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Evaluation of Legacy Hydrochemical Data Using Statistics, Graphical Methods, and Equilibrium Modeling—Platte River Watershed, Nebraska, USA

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Abstract

The Platte River watershed, the largest river basin in Nebraska (1.06×10^5 km^2), crosses the entire state along its W-E course in the approximate N-S center of Nebraska. A plethora of historical (1968-1975) hydrochemistry data [major cations and anions, primarily] resulting from collection and analysis by the Nebraska Department of Environment and Energy (NDEE) were statistically and graphically analyzed and subjected to geochemical modeling. Interpretation of this large legacy dataset (31 Platte River systems sampling stations and 34 sampling sites on 22 tributaries) revealed several hydrochemical facies (Ca-HCO_3 and three additional ones, encompassing Ca-SO_4 and Na-SO_4 facies solely in South Platte River discharge), and slight calcite and dolomite supersaturation comprising a line of evidence for the near thermodynamic equilibrium of the studied surface waters. Scatter plots of selected cations versus anions reveal the impact of silicate minerals (e.g., feldspars) weathering on the aqueous hydrochemistry throughout the watershed. Relatively high concentrations of sulfate (up to 1100 mg/L) in numerous samples from the South Platte River are probably sourced by agricultural fertilizer, irrigation water, and dissolution of gypsum/anhydrite. NETPATH geochemical modeling identified 10 plausible models to simulate the significant decrease in SO_4 levels downstream along the South Platte River.

Keywords

Hydrochemical Facies, Surface-Water Quality, NETPATH, Visual MINTEQ, Silicate (Feldspar) Weathering

1. Introduction

From the late 1960s through approximately 1991, 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), in collaboration with USEPA Region 7, sampled numerous river and stream discharges throughout the state, typically monthly, to characterize state-wide surface-water quality and potential contamination. The grab samples were analyzed for all major ions, total dissolved solids (TDS), nitrate, 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).

