \times 10^6$ acre-ft/year). Overland runoff downstream becomes an increasing proportion of the average river discharge.

The USGS has measured Niobrara River flow at nine stations in Nebraska for many years (Table 1). Mean discharge ranges from 0.12 m³/s (4.4 ft³/s) at the Wyoming–Nebraska state line to 72.2 m³/s (2550 ft³/s) near Butte [27].

| Stream gage site number | Gage location | Legal description | Mean discharge (cfs)[a] | Mean discharge (cms)[b] |
|---|---|---|---|---|
| 06454000 | at WY–NE line | 42.6252° N −104.05160° W | 4.41 | 0.12 |
| 06454050 | at 33 Ranch | 42.57550° N −103.93530° W | 6.94 | 0.20 |
| 06454100 | at Agate | 42.42353° N −103.79250° W | 14.0 | 0.40 |
| 06454500 | above Box Butte Reservoir | 42.45971° N −103.17110° W | 25.2 | 0.71 |
| 06455500 | below Box Butte Reservoir | 42.45654° N −103.06930° W | 25.6 | 0.72 |
| 06456500 | nr[c] Hay Springs | 42.48250° N −102. 69410° W | 26.6 | 0.75 |
| 06457500 | nr Gordon | 42.63992° N −102.21070° W | 125 | 3.5 |
| 06459025 | nr Nenzel | 42.80469° N −101.12290° W | 457 | 12.9 |
| 06464930 | nr Butte | 42.84350° N −98.85054° W | 2550 | 72.2 |

[a] cfs = cubic feet/second.

[b] cms = cubic meter/second.

[c] nr = near.

**Table 1: Niobrara River Mean Discharge for Nine Monitoring Stations**

### 1.7. Multipurpose Dams and Reservoirs

Box Butte Dam (Fig. 1) is in the arid northwestern panhandle area of Box Butte County (42.4583°N −103.0847°W). The earthen dam, containing 1,087,197 m$^3$ (1,422,000 yd$^3$) of earthen material, was constructed from 1941–1946 by the US Bureau of Reclamation. [It impounds the Niobrara River for flood control, part of the Bureau's Mirage Flats Project for irrigation water storage. It has a structural height of 26 m (87 ft) and a crest length of 1679 m (5,508 ft). The impoundment it creates, Box Butte Reservoir, has a total capacity of 3.83 × 10$^7$ m$^3$ (31,060 acre-ft), with an active capacity of 3.55 × 10$^7$ m$^3$ (28,785 acre-ft), a surface area of 648 ha (1,600 acres), and a drainage area of 3781 km$^2$ (1460 mi$^2$) [28].

Box Butte Dam and Reservoir lie entirely within a sandy siltstone of the Arikaree Group of Tertiary age. At the site of the dam, the Niobrara River has incised a broad channel approximately 427 m (1,400 ft) wide along the bottom of the valley [29].

Merritt Dam and Reservoir (Fig. 1) in Cherry County approximately 42 km (26 mi) southwest of Valentine (42.63282° N −100.86936° W). The 38-m (126-ft) earthen dam impounds the Snake River where the valley narrows and becomes entrenched. The dam was built in 1961–1964 by the US Bureau of Reclamation for irrigation purposes. The crest length is 982 m (3222 ft), and the total capacity is almost 9.3 × 10$^7$ m$^3$ (75,000 acre-ft), with 1,176 ha (2,905 acres) of surface water.

The dam is built mostly within and on the Ogallala Group beds of the upper Tertiary. The nearby sand dunes and limited sediments in the small floodplain are of Recent or Pleistocene age.

### 1.8. Niobrara National Scenic River

A 122-km (76-mi) course of the Niobrara River in northcentral Nebraska, that extends from ~3 km (~2 mi) southeast of Valentine (northeastern Cherry County) northeast and eastward to about 42.783°N −99.336°W, in northeastern Rock County [~19 km (~12 mi) east of Riverview], has been designated as the Niobrara National Scenic River (NNSR) since 1991. It is managed by the Department of the Interior (US Fish and Wildlife Service and National Park Service) to protect the: water quality, geologic, paleontological (fossils), fish and wildlife, scenic, and recreation values [30].

Most of the lands within the boundary of the NNSR are in private ownership and will remain so into the indefinite future. Management is based upon working with private, county, state, and federal landowners, and stakeholders to coordinate protection of the river while ensuring a high-quality experience for river visitors. The US Fish and Wildlife Service manages the ~14 km (~9 mi) of river that flow through the Fort Niobrara Refuge (predominantly on the north side of the river and centered at ~42.92°N −100.43°W) primarily for wilderness and wildlife habitat but allows recreation in about the downstream two thirds of the refuge. The National Park Service manages the remaining 108 km (67 mi), acting as a facilitator for resource protection by landowners and river users, providing law enforcement and visitor education services, and coordinating resource management activities.

Five present study Niobrara River sampling sites occur in the NNSR: Valentine SE, Valentine NE, Sparks, Norden, and Riverview.

## 2. Materials and Methods

Major-ion and related water-quality analyses were obtained primarily from the WQP (STORET). These data resulted from the NDEE sampling and analysis efforts) for the approximate period 1968 through 1991.

To evaluate and enhance major-ion data quality, concentrations expressed in milliequivalents per liter (meq/L) for the major ions, cation-anion balance (CAB) errors, and numerous quality-assurance algorithms [e.g., SC (in µS/cm)*0.65 = calculated TDS (in mg/L), (0.01)*(SC) = sum of anions in meq/L, (0.01)*(SC) = sum of cations in meq/L], were used to evaluate and enhance major-ion data quality [31- 33]. The USGS considers ion balances within the ±6% range to indicate major-ion analyses of good quality; however, ion balances up to 12% are considered acceptable [34]. For NRW analyses that exceeded 5% CAB errors, ion concentrations were revised using computer-based algorithms, and revisions were constrained by measured TDS concentrations, SC values, and several empirical water-quality ratios as described above.

Visual MINTEQ, a Microsoft Windows version of the DOS-based computer code MINTEQA2 prepared for the USEPA, is an equilibrium speciation model [35, 36]. This public-domain software, which contains an extensive and updated thermodynamic database, was used to calculate aqueous mineral saturation indices and partial pressure of carbon dioxide (pCO$_2$) values for numerous Niobrara River, contributing creek, and tributary river water samples.

The chemical composition and classification (i.e., hydrochemical facies) of surface water and groundwater can be graphically depicted with a Piper trilinear diagram [37]. Percentages of major ion concentration (meq/L) data for numerous Niobrara River and contributing stream analyses were plotted on respective Piper trilinear diagrams. A major limitation of the Piper diagram is that it does not depict individual concentrations of major cations and anions and does not give an indication of TDS. GW_Chart, computer software available for download on the USGS website, was used to build the study area Piper trilinear diagrams [38].

Stiff diagrams depict major ion composition as meq/L and are useful in comparing the ionic composition (hydrochemical facies) and TDS of streams or aquifers of interest [39]. The size of the polygon comprising the Stiff diagram is a relative indication of the dissolved solid concentration.

One-way analysis of variance (abbreviated one-way ANOVA) is a statistics technique that can be used to compare means of three or more sample groups (using the F distribution). The ANOVA tests the null hypothesis, which states that samples in all groups are drawn from populations with the same mean values. To do this, two estimates are made of the population variance. The one-way ANOVA produces an F-statistic, the ratio of the variance calculated among the means to the variance within the samples. The smaller the F statistic the more likely the sample means are equal. The one-way ANOVA test is followed up by running a post hoc test to identify means that are different from each other. For this study, Tukey's honestly significant difference (HSD) post hoc test was used when performing one-way ANOVA testing [40].

Descriptive statistics, e.g., median, mean, standard deviation, range, were used to describe the water quality on the sampling site level and on the watershed-wide level. Microsoft (MS) Excel was used to generate these statistics. The MS Excel formula STANDARDIZE, in conjunction with mean and standard deviation values, was utilized to calculate hydrochemical parameter z-scores.