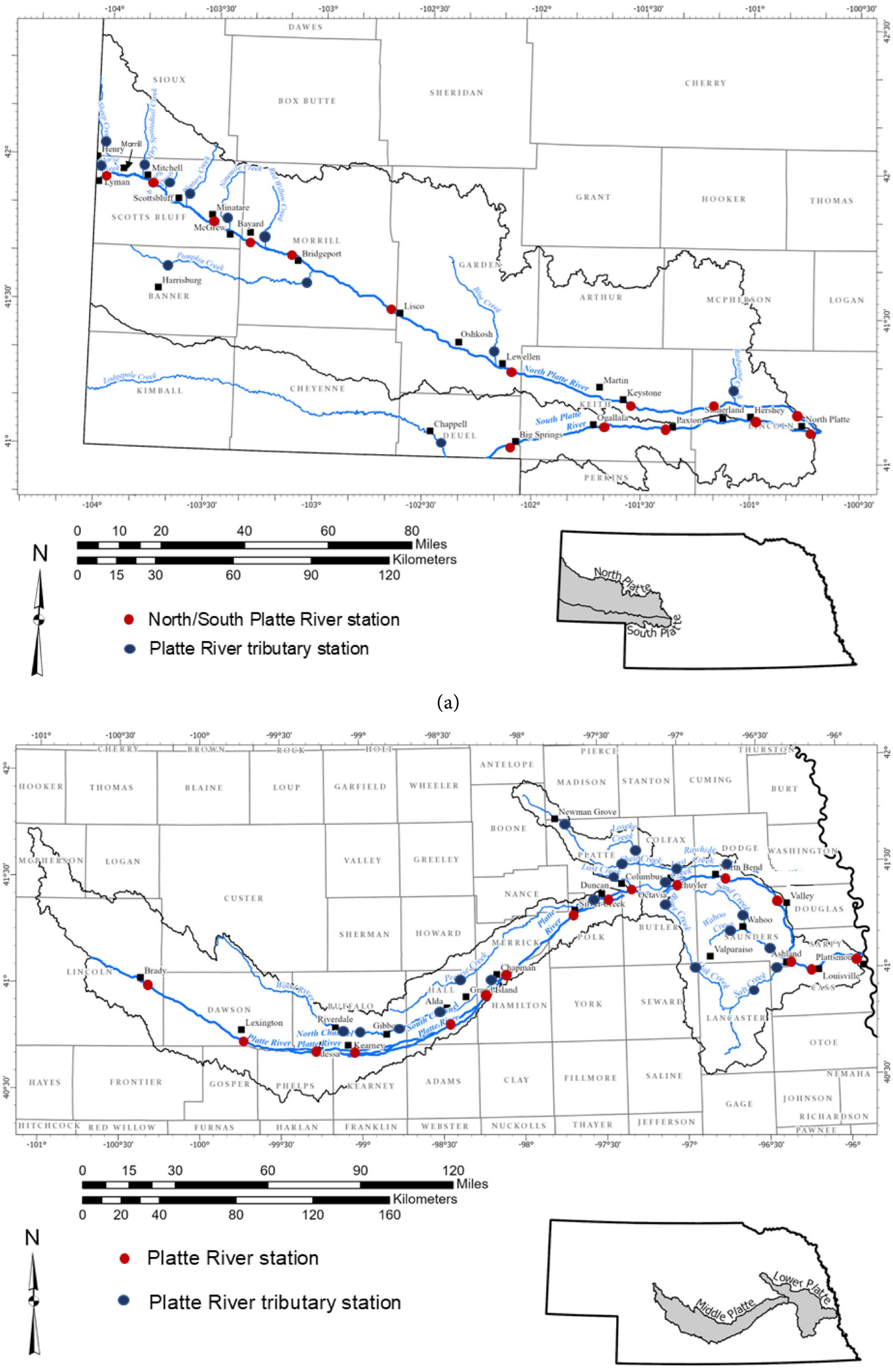
This study evaluates historical major-ion data collected by the NDEC for the expansive Platte River watershed located throughout N-S central Nebraska from its western to its eastern (downgradient) boundaries. Major-ion data for the three river systems and 22 tributaries, collected during the period April 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 Platte River systems occur in the central Great Plains of North America.

The objective of this study was to comprehensively evaluate and interpret the hydrogeochemical properties of the extensive legacy STORET (STOrage and RETrieval) data and to integrate pertinent geological and hydrological information for the Platte River watershed 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 expansive Platte River watershed.

2. Study Area Description

The study area, the Platte River watershed in Nebraska (**Figures 1(a)-(b)**), encompasses almost all or parts of the following counties: Sioux, Banner, Morrill, Cheyenne, Garden, Deuel, Arthur, Keith, McPherson, Lincoln, Custer, Frontier, Gosper, Phelps, Buffalo, Kearney, Howard, Hall, Adams, Boone, Nance, Merrick, Hamilton, Platte, Polk, Colfax, Butler, Dodge, Saunders, Lancaster, Douglas, Sarpy, and Cass, and covers approximately 1.06 × 10^5 km^2 (40,800 mi^2) (MRBC 1976).

French explorers in the early 1700s named the Platte River *rivière plate* ("flat river"), the probable origin of the name Platte River. An American Indian tribe, the Otoe, named the Platte River *flat water*. The Platte, over most of its length, is a broad, shallow, meandering, braided stream with a sandy bottom and many islands. During the pioneer days of the 1800s, a humorous description of the Platte was "a mile wide at the mouth, but only six inches deep."



(a)

(b)

Figure 1. Platte River watershed in Nebraska showing the surface-water sampling locations and tributary streams.

The Platte River watershed in Nebraska encompasses 11 hydrologic unit subbasins contained collectively in the 1018 North Platte subregion, 1019 South Platte subregion, and 1020 Platte subregion. Each hydrologic unit possesses an eight-digit hydrologic unit code (HUC) (USGS, 1976).