### 2.1. Niobrara River Watershed Sampling Stations
NDEE established 17 water-quality monitoring stations along the Niobrara River (Fig. 1) and then collected and analyzed numerous water samples from them over a period of several years in the late 1960s, 1970s, and 1980s. Stations at Harrison and Agate are located in Sioux County; the Marsland and Dunlap stations are in Box Butte/Dawes Counties; the stations at Hay Springs, Rushville, and Gordon occur in Sheridan County; Cherry County contains the Merriman, Nenzel, three Valentine, and Sparks monitoring stations; the Norden sampling site occurs in Keya Paha/Brown Counties; the Riverview site occurs in Keya Paha/Rock Counties; and Knox County contains the Verdel and Niobrara stations.

Fifteen tributary sampling stations were established on six creeks, two rivers, and Merritt Reservoir. The two sampled tributary rivers are the Snake and the Keya Paha. The numerous water-quality analyses for these 32 aggregated Niobrara River and tributary sampling stations comprise the aqueous chemical data source evaluated for this study.

### 3. Results and Discussion
### 3.1. Saturation index, Solubility Product Constants, and Partial Pressure of Carbon Dioxide (pCO₂)
Interaction between surface water, groundwater, and rock formations controls the hydrogeochemistry of rivers and streams in the Niobrara River watershed. The saturation index (SI) indicates the degree of saturation in a particular mineral phase compared with the aqueous solution in contact with it. SI has been defined by as the ability of water to precipitate (for super saturated water with SI > 0) or dissolve calcium carbonate (for under saturated water with SI < 0 [41]. The SI allows prediction of the reactive mineralogy of surface water in the NRW based on its hydrochemistry data. The SI, calculated using the computer geochemical program Visual MINTEQ for surface-water samples, is defined as

$$SI = \log (IAP)/Ksp \qquad (1)$$

where IAP is the ion activity product (IAP), and $Ksp$ is the solubility product constant (equilibrium constant). This equation documents an inverse relationship between SI and $Ksp$. Hydrochemical equilibrium is indicated when SI = 0; the surface water is supersaturated when SI > 0, which shows that precipitation is necessary to achieve equilibrium. If SI < 0, the surface water is undersaturated; this indicates that dissolution is required to reach equilibrium [42].

Common minerals possess highly variable $Ksp$ values. Calcite has a relatively high $Ksp$ for carbonates of $3.31 \times 10^{-9}$. The Ksp for dolomite or dolostone, a geochemically similar carbonate, is much lower at $8.13 \times 10{-}18$. Gypsum ($CaSO_4.2H_2O$), an evaporite mineral, often layered in sedimentary rocks with calcite and dolomite, has a Ksp significantly higher than that of calcite and dolomite, $2.45 \times 10{-}5$. The solubility of gypsum at pH 7.0 is 2100 mg/L, notably higher than that for calcite and dolomite (500 and 480 mg/L, respectively) [43]. No calculated gypsum SI values approach saturation or supersaturation in the NRW sampled waters.

For 263 Niobrara River samples, the median calcite SI is 0.296 (supersaturated), and the minimum and maximum values are −1.078 (undersaturated) and 1.218, respectively, at Norden and at Hay Springs. One hundred ninety-five of these water analyses (74%) yielded SI values greater than 0.0 (supersaturated). Calculated dolomite SI values for 263 analyses are: a median of 0.048, and minimum and maximum values are −2.69 and 2.11 at Norden and at Dunlap, respectively. One hundred thirty-three of these tributary water analyses (51%) yielded dolomite SI values greater than 0.0 (supersaturated). A 23% occurrence difference results when subtracting the dolomite SI occurrence from calcite SI occurrence percentage.

For 181 NRW creek, secondary river, and reservoir legacy (STORET) samples, the median calcite SI is −0.018 (unsaturated), and the minimum and maximum values are −1.59 and 1.16, respectively, at sampling sites on Long Pine Creek at Long Pine and Verdigre Creek at Royal, respectively. Ninety-three of these water analyses (51%) yielded calcite SI values greater than 0.0 (supersaturated). For dolomite, the median SI is −0.59 and minimum and maximum levels are −3.41 and 1.77 reported at Long Pine Creek at Long Pine and Verdigre Creek at Royal, respectively. Fifty-six of these water analyses (31%) yielded dolomite SI values greater than 0.0 (supersaturated). This results in a 20% occurrence difference when subtracting the dolomite positive SI percentage from calcite positive SI occurrence percentage.

Comparing the percentage of positive calcite SI occurrence values for the Niobrara River analyses with those for the creek-tributary-rivers-reservoir category, 74% compares with 51%, respectively. This is equivalent to a positive SI ratio of 1.45:1. Comparing the percentage of positive dolomite SI occurrence values for the

Niobrara River analyses with those for the creek-tributary river category, 51% compares with 31%, respectively. This is equivalent to a positive SI dolomite ratio of 1.65:1. Apparently, geochemical conditions existing in the Niobrara River are more conducive to carbonate (calcite and dolomite) precipitation than in the sampled creeks and tributary rivers.

The explanation for these Niobrara River/(creeks, tributary rivers) SI ratios greater than 1 is unknown; however, the ratio of the median $pCO_2$ value ($1.07 \times 10^{-3}$) for the Niobrara River analyses to the median $pCO_2$ value ($1.40 \times 10^{-3}$) for the creek-tributary-river category analyses is 0.76:1. Thus, an inverse relationship appears to exist comparing SI ratios with $pCO_2$ ratios.

SI of calcite is equal to the result of a complex equation containing log values of $pCO_2$, $HCO_3$, equilibrium constants (temperature dependent), and the ratio of Ca to $HCO_3$ activities [44]. Scatter plot diagrams for two Niobrara River sampling stations, Harrison (upstream) and Verdel (downstream), reveal an inverse relation for $pCO_2$ versus SI for calcite. Fig. 3 displays this relationship for the Verdel sampling site. This linear regression analysis has high coefficient of determination ($R^2$) values 0.72 and 0.83 for Harrison and Verdel, respectively, and p-values well below the 0.05 confidence level ($\alpha < 0.05$).
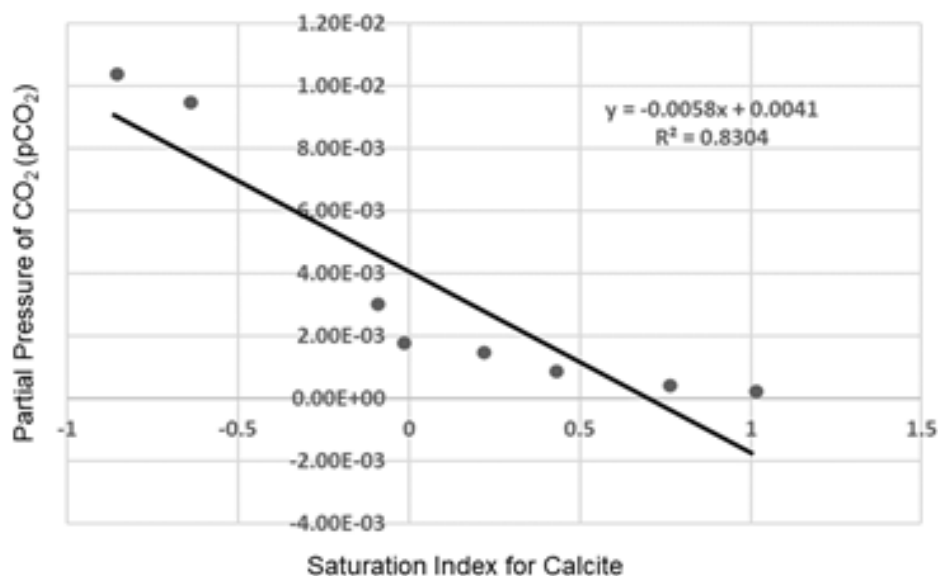


**Figure 3:** Linear Relationship of Calcite SI Verses $pCO_2$ for the Niobrara River at the Verdel Sampling Site.

Plotting SI values for dolomite (x-axis) versus calcite SI values (y-axis) for the Niobrara River at Sparks (n = 17) suggests a strong linear correlation with an $R^2$ of 0.94. This positive linear regression reflects the similar chemistry and comparable solubility concentrations of calcite and dolomite (500 mg/L for calcite versus 480 mg/L for dolomite).

### 3.2. Hydrochemical Characterization for the Niobrara River Watershed

The hydrochemical facies of the Niobrara River watershed discharge are largely classified as the Ca-$HCO_3$ type [45]. Noted that, in general, most groundwater in Nebraska is of the Ca-$HCO_3$ type [46]. Like groundwater, most surface-water bodies in Nebraska also are the Ca-$HCO_3$ type with low to moderate (i.e., < ~700 mg/L) TDS content.

Only a handful of hydrochemical analyses for the study area fall outside the predominant hydrochemical facies Ca-$HCO_3$. A sample from the Niobrara River at Gordon possesses a facies type Mg-$HCO_3$. The Niobrara River at Niobrara yielded a sample with hydrochemistry of Na-HCO3. A sample from the Snake River at Nenzel is classified as a Mg-$HCO_3$ type water. One sample from Minnechaduza Creek at Kilgore is a Na-$HCO_3$ type, and a second sample is a Ca-$SO_4$ water. One sample from the Long Pine Creek at Riverview is Mg-$HCO_3$ type water. For the Keya Paha River at Mills, two samples are also the Mg-$HCO_3$ facies. The Mg in the Mg-$HCO_3$ facies water samples probably originates in dolomite rock layers.

Typical single sample analyses for 12 Niobrara River sampling stations are depicted on a Piper diagram (Fig. 4) showing that all analyses are Ca-$HCO_3$ hydrochemistry facies plotting in a relatively small pattern. The Niobrara River at Harrison and at Niobrara points are slightly separated from the remainder of points in the Piper diamond plot because of slightly higher Ca plus Mg percentages. Twelve typical analyses for the Niobrara River tributary creeks and rivers (Fig. 5) also plot in a relatively tight pattern in the Ca-$HCO_3$ regions of the diagram. The only noticeable differences in the plotted points are the higher cation percentages for Mg (about 35% versus 5%–20%) for samples from Long Pine Creek at Riverview and the Keya Paha River at Mills.
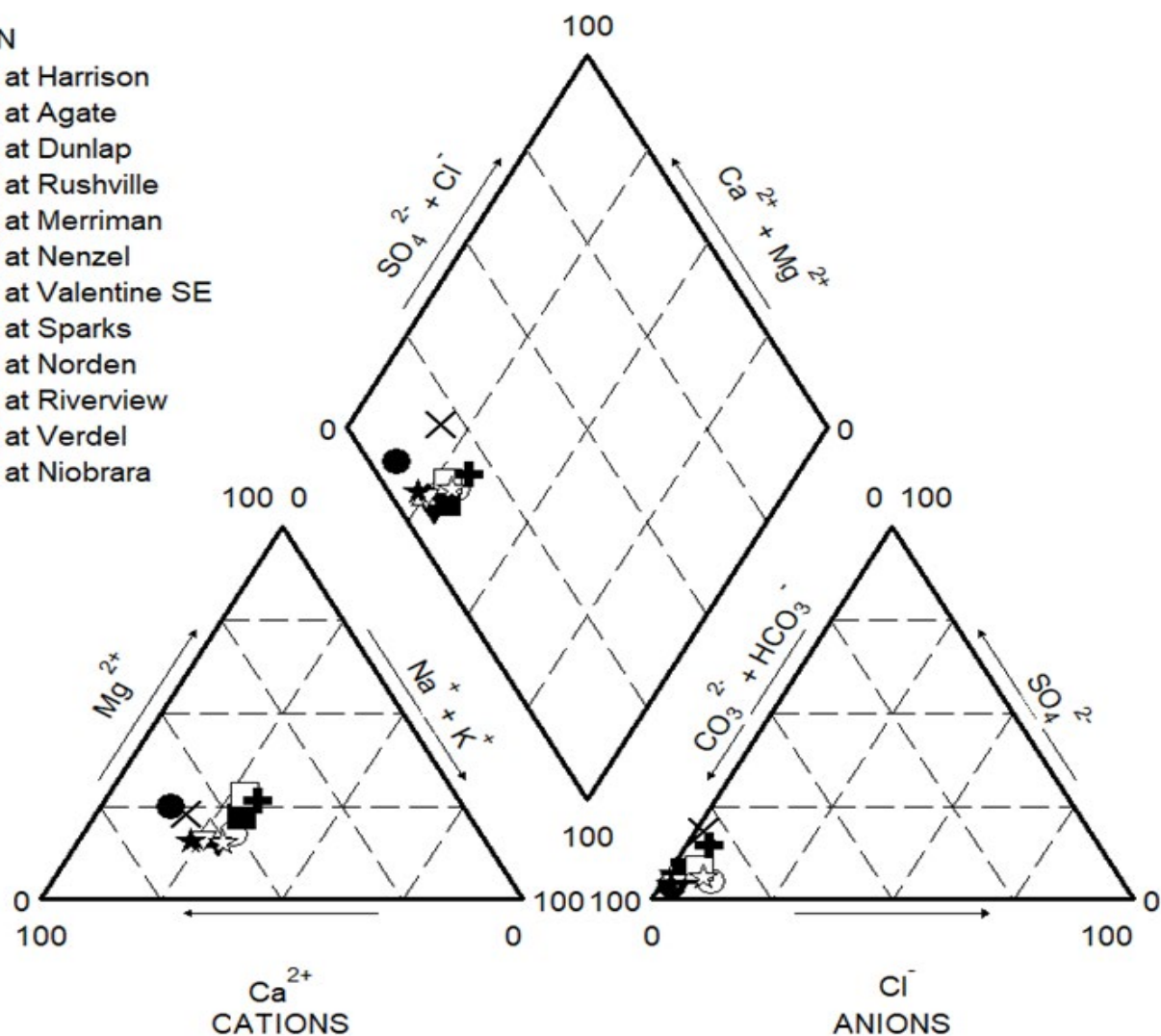
**Figure 4:** Piper Trilinear Diagram Illustrating Hydrochemistry of 12 Sampling Stations on the Niobrara River.

**Figure 5:** Piper Trilinear Diagram Illustrating Hydrochemistry of 12 Sampling Stations on Niobrara River Tributary Creeks and Rivers.

Two hundred forty-two sample analyses (from 17 sampling locations) for the Niobrara River were used to rank and order SC values to identify representative analyses for depiction on Stiff diagrams. Sample analyses falling on the 5th, 50th, and 95th percentiles were chosen. SC values for these three samples are 180, 250, and 420 µS/cm, respectively. These three analyses are associated with grab samples from the sampling stations at Hay Springs, Harrison, and Riverview, respectively. Fig. 6 reveals that $HCO_3$ is the major ion with the highest concentrations and that