The Platte River watershed resides in the Great Plains physiographic province in North America (Fenneman, 1946). The study area lies predominantly within the following topographic regions of Nebraska: 1) valley; 2) valley side slopes; and 3) bluffs and escarpments (Korus et al., 2013). The valley side slopes occur primarily in Sioux, Scotts Bluff, Banner, and Morrill Counties. Bluffs and escarpments occur in Sioux, Scotts Bluff, Banner, Morrill, Garden, Keith, Lincoln, Hamilton, Polk, Butler, Saunders, Washington, Douglas, Sarpy, and Cass Counties. The North Platte River in Scotts Bluff County flows in a valley about 305 m (1000 ft) deep. The valley floor is 8-13 km (5-8 mi) wide (Yost et al., 1968).

The study area has a temperate, subhumid, midcontinental climate that is characterized by wide seasonal variation. Winter temperatures below −18˚C (0˚F) and summer temperatures higher than 35˚C (95˚F) are common. The average annual temperature is about 11˚C (51˚F) (Paden, 1978). The mean annual precipitation in the watershed ranges from about 38 cm (15 in.) in the extreme west to about 76 cm (30 in.) in the east (Oregon State University, 2022). Precipitation is highest during May, June, and July in response to seasonal weather patterns. Annual free-water evaporation averages about 137 cm (54 in.), and approximately 74% of the total (~100 cm) occurs during the six-month period from May through October (Mitchell et al., 1974).

2.1. Geology

The uppermost Mesozoic (encompassing the Cretaceous Period) and Cenozoic (Tertiary and older) geological bedrock units found in the study area encompass, from younger to older, the: Ogallala Group, Arikaree Group, White River Group, Pierre Shale (Mesozoic age), Niobrara Formation, Carlile Shale, Greenhorn Limestone (not described), Graneros Shale (not described), and Dakota Group (**Figure 2**).

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 the Late Cretaceous (Condra & Reed, 1959; Brown et al., 1980; Engberg, 1984). This formation approaches 43 m (98 ft) in thickness in eastern Nebraska (Druliner & Mason, 2001). The Dakota is the uppermost bedrock in the Platte River valley in Dodge and Saunders 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, 2019).

The Niobrara Formation is the uppermost bedrock in the Platte River valley in parts of Hamilton, Merrick, and Polk Counties. It consists primarily of chalk, limestone, and shale with a 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, 2019).