varies the most. The skewness for the $HCO_3$ population is 1.10. Skewness for the population of SC values is 0.58 indicating the right side of the distribution curve is skewed, and the SC data fail the Shapiro-Wilk test of normality. The difference in skewness values (0.52) most likely explains the greater percent difference in SC and $HCO_3$ concentrations from the 50th to the 95th percentile (66% for SC, 75% for $HCO_3$) compared with that percent difference in concentrations between the 5th and 50th percentiles (34% for SC, 25% for $HCO_3$).
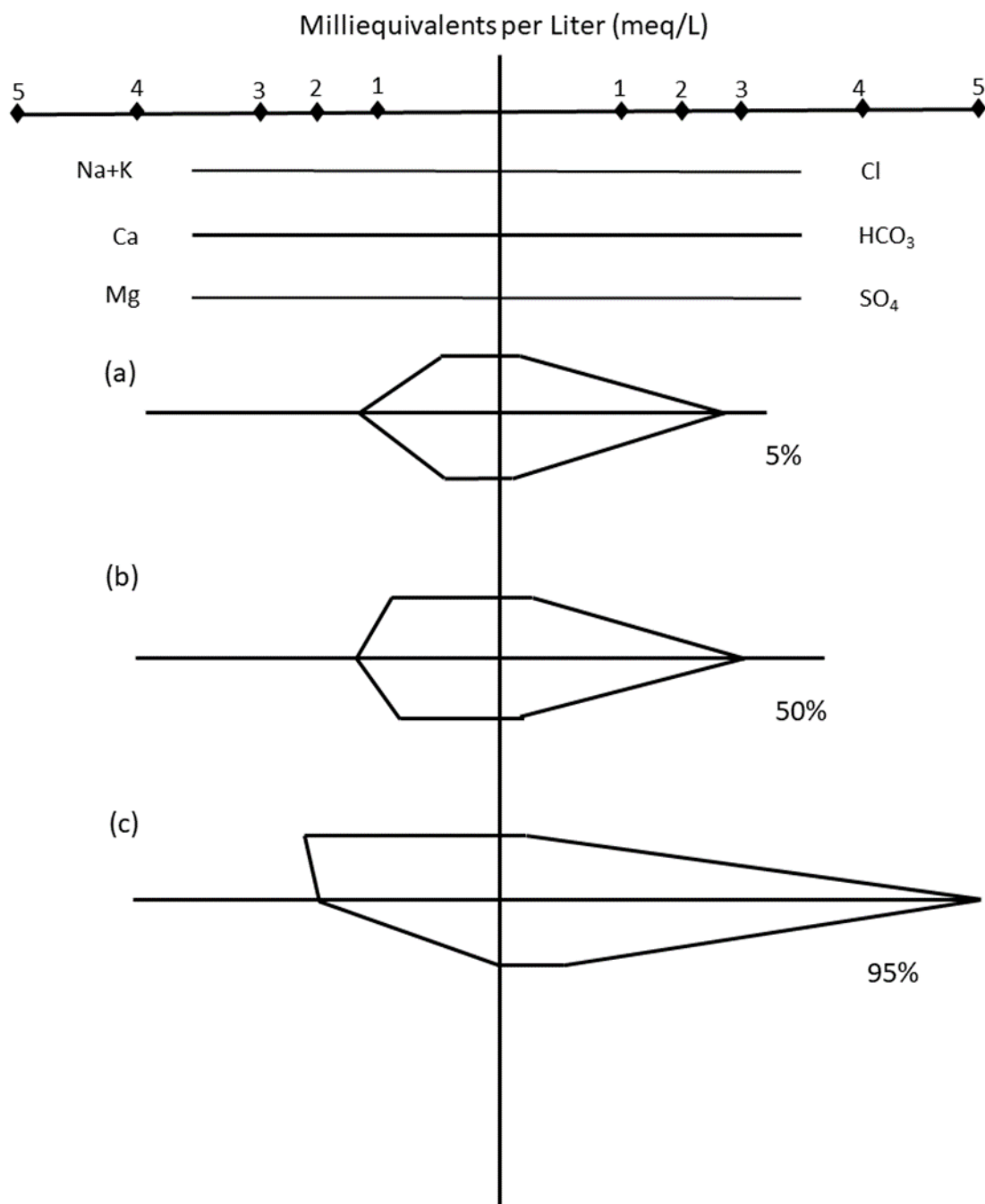
**Figure 6:** Stiff Diagram Illustrating Hydrochemistry of the Niobrara River Sampling Stations.

For 322 samples from the Niobrara River, the median SC value is 260 µS/cm (~170 mg/L TDS). The minimum value recorded is 130 µS/cm (~85 mg/L TDS), recorded for a Valentine sampling station, and the maximum is 490 µS/cm (~320 mg/L TDS) recorded for the Dunlap site.

For the Niobrara River aggregated samples, the median value for calcium is 34 mg/L. The minimum content recorded is 16 mg/L at Dunlap; the maximum Ca value is 80 mg/L for the Niobrara

sampling station.

The median Mg value is 7 mg/L; the minimum Niobrara River value is 1 mg/L recorded for several stations including Norden and Merriman, and the maximum Mg value, 19 mg/L, was reported for the Niobrara sampling station. For Na values for the Niobrara River, the median is 12 mg/L. The minimum value of 6.0 mg/L was reported for a Valentine site and for the Niobrara station, and the maximum of 53 mg/L was recorded for the Marsland sampling site.

The median K concentration for the aggregated Niobrara River sites is 7.0 mg/L. The minimum K level is 3,0 mg/L recorded for the Niobrara station, and the maximum content is 19 mg/L for the Gordon site.

For 322 Niobrara River samples, the median $HCO_3$ value is 163 mg/L. The minimum content is 122 mg/L reported for the Niobrara sampling site, and the maximum $HCO_3$ value is 299 mg/L belonging to the Hay Springs sampling site.

The median Cl value for the Niobrara River is 3.0 mg/L. The minimum level is 0.5 mg/L for the Nenzel site, and the maximum value of 18 mg/L occurs at the Agate sampling station.
For the 322 Niobrara River $SO_4$ analyses, the median is 10 mg/L. The minimum is 1.0 mg/L reported for the Harrison site, and the maximum concentration, 115 mg/L, belongs to the Niobrara sampling site.

Although silica ($SiO_2$) was not an analyte for the surface-water sample analyses evaluated for this study, legacy analyses for dissolved $SiO_2$ content for 2008–2019 are archived on the internet-based WQP. For 13 Niobrara River samples collected in Sioux, Dawes, and Cherry Counties, $SiO_2$ content ranged from 13–59 mg/L, with a median of 53 mg/L. These concentrations are considered high; by comparison, for five Elkhorn River sample stations, characterized median levels ranging from 21–44 mg/L as high silica content [47].

Only a few hydrochemical analyses for the tributaries and one impoundment (Merritt Reservoir), fall outside the predominant hydrochemical facies Ca-$HCO_3$. One sample from the Minnechaduza Creek at Kilgore is a Na-$HCO_3$ facies and a second is a Ca-$SO_4$ facies. The Long Pine Creek at Riverview recorded a sample with Mg-$HCO_3$ hydrochemical facies. The two samples from the Keya Paha River at Mills are classified as Mg-$HCO_3$ facies.

For 181 samples for the aggregated tributary sampling stations (creeks, two rivers, one reservoir), the median SC value is 240 µS/cm (~160 mg/L TDS). The minimum value, 101 µS/cm (~65 mg/L TDS), was reported for the Long Pine Creek at Long Pine South station, and the maximum level of 560 µS/cm (~370 mg/L TDS) belongs to the Minnechaduza Creek at Kilgore.

The median for Ca content is 29 mg/L for all tributaries. The minimum Ca value is 8.0 mg/l recorded for Long Pine Creek at Long Pine South; 67 mg/L is the maximum calcium value, and it occurred at the Minnechaduza Creek at Kilgore.

For the aggregated tributary analyses, the median Mg value is 6.0 mg/L. The minimum Mg value is 1.0 mg/L that occurred at the Snake River station at Valentine; the maximum Mg concentration, 24 mg/L, was reported for the Keya Paha River at Mills.

For the 181 Na analyses, the median is 11 mg/L. The minimum concentration, 4.0 mg/L, was recorded for the sampling site on the Long Pine Creek at Long Pine; the maximum Na value is 33 mg/L

reported for the Keya Paha River at Mills.

The median for K content along the tributaries is 6.0 mg/L. The minimum concentration of K is 1.0 mg/L occurring on the Snake River at Valentine; the maximum content, 21 mg/L, was reported for Verdigre Creek at Verdigre.

For the aggregated $HCO_3$ analyses, the median value is 141 mg/L. The minimum reported concentration is 65 mg/L for the Long Pine Creek at Long Pine; the maximum $HCO_3$ concentration is 282 mg/L, occurring on the Minnechaduza Creek at Kilgore.
The Cl median for the tributaries is 3.0 mg/L. The minimum chloride value is 1.0 mg/L, occurring at numerous sampling sites; the maximum Cl content is 10 mg/L recorded for the Minnechaduza Creek at Valentine and the Verdigre Creek at Verdigre.