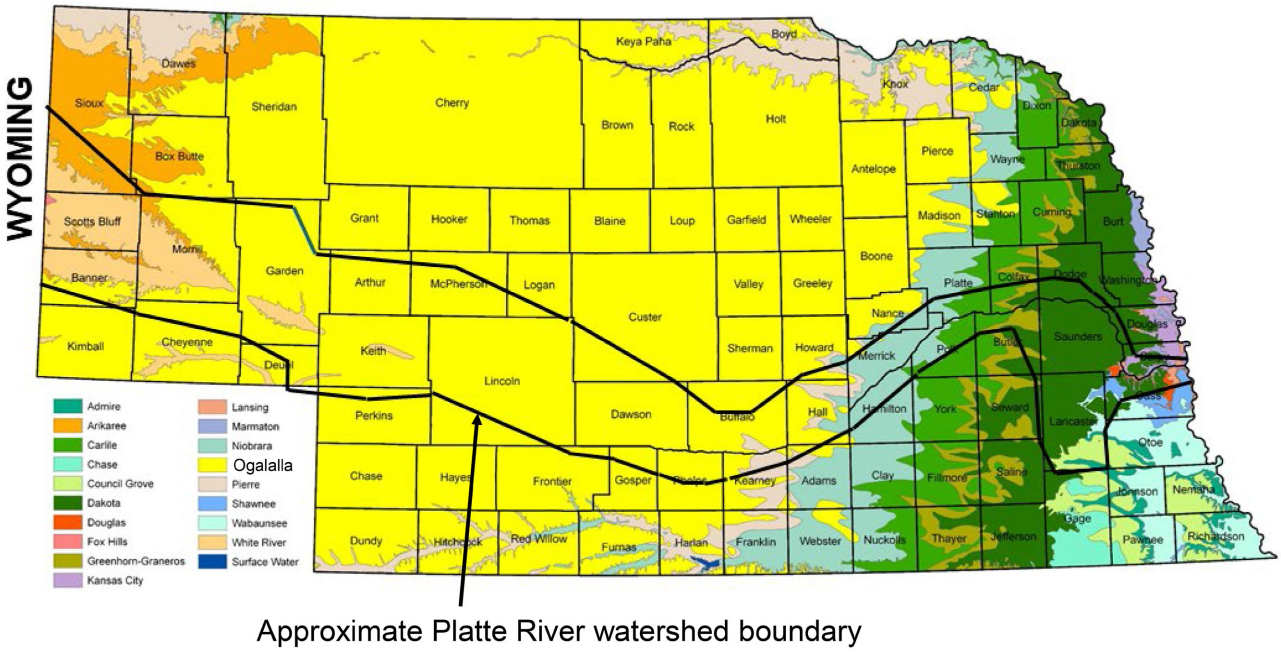


Figure 2. Uppermost geologic units in the Platte River watershed in Nebraska.

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

The Cenozoic (66 million years ago and younger) includes the Neogene and Paleogene periods (collectively referred to as the Tertiary age) bedrock units found in the study area and encompasses, from younger to older: the Ogallala Group, Arikaree Group, and White River Group (**Figure 2**).

The White River Group consists of clay, claystone, silt, and siltstone deposited in fluvial, eolian, and lacustrine environments. It is predominantly volcaniclastic but includes light-colored bentonitic variations (USGS, 2019). This Tertiary-age stratigraphic group represents the oldest deposition following the retreat of the Western Interior Seaway (Condon, 2005). The White River Group is the uppermost bedrock under the North Platte River valley in Scotts Bluff, Banner, and Morrill Counties and in narrow bands in Garden and Keith Counties. The Brule Clay (the anchor geologic unit for the Kingsley Dam) is a subunit of the White River Group.

The Arikaree Group is a very fine to fine-grained sandstone. This unit, fluvial and eolian in origin, has typically been eroded away within the study area, but outcrops along the northern boundary of the North Platte River valley in Sioux and Morrill Counties (Swinehart et al., 1985).

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 the Tertiary period. Much of the Ogallala is cemented by calcium carbonate (Eversoll et al., 1988; Goeke et al., 1992).

Unconsolidated silts, sands, and gravels of the Quaternary Period (Holocene and Pleistocene Epochs) overlie the Ogallala Group bedrock in the western and central portions 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 some plains and dissected plains adjacent to the North Platte River and in areas between the North and South Platte Rivers, the Ogallala Group is absent. In these areas, Pleistocene loess (wind-blown silt and clay, predominantly) and 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, which occurred from the Late Cretaceous to the 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).

2.2. Surface-Water and Groundwater Hydrology

The North Platte River system is approximately 300 km (190 mi) in length from the Nebraska-Wyoming border (near Henry, NE) to the confluence with the South Platte River system slightly east of North Platte, Nebraska. The South Platte River system flows about 100 km (62 mi) from the Nebraska–Colorado boundary (Deuel County) to its confluence with the North Platte River near the city of North Platte. The Platte River system stretches approximately 500 km (310 mi) from the confluence of the North and South Platte River systems to its confluence with the Missouri River near Plattsmouth, Nebraska (UN-L, 2023). The Platte River systems and their tributaries drain the largest part of Nebraska and account for most of the state's outflow to the Missouri River (Bentall, 1991).

Tributaries in Nebraska that feed the North Platte River include: Horse Creek, Sheep Creek, Winters Creek, Nine Mile Creek, Blue Creek, Pumpkin Creek, Birdwood Creek, and Rush Creek. Lodgepole Creek is the major tributary of the South Platte River in Nebraska. The headwaters of Lodgepole Creek are located east of Laramie, Wyoming, and its confluence with the South Platte River is at Ovid, Colorado (UN-L, 2023). Discussion of major ion chemistry for the Lodgepole Creek watershed is outside the scope of this article but is found in Atkinson (2018).

Discharge in the Platte River systems and streams tributary to it fluctuates greatly and depends on groundwater/springs, rains, and snowmelt. Brown et al.

(1980) and Buller et al. (1974) reported that the Platte River in Dawson and Buffalo Counties is often dry in the summer. Loss of Platte River flow between Overton and Grand Island monitoring stations is probably due to seepage of river water to the underlying and adjoining aquifer (Bentall, 1991). North Platte River flow is regulated by the release of water from the Kingsley Dam/Lake McConaughy in Keith County. Long-term average (≥30 years) discharge for the North Platte and Platte River systems ranges from 22.9 m^3/s (810 ft^3/s) near the Nebraska-Wyoming border (near Henry) to 187 m^3/s (6590 ft^3/s) at Louisville near the mouth at the Missouri River (**Figure 3**).

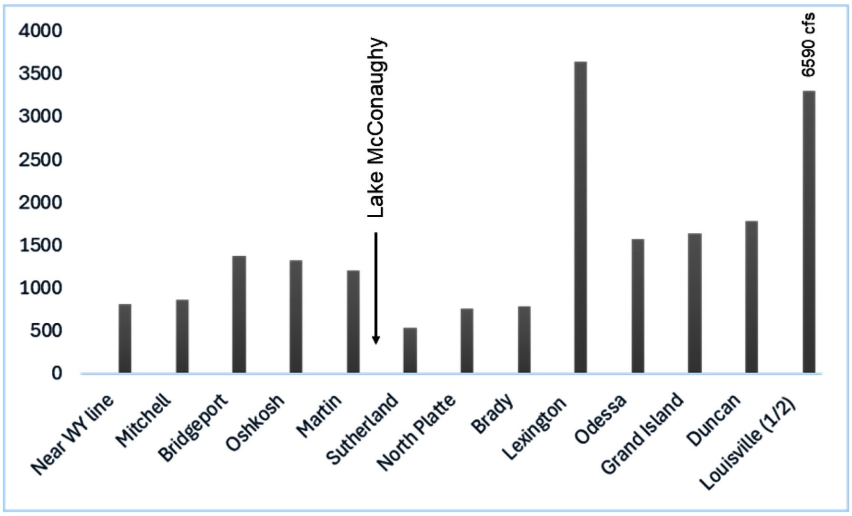


Figure 3. Long-term average discharge values for monitoring sites on the Platte River systems.

2.3. Multipurpose Dams and Reservoirs

Kingsley Dam, in Keith County (41˚13'N - 101˚40'W), was constructed across the North Platte River during the period 1936-1941, and is the largest and tallest dam in Nebraska with a maximum storage capacity of 2.71×10^9 m^3 (2.2×10^6 acre-feet) and a height of 50 m (163 ft). The location of the dam was chosen to be west of Keystone because of the Brule Clay (Paleogene or Tertiary age) present in the area. The first construction step was driving large interlocking sheets of metal over 30 m (100 ft) into the Brule Clay. Loess soil was pumped over these sheets where it hardened to form the dam's structure. Lake Ogallala, immediately downgradient of the dam, was formed from the pumping of the loess soil into Kingsley Dam. The dam is 5 km (3.1 mi) long and contains 2.0×10^6 m^3 (2.6×10^7 yd^3) of loess and clay (Visit Keith County, 2024).