For the 181 sample analyses, the median $SO_4$ concentration is 7.0 mg/L. The minimum content for all the tributaries is 1.0 mg/L occurring at several sampling sites encompassing Pine Creek at Rushville. The maximum $SO_4$ value is 152 mg/L reported for Minnechaduza Creek at Kilgore.

Comparing median hydrochemistry parameter values, Niobrara River values are slightly higher than the tributary median values (excepting Cl), e.g., 34 versus 29 mg/L for Ca, 163 versus 141 mg/L for $HCO_3$. Median mineralization is slightly higher for the Niobrara River samples (TDS of 192 mg/L verses 129 mg/L for the tributaries).

### 3.3. Hydrochemical Comparison with Adjacent River Watershed
The Elkhorn River (ER) [about 18,130 km² (7000 mi²)] lies immediately south of the NRW. ER water is Ca-$HCO_3$ facies exclusively and has moderate to high silica content (~3.2–62 mg/L). Measured TDS ranges from ~127–529 mg/L. Median TDS of ER water is 153 mg/L at the most upgradient sampling station and mineralization gradually increases to a median of 328 mg/L near the mouth (Waterloo, NE). By contrast, the mineralization level of Niobrara River water is essentially constant from upstream to downstream (at the mouth). Median SC for Harrison is 319 µS/cm (~210 mg/L TDS), and the Niobrara station (at mouth) owns a median SC of 300 µS/cm (~200 mg/L TDS).

### 4. Statistical Analysis
### 4.1. Descriptive Statistics
The hydrochemical data for the Niobrara River were evaluated using the descriptive statistics algorithm contained in MS Excel. Statistical parameters obtained for the 17 river sampling locations encompass: mean, median, standard deviation, and skewness. The hydrochemical parameters evaluated are: Ca, Mg, Na, K, $HCO_3$, Cl, $SO_4$, and SC. Using the means calculated for the 17 river sampling stations, aggregated or river-wide means and standard deviations were calculated for the eight hydrochemical parameters. These river-wide means and standard deviations were input to the Excel formula STANDARDIZE to calculate the standard scores called z-scores for the eight hydrochemical parameters. The z-score measures the

percentage of the standard deviation a value is from the average. Positive z-scores document sample station means that exceed the river-wide means by a proportion of the standard deviation; negative z-scores reflect sample station mean values smaller than river-wide mean values.

Three Niobrara River sampling stations (Dunlap, Hay Springs, Rushville) recorded all positive z-scores, indicating that all means exceeded the river-wide means (Table 2). And only one small negative z-score occurs for the Agate station. Downstream, eight sampling stations (Merriman, Nenzel, Valentine SW, Valentine SE, Valentine NE, Sparks, Norden, and Riverview) are associated with all negative z-scores revealing all means lower than the river-wide means and lower salinities than the four stations possessing all positive z-scores excepting only one small negative one.

| Parameter | Riverwide mean (Std Dev) | Niobrara R – Harrison | Niobrara R – Agate | Niobrara R – Marsland | Niobrara R – Dunlap | Niobrara R – Hay Springs | Niobrara R – Rushville | Niobrara R – Gordon | Niobrara R – Merriman | Niobrara R – Nenzel | Niobrara R – Valentine SW | Niobrara R – Valentine SE | Niobrara R – Valentine NE | Niobrara R – Sparks | Niobrara R – Norden | Niobrara R – Riverview | Niobrara R – Verdel | Niobrara R – Niobrara |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n = 18 | n = 8 | n = 8 | n = 18 | n = 8 | n = 18 | n = 8 | n = 18 | n = 17 | n = 16 | n = 17 | n = 9 | n = 17 | n = 16 | n = 18 | n = 8 | n = 17 |
| Ca | 35 (6.2) | 48 (2.10) | 47 (1.94) | 38 (0.48) | 36 (0.15) | 43 (1.29) | 37 (0.31) | 35 (-0.01) | 32 (-0.50) | 30 (-0.82) | 28 (-1.14) | 30 (-0.82) | 33 (-0.33) | 29 (-0.98) | 32 (-0.50) | 31 (-0.66) | 29 (-0.98) | 38 (0.48) |
| Mg | 7.4 (2.3) | 12 (2.01) | 11 (1.57) | 7.4 (-0.01) | 11 (1.57) | 10 (1.14) | 7.9 (0.21) | 6.6 (-0.36) | 5. (-0.67) | 5.2 (-0.97) | 6.1 (-0.58) | 6.0 (-0.62) | 5.2 (-0.97) | 5. (-0.67) | 4.9 (-1.11) | 5.5 (-0.84) | 8.0 (0.26) | 7.5 (0.04) |
| Na | 17 (7.6) | 13 (-0.49) | 26 (1.23) | 14 (-0.36) | 32 (2.02) | 36 (2.55) | 19 (0.30) | 18 (0.17) | 15 (-0.23) | 14 (-0.36) | 12 (-0.62) | 11 (-0.75) | 10 (-0.89) | 12 (-0.62) | 11 (-0.75) | 12 (-0.62) | 15 (-0.23) | 14 (-0.36) |
| K | 7.7 (1.6) | 7.4 (-0.46) | 11 (2.03) | 6.8 (-0.59) | 8.4 (0.41) | 11 (2.03) | 8.9 (0.72) | 10 (1.41) | 7.6 (-0.09) | 7.2 (-0.34) | 7.3 (-0.28) | 6.5 (-0.77) | 6.1 (-1.02) | 6.5 (-0.77) | 6.4 (-0.84) | 6.2 (-0.96) | 8.0 (0.16) | 6.7 (-0.65) |
| HCO$_3$ | 183 (45) | 233 (1.13) | 241 (1.31) | 258 (1.69) | 230 (1.06) | 262 (1.78) | 189 (0.15) | 186 (0.08) | 164 (-0.42) | 155 (-0.62) | 151 (-0.71) | 148 (-0.77) | 124 (-1.31) | 148 (-0.77) | 145 (-0.84) | 148 (-0.77) | 154 (-0.64) | 167 (-0.35) |
| Cl | 3.9 (3.1) | 4.9 (0.30) | 15 (3.60) | 3.2 (-0.20) | 5.1 (0.40) | 4 (0.05) | 5.6 (0.60) | 1.9 (-0.63) | 2.7 (-0.38) | 1.5 (-0.76) | 2.2 (-0.54) | 2.8 (-0.34) | 2.2 (-0.54) | 2.7 (-0.38) | 2.5 (-0.44) | 2.8 (-0.34) | 3.3 (-0.18) | 3.2 (-0.21) |
| SO$_4$ | 10 (5.2) | 5.7 (-0.84) | 9.8 (-0.05) | 18 (1.53) | 13 (0.57) | 15 (0.95) | 14 (0.76) | 8.9 (-0.22) | 7. (-0.59) | 6.3 (-0.72) | 5.4 (-0.89) | 5.6 (-0.85) | 5.2 (-0.93) | 5.8 (-0.82) | 6.8 (-0.62) | 6.2 (-0.74) | 17 (1.34) | 21 (2.11) |
| SC[a] | 277 (54) | 319 (0.78) | 361 (1.55) | 302 (0.46) | 341 (1.18) | 393 (2.14) | 321 (0.81) | 260 (-0.31) | 257 (-0.36) | 237 (-0.73) | 231 (-0.84) | 227 (-0.92) | 230 (-0.86) | 227 (-0.92) | 225 (-0.95) | 227 (-0.92) | 247 (-0.55) | 300 (0.43) |
| Calc TDS | 176 (42) | 207 (0.73) | 239 (1.49) | 237 (1.43) | 220 (1.04) | 251 (1.77) | 187 (0.26) | 173 (-0.07) | 153 (-0.54) | 142 (-0.80) | 135 (-0.97) | 136 (-0.94) | 137 (-0.92) | 136 (-0.94) | 137 (-0.92) | 137 (-0.92) | 158 (-0.42) | 207 (0.73) |

[a]SC = Specific conductance.