Lake McConaughy, created by Kingsley Dam, is 35 km (22 mi) long, 4.8 km (3 mi) wide in some areas, and up to 43 m (142 ft) deep. At 12,140 ha (30,000 acres), it is Nebraska's largest reservoir. This lake is the source of irrigation water for thousands of hectares (acres) in the Platte River valley (Low Impact Hydropower Institute, 2024).

3. 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. In April 2022, hydrochemical data for this study were retrieved from the STORET Water Quality Portal (WQP), which replaced the Legacy Data Center. The WQP is a cooperative service sponsored by the USGS and USEPA (WQP, 2019).

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). For all analytical results evaluated, an Excel program created by the author calculated the sum of cations (Ca + Mg + Na + K) in meq/L and the sum of anions (HCO_3 + Cl + SO_4) in meq/L and then calculated ion balance errors for each sample analysis. If the difference in the ratios of these two sums (balance error) exceeded about ±5%, individual concentrations were inspected for simple transcription error(s) (TE). If no apparent TE was observed, then the [(0.01) (SC)/∑cations] and/or [(0.01) (SC)/∑anions] ratios were modified accordingly to reduce balance error (∑cations)/∑anions) to < 5%. These quality assurance checks do not resolve all inaccuracy/uncertainty in ion concentrations but are a significant improvement in analytical accuracy for sample analyses with cation-anion balance errors that exceed about 10%. The USGS takes pride in producing sample chemical analyses that result in cation-anion balance errors < 5%.

The USGS considers ion balances within the ±6% range to indicate major-ion analyses of useful quality; however, CABs up to ±12% are still considered acceptable by the USGS (Bartos & Ogle, 2002). Errors over ±12% are outside USGS guidelines, but adjustments were made using the above-described algorithms. The adjusted values were not validated against modern or independent datasets or analytical standards.

For this study, CAB errors for the Platte River range from approximately ±0.1% to +71% (South Platte River at Big Springs). Most high CAB errors are associated with samples collected and analyzed in 1968-1969. For samples collected in 1970-1975, many errors range from about ±1% to ±20%. For analyses that exceeded about ±5% 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.

Visual MINTEQ (Gustafsson, 2009), a Microsoft Windows version of the DOS-based computer code MINTEQA2 prepared for the 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 several Platte River systems and tributary sampling stations.

The hydrogeochemical composition and classification (i.e., hydrochemical facies) of surface water and groundwater are typically illustrated with a Piper trilinear diagram (Piper, 1944). Percentages of major ion concentration data for numerous Platte River and contributing stream analyses were plotted on respective Piper diagrams. A major limitation of the Piper diagram is that it does not depict individual concentrations (only *relative* percentages) of major cations and anions nor indicate TDS. GW_Chart, computer software available for download on the USGS website (USGS, 2012), was used to build the study area Piper trilinear diagrams.

Stiff diagrams (Stiff, 1951) depict major ion composition (as meq/L) and are useful in comparing the ionic composition (hydrochemical facies) and TDS for streams of interest. The polygon size comprising the Stiff diagram is a relative indication of the dissolved solid concentration (Bartos & Ogle, 2002; Atkinson, 2018).

NETPATH (Plummer et al., 1994) is an interactive, public domain program (Fortran 77) used to interpret net mass balance reactions. NETPATH calculates different species of solutions, molal concentrations, and ion activities. It also models chemical reactions and mass transfers along the flow path. It incorporates three USGS aqueous speciation computer codes (WATEQ, WATEQF, and WATEQ4F). The SIs of the phases based on the input of analytical data can also be calculated.

NDEC established a notable number of water-quality monitoring stations along the Platte River systems and their tributaries, then collected numerous water samples from May 1968 to November 1975 and analyzed them in the field and laboratory. The 31 river stations extend geographically from near the town of Henry (close to the Nebraska-Wyoming boundary) to Plattsmouth near the mouth of the river (**Figures 1(a)-(b)**). Also depicted on **Figures 1(a)-(b)** are 34 sampling stations on 22 tributary streams.