**Table 2: Z-Scores for Eight Hydrochemical Parameters, Niobrara River Sampling Stations**

The hydrochemical data (181 samples) for the Niobrara River tributaries were also evaluated using the descriptive statistics algorithm and STANDARDIZE equation. Two sampling stations yielded all positive z-scores (Keya Paha River at Mills and Verdigre Creek at Verdigre) and one sampling site recorded only one negative z-score (Minnechaduza Ck at Kilgore) (Table 3).

Interestingly, six sampling stations recorded all negative z-scores [Pine Creek at Rushville, Snake River at Nenzel, Merritt Reservoir, Long Pine Creek at Long Pine South, and Long Pine Creek at Riverview], and two sampling points (Snake River at Valentine and Plum Creek at Meadville) yielded only one positive z-score.

| Parameter | Study Area wide Mean (Std Dev) | Pine Ck at Rushvill | Snake R at Nenzel | Minnechaduza Ck at Kilgore | Merritt Reservoir | Snake R at Valentine | Minnechaduza Ck at Valentine | Bone Ck nr Long Pine Ck | Plum Ck at Meadville | Long Pine Ck at Long Pine | Long Pine Ck at Long Pine S | Long Pine Ck at Riverview | Keya Paha R at Mills | Verdigre Ck Royal | Verdigre Ck Royal | Verdigre Ck at Verdigre |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | n = 16 | n = 8 | n = 15 | n = 6 | n = 13 | n = 19 | n = 4 | n = 18 | n = 7 | n = 15 | n = 18 | n = 2 | n = 9 | n = 18 | n = 13 |
| Ca | 32 (11.2) | 25 (-0.63) | 26 (-0.54) | 48 (1.43) | 22 (-0.89) | 26 (-0.54) | 47 (1.34) | 36 (0.36) | 30 (-0.18) | 17 (-1.34) | 15 (-1.52) | 23 (-0.80) | 33 (0.09) | 45 (1.16) | 44 (1.07) | 43 (0.98) |
| Mg | 7 (4.7) | 4 (-0.65) | 5.9 (-0.24) | 8.5 (0.31) | 3 (-0.86) | 4.6 (-0.52) | 7.1 (0.01) | 6 (-0.22) | 5.6 (-0.31) | 5.3 (-0.37) | 4.5 (-0.54) | 5.6 (-0.31) | 23 (3.39) | 5.6 (-0.31) | 8 (0.20) | 8.9 (0.39) |
| Na | 12.6 (6.8) | 8 (-0.68) | 12 (-0.09) | 21 (1.23) | 7.2 (-0.80) | 8.8 (-0.57) | 15 (0.35) | 11 (-0.24) | 10 (-0.39) | 7.4 (-0.77) | 7.1 (-0.82) | 9 (-0.54) | 33 (3.00) | 15 (0.35) | 12 (-0.09) | 13 (0.04) |
| K | 6.8 (2.7) | 5 (-0.68) | 6.6 (-0.08) | 9.8 (1.11) | 6 (-0.31) | 4.8 (-0.76) | 7.7 (0.33) | 7 (0.06) | 5.7 (-0.42) | 4.6 (-0.83) | 4.5 (-0.87) | 5.3 (-0.57) | 15 (3.06) | 7 (0.06) | 6 (-0.31) | 7.4 (0.21) |
| HCO$_3$ | 156 (52) | 116 (-0.76) | 138 (-0.34) | 224 (1.31) | 95 (-1.16) | 124 (-0.61) | 214 (1.12) | 157 (0.02) | 143 (-0.24) | 96 (-1.14) | 86 (-1.33) | 120 (-0.68) | 257 (1.94) | 195 (0.75) | 177 (0.41) | 194 (0.73) |
| Cl | 3.2 (1.1) | 2.1 (-1.00) | 2.5 (-0.64) | 2.7 (-0.46) | 1.1 (-1.89) | 2.2 (-0.91) | 3.2 (-0.01) | 4 (0.71) | 3.3 (0.01) | 2.7 (-0.46) | 2.8 (-0.37) | 3.2 (-0.01) | 5.5 (2.06) | 4.6 (1.25) | 4 (0.71) | 4.2 (0.89) |
| SO$_4$ | 12 (12.0) | 5.3 (-0.56) | 7.5 (-0.38) | 22 (0.83) | 10 (-0.17) | 5.3 (-0.56) | 6.6 (-0.45) | 10 (-0.17) | 5.4 (-0.55) | 2.4 (-0.80) | 3.1 (-0.74) | 3.8 (-0.68) | 48 (2.99) | 8.9 (-0.26) | 25 (1.08) | 17 (0.41) |
| SC[a] | 249 (81) | 177 (-0.89) | 203 (-0.57) | 370 (1.49) | 175 (-0.91) | 254 (0.06) | 305 (0.69) | 248 (-0.01) | 229 (-0.25) | 143 (-1.31) | 140 (-1.35) | 184 (-0.80) | 410 (1.99) | 298 (0.60) | 292 (0.53) | 308 (0.73) |

[a]SC = Specific conductance.

**Table 3: Z-Scores for Eight Hydrochemical Parameters, Niobrara River Tributary Creek and River Sampling Stations**

### 4.2. One-Way ANOVA

To examine the statistical relationships for the eight hydrochemical parameters along the Niobrara River sample stations, one-way ANOVA analysis was performed for three groups of five sampling stations spread out along the course of the river. The first group, in downstream order, is: Harrison (G1); Rushville (G2); Valentine NE (G3); Riverview (G4); and Niobrara (G5) [Table 4(a)]. Thirty-nine parameter pairs (49%) yielded results where $p < 0.05$, indicating statistically significant mean differences at a 0.05 confidence level ($\alpha = 0.5$). Pairs G2–G3 (Rushville–Valentine NE) and G2–G4 (Rushville–Riverview) each yielded six statistically significant parameter pairs encompassing $HCO_3$ and SC. For the G3–G4 (Valentine NE–Riverview) pair, all parameter pairs are the null hypothesis (NH) ($p > 0.05$). The pair G1–G5 represents the most upstream and most downstream river sampling stations. For this pair, Ca, Mg, $HCO_3$, and SO4 values were statistically different; the other four pair differences were not statistically different or NH.

| Parameter | F statistic | G1–G2 | G1–G3 | G1–G4 | G1–G5 | G2–G3 | G2–G4 | G2–G5 | G3–G4 | G3–G5 | G4–G5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 14.5 | 0.0002 | 0.0000 | 0.0000 | 0.0005 | — | — | — | — | — | 0.0382 |
| Mg | 17.9 | 0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0135 | 0.0323 | — | — | — | — |
| Na | 7.23 | 0.0024 | — | — | — | 0.0000 | 0.0002 | 0.0132 | — | — | — |
| K | 8.24 | —[a] | — | — | — | 0.00002 | 0.0001 | 0.0017 | — | — | — |
| $HCO_3$ | 40.4 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0479 | — | — | — |
| Cl | 7.48 | — | 0.0038 | 0.0375 | — | 0.0002 | 0.0030 | 0.0162 | — | — | — |
| SO_4 | 16.1 | — | — | — | 0.0004 | — | — | — | — | 0.0002 | 0.0006 |
| SC[b] | 20.1 | — | 0.0000 | 0.0000 | — | 0.0000 | 0.0000 | — | — | 0.0001 | 0.0000 |

[a] $p > 0.05$.
[b] SC = Specific conductance.
Note: G1 = Harrison; G2 = Rushville; G3 = Valentine NE; G4 = Riverview; G5 = Niobrara.

**Table 4(a): One-way ANOVA p-values Calculated for Group 1 Niobrara River Sampling Stations**

For a second group of five Niobrara River sampling stations—Marsland (G1); Dunlap (G2); Merriman (G3); Norden (G4); and Verdel (G5) in downstream order—36 parameter pairs (45%) yielded results where $p < 0.05$, reflecting statistically significant mean differences [Table 4(b)]. Again, for G3–G4 (Merriman–Norden), all parameter pairs are the NH, and only a few statistically significant pairs for groups G3–G5 (Merriman–Verdel) and G4–G5 (Norden–Verdel) occur. These numerous NH results for both river groups suggest that Niobrara River hydrochemical parameters possess low variability in the downstream direction.

| Parameter | F statistic | G1–G2 | G1–G3 | G1–G4 | G1–G5 | G2–G3 | G2–G4 | G2–G5 | G3–G4 | G3–G5 | G4–G5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 4.33 | —[a] | 0.0194 | 0.0093 | 0.0006 | — | — | — | — | — | — |
| Mg | 13.0 | — | 0.0039 | 0.0002 | — | 0.0008 | 0.0000 | — | — | — | 0.0483 |
| Na | 39.9 | — | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | — | — | — |
| K | 4.94 | — | 0.0496 | 0.0005 | — | — | — | — | — | — | — |
| $HCO_3$ | 101.3 | 0.0018 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | — | — | — |
| Cl | 5.41 | — | — | — | — | 0.0237 | 0.0111 | — | — | — | — |
| SO_4 | 7.88 | — | — | — | 0.0018 | — | 0.0293 | — | — | 0.0005 | 0.0001 |
| SC[b] | 42.1 | 0.0195 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | — | — | — |

[a] $p > 0.05$.
[b] SC = Specific conductance.
Note: G1 = Harrison; G2 = Rushville; G3 = Valentine NE; G4 = Riverview; G5 = Niobrara.

**Table 4(b): One-way ANOVA p-values Calculated for Group 2 Niobrara River Sampling Stations**

For a third group of five Niobrara River sampling stations—Agate (G1); Hay Springs (G2); Gordon (G3); Nenzel (G4); and Sparks (G5)—52 parameter pairs (65%) yielded statistically significant differences ($p < 0.05$) [Table 4(c)]. The G4–G5 parameter pair, however, has all NH values. This group possesses more parameter variability than the first two groups based on one-way ANOVA results (65% with $p < 0.05$ versus 49% and 45% for groups 1 and 2, respectively).

| Parameter | F statistic | G1–G2 | G1–G3 | G1–G4 | G1–G5 | G2–G3 | G2–G4 | G2–G5 | G3–G4 | G3–G5 | G4–G5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 21.3 | —[a] | 0.0000 | 0.0000 | 0.0000 | 0.0110 | 0.0000 | 0.0000 | — | — | — |
| Mg | 8.86 | — | 0.0147 | 0.0003 | 0.0022 | 0.0447 | 0.0013 | 0.0081 | — | — | — |
| Na | 31.1 | 0.0018 | 0.0124 | 0.0002 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | — | — | — |
| K | 13.8 | — | — | 0.0034 | 0.0003 | — | 0.0002 | 0.0000 | 0.0078 | 0.0007 | — |
| HCO$_3$ | 121.0 | 0.0255 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0003 | 0.0000 | — |
| Cl | 67.4 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | — | 0.0499 | — | — | — | — |
| SO$_4$ | 16.73 | 0.0003 | — | — | — | 0.0000 | 0.0000 | 0.0000 | — | — | — |
| SC[b] | 89.35 | 0.0406 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0061 | 0.0012 | — |

[a]$p > 0.05$.

[b]SC = Specific conductance.

Note: G1 = Harrison; G2 = Rushville; G3 = Valentine NE; G4 = Riverview; G5 = Niobrara.

**Table 4(c): One-way ANOVA p-values Calculated for Group 3 Niobrara River Sampling Stations**

One-way ANOVA analysis also was employed for the three sampling stations along Long Pine Creek [Table 4(d)]. Only six of 24 parameter pairs (25%) are statistically significant suggesting relatively low ion variability along this tributary. However, these statistical results ($\alpha = 0.05$) confirm increasing mineralization (salinity) in the downgradient direction (G1–G3) for SC, Ca, and HCO$_3$.

| Parameter | F statistic | G1–G2 | G1–G3 | G2–G3 |
|---|---|---|---|---|
| Ca | 19.2 | [a]__ | 0.0008 | 0.0001 |
| Mg | 0.95 | — | — | — |
| Na | 3.57 | — | — | — |
| K | 1.21 | — | — | — |
| HCO$_3$ | 30.5 | — | 0.0002 | 0.0000 |
| Cl | 0.05 | — | — | — |
| SO$_4$ | 1.86 | — | SCb — | — |
| SC[b] | 12.5 | — | 0.0028 | 0.0012 |

[a]$p > 0.05$.

[b]SC = Specific conductance.

Note: G1 = Long Pine Ck at Long Pine; G2 = Long Pine Ck at Long Pine S; G3 = Long Pine Ck at Riverview.

**Table 4(d): One-way ANOVA p-values Calculated for Three Sampling Stations on Long Pine Creek**

### *4.3. Chemical Weathering Processes Impacting Major Ion Chemistry*

Weathering of carbonates likely is a significant process contributing to the geochemistry of most surface waters in the study area. Limestone and other calcium-rich deposits which are composed primarily of calcite are abundant in the NRW. Consequently, the dissolution of calcite in water saturated with CO$_2$ should give a Ca/HCO$_3$ molar ratio equal to 0.5 as shown in the following reaction [48] [Eq. (2)]:
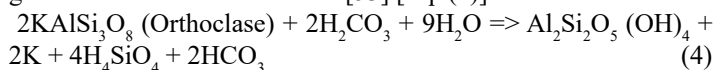
$$CaCO_3 + H_2O + CO_2 => Ca + 2HCO_3 \qquad (2)$$
Calcite
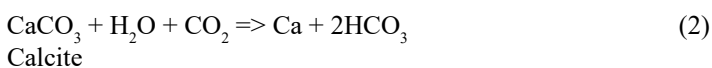
Calcite can also dissociate or weather in the presence of an acid, e.g., H$_2$CO$_3$, commonly resulting in precipitation of Ca [Eq. (3)]:

$$CaCO_3(s) + H^+ => Ca^{2+} + HCO_3^{-1} \qquad (3)$$
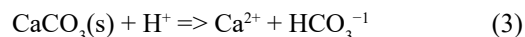
For the (Ca + Mg) (y axis) versus (HCO$_3$ + SO$_4$) (x-axis) scatter diagram, the ionic concentrations (meq/L) plotting above the 1:1 equiline result from carbonate weathering, whereas those falling along the equiline are attributable to both carbonate and crystalline or silicate (e.g., feldspar) weathering [49]. Sample analyses that plot below the 1:1 line reflect silicate [alkali (K, Na) feldspar] weathering as the dominant hydrogeochemical process [50]. Several researchers assert that the plot of (Ca + Mg) versus (HCO$_3$ + SO$_4$) (in meq/L) will be close to the 1:1 line if the dissolution of calcite, dolomite, and gypsum are the dominant reactions in a hydrologic system [51, 52].

Silicate rock weathering increases the concentration of HCO$_3$ in

groundwater and surface water [53] [Eq. (4)]:

$$2KAlSi_3O_8 \text{ (Orthoclase)} + 2H_2CO_3 + 9H_2O => Al_2Si_2O_5 (OH)_4 + 2K + 4H_4SiO_4 + 2HCO_3 \quad (4)$$

Most likely, the notably high dissolved silica content in the Niobrara River samples is the result of chemical breakdown of silicate minerals [feldspars (encompassing plagioclases), amphiboles, micas] in the processes of weathering [54]. Concentrations of silica concentrations of silica measured in natural water commonly ranges from 1–30 mg/L; however, levels up to 100 mg/L occur in groundwater in some areas. For the dissociation of silica (quartz) in water [$SiO_4 + 2H_2O = Si(OH)_4$)], the solubility at pH 7.0 is 12 mg/L. However, for amorphous silica, solubility is 120 mg/L.

Ion exchange typically is one of the important geochemical processes responsible for the concentration of major ions in surface water and groundwater. According to, cation exchange between the groundwater and its host environment during residence or travel can be chloro-alkaline disequilibrium [55- 58]. During this cation-exchange process, the host rocks are the primary sources of dissolved solids in the water. How ion exchange has probably impacted surface water in the NRW is discussed later.

The scatter diagrams of (Ca + Mg) (y-axis) versus ($HCO_3$ + $SO_4$) (x-axis) (in meq/L) for the Niobrara River and its tributaries for this study depict all samples plotting below the 1:1 equiline (Fig. 7). This ratio for the Niobrara River samples varies from 0.47–0.93 with a median value of 0.77. For 181 tributary river and creek samples, the (Ca + Mg):($HCO_3$ + $SO_4$) ratio ranges from 0.59–0.93 with a median of 0.80. These values for this hydrogeochemical ratio most likely confirm the thesis asserted by Datta and Tyagi, Dehnavi et al., and Gomaa et al., that weathering of silicate minerals (e.g., alkali feldspar) is a dominant geochemical process in the study area. As briefly discussed in the "Geology and hydrogeology" section, the Laramide Orogeny provided a source of igneous rocks and silicate minerals (i.e., feldspars) transported by rivers and streams during the Late Cretaceous and Tertiary time eastward into Nebraska and the NRW.
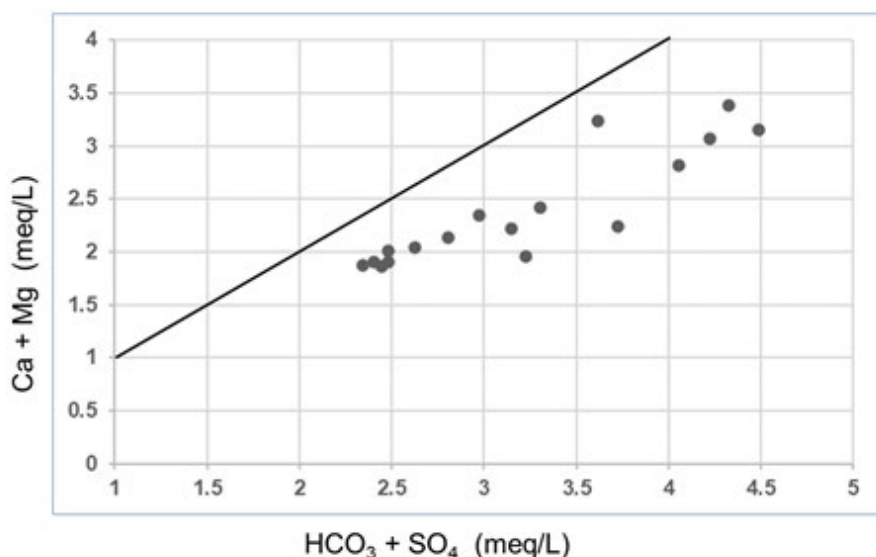


**Figure 7:** (Ca + Mg) (meq/L) versus ($HCO_3$ + $SO_4$) (meq/L) Concentrations for 17 Niobrara River Sampling Stations.

Another explanation for the calculated ratios below 1.0 is ion exchange as described in the literature as briefly summarized above, where calcium in the water is exchanged for Na residing in soils and aquifer materials. Several investigators have noted that scatter diagrams of (Ca + Mg) versus ($HCO_3$ + $SO_4$) (all concentrations in meq/L) provide insight into the ion exchange process [59]. Specifically, cation exchange (Ca for Na) tends to shift the points below the 1:1 line resulting from an excess of ($HCO_3$ + $SO_4$) relative to (Ca + Mg). The scatter diagram (Fig. 7) is prima facie evidence that positive cation exchange (aqueous Ca for crystalline Na) is a geochemical mechanism most likely occurring in the monitored surface-water of the NRW. If this hydrogeochemical process were reverse ion exchange, it would shift the points (values) above the equiline owing to the excess of (Ca + Mg) over ($HCO_3$ + $SO_4$) in solution.

### 4.4. Suitability for Drinking Water and Other Beneficial Uses
The USEPA secondary (aesthetic quality) maximum contaminant levels (SMCLs) in drinking water supplies for the following chemicals encompass: TDS—500 mg/L and for Cl and $SO_4$—250 mg/L [60]. Due to the low mineralization in Niobrara River and most of its tributaries, these waters comply with the above SMCLs. Further, most surface waters occurring in the NRW are excellent sources of agricultural (e.g., irrigation water) and industrial uses (e.g., cooling water) [61].

## 5. Summary and Conclusions

The NRW drains the northwestern and northcentral portions of Nebraska (approximately 4,130 km²), encompassing the ancient and unique Sand Hills and Niobrara National Scenic River course. The study findings are summarized as follows:

- Mineralization (salinity) for 17 sampling stations on the Niobrara River varies from a low SC of 130 µS/cm (~85 mg/L TDS) to a maximum of 490 µS/cm (~320 mg/L TDS) with a median SC value of 260 µS/cm (~170 mg/L TDS). All but a few of the water samples for the NRW belong to the Ca-HCO$_3$ hydrochemical facies.

- Mineralization for the 15 sampling stations on NRW tributary creeks and two rivers varies from a low SC of 101 µS/cm (~65 mg/L TDS) to a maximum level of 560 µS/cm (~370 mg/L TDS) with a median SC of 240 µS/cm (~160 mg/L TDS).

- For the graphical relationship (Ca + Mg) (y-axis) versus (HCO$_3$ + SO$_4$) (x-axis) concentrations (in meq/L), all the Niobrara River and tributary creek and river data points fall below the 1:1 equiline, suggesting predominant silicate (feldspar) rock and mineral weathering/dissolution. Cation exchange (aqueous Ca for Na in streambed sediment) is a second hydrochemical mechanism accounting for points falling below the 1:1 equiline.

- About 74% of Niobrara River water samples yielded calcite SI values slightly greater than 0.0 (supersaturated conditions). Approximately 51% of Niobrara River water samples yielded dolomite SI values slightly greater than 0.0, documenting supersaturated conditions, a depositional environment.

- About 51% of NRW creek and tributary river water samples yielded calcite SI values slightly greater than 0.0 (supersaturated conditions). Approximately 31% of NRW creek and tributary river water samples yielded dolomite SI values slightly greater than 0.0, documenting supersaturated conditions, a depositional environment. All NRW water samples yielded gypsum SI values significantly less than 0.0, documenting undersaturated (dissolving) conditions.

- Scatter plot diagrams for two Niobrara River sampling stations, one upstream and one downstream, reveal an inverse relation for pCO2 versus calcite SI values. This linear regression analysis has high R² values 0.72 and 0.83, respectively, and p-values well below the 0.05 confidence level ($\alpha < 0.05$).

- A 122-km (76-mi) course of the Niobrara River in northcentral Nebraska has been designated as the NNSR since 1991. Five sampling stations for the present study occur in the NNSR.

- The Elkhorn River (ER) watershed [about 18,130 km² (7000 mi²)] lies immediately south of the NRW. ER water is Ca-HCO$_3$ facies exclusively; TDS ranges from ~127–529 mg/L. Median TDS of ER water is 153 mg/L at the most upgradient sampling station, and mineralization gradually increases to a median of 328 mg/L near the mouth (Waterloo, NE). By contrast, the mineralization level of Niobrara River water is essentially constant from upstream to downstream [244 mg/L (median) TDS at headwater to 202 mg/L (median) TDS at mouth]. The NNSR, possessing low agricultural, industrial, and commercial development, probably contributes to this consistent upstream–downstream mineralization.

- For 13 Niobrara River samples originating collectively in Sioux, Dawes, and Cherry Counties for the period 2008–2019, dissolved SiO$_2$ content ranged from 13–59 mg/L, with a median of 53 mg/L. This mineralization level is considered high for rivers and creeks in Nebraska.

- Hopefully, this historical hydrogeochemical evaluation will provide a sound scientific basis and background for comparison and contrast with present-day hydrogeochemistry of the NRW.

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