4. Results and Discussion

Each of the three Platte River systems has distinct major ion chemistry. Median TDS (calculated) for the North Platte is 410 mg/L, median SO_4 is 101 mg/L, with predominant hydrochemical facies Na-HCO_3 followed closely by Ca-HCO_3 (**Table 1**). For the South Platte, median TDS (calculated) is 1022 mg/L; median SO_4 is 476 mg/L, with predominant hydrochemical facies Ca-SO_4. Minimum and maximum recorded SO_4 concentrations for the South Platte River are 92 mg/L (North Platte station) and 1100 mg/L (Big Springs), respectively. For the Platte River system (downgradient of the confluence of the North Platte with the South Platte), median TDS (calculated) is 482 mg/L, median SO_4 is 160 mg/L, with predominant hydrochemical facies Ca-HCO_3 followed by Ca-SO_4. The significant 58% increase in median SO_4 concentrations for the North Platte and Platte River systems is likely due to mixing of South Platte and Platte River waters.

Table 1. Distribution of four hydrochemical facies across the three Platte River systems.

	Hydrochemical Facies			
River Reach	Ca-HCO_3	Na-HCO_3	Ca-SO_4	Na-SO_4
North Platte River				
State line-Henry	46	27	—	—
Henry-Mitchell	20	68	—	—
Mitchell-Minatare	32	64	—	—
Minatare-Bayard	50	38	—	—
Bayard-Bridgeport	46	50	—	—
Bridgeport-Lisco	48	44	—	—
Lisco-Lewellen	42	58	—	—
Lewellen-Keystone	38	57	—	—
Keystone-Sutherland	41	59	—	—
Sutherland-North Platte	62	36	—	—
South Platte River				
State line-Big Springs	—	—	59	39
Big Springs-Ogallala	—	—	90	10
Ogallala-Paxton	—	—	50	50
Paxton-Hershey	—	—	75	17
Hershey-North Platte	—	—	53	29
Platte River				
North Platte-Brady	40	48	—	—
Brady-Lexington	65	25	11	—
Lexington-Odessa	15	38	19	27
Odessa-Kearney E	22	—	67	—
Kearney E-Alda	—	—	67	22
Alda-Grand Island	—	23	23	38
Grand Island-Chapman	—	—	62	38
Chapman-Silver Creek	—	—	67	33
Silver Creek-Duncan	26	26	30	19
Duncan-Columbus	—	—	50	42
Columbus-Schuyler	80	11	—	—
Schuyler-North Bend	80	10	10	—
North Bend-Valley	79	18	—	—
Valley-Ashland	96	—	—	—
Ashland-Louisville	85	—	—	—
Louisville-Plattsmouth	28	60	—	—

Note: Numbers represent the number of sample analyses.

No sampled tributary sites yielded SO_4 levels nearly as high as those recorded for the South Platte River. Horse Creek at Lyman (Scotts Bluff County) possesses the highest median SO_4 content for the sampled tributaries (210 mg/L), is associated with a median TDS of 685 mg/L, and is a Na-HCO_3 hydrochemical facies.

Salt Creek at Ashland (Saunders County) has the most mineralized flow among the tributaries, with a median Cl content of 1156 mg/L, a median TDS of 2492 mg/L, and a median SO_4 level of 196 mg/L.

The range or delta in SO_4 content station-wide for the 31 Platte River systems stations is significant and highest for the South Platte stations, reaching 972 mg/L at Big Springs and equaling 796 mg/L at the downstream Paxton station. Additionally, numerous North Platte and Platte River stations recorded notable delta SO_4 levels, encompassing 188 mg/L at Minatare (North Platte River) and down-gradient for the Platte River exceeding 180 mg/L at Schuyler and the North Bend station (**Figure 4**). The variations in TDS levels at these sampling stations display similar patterns to the highly variable SO_4 concentrations.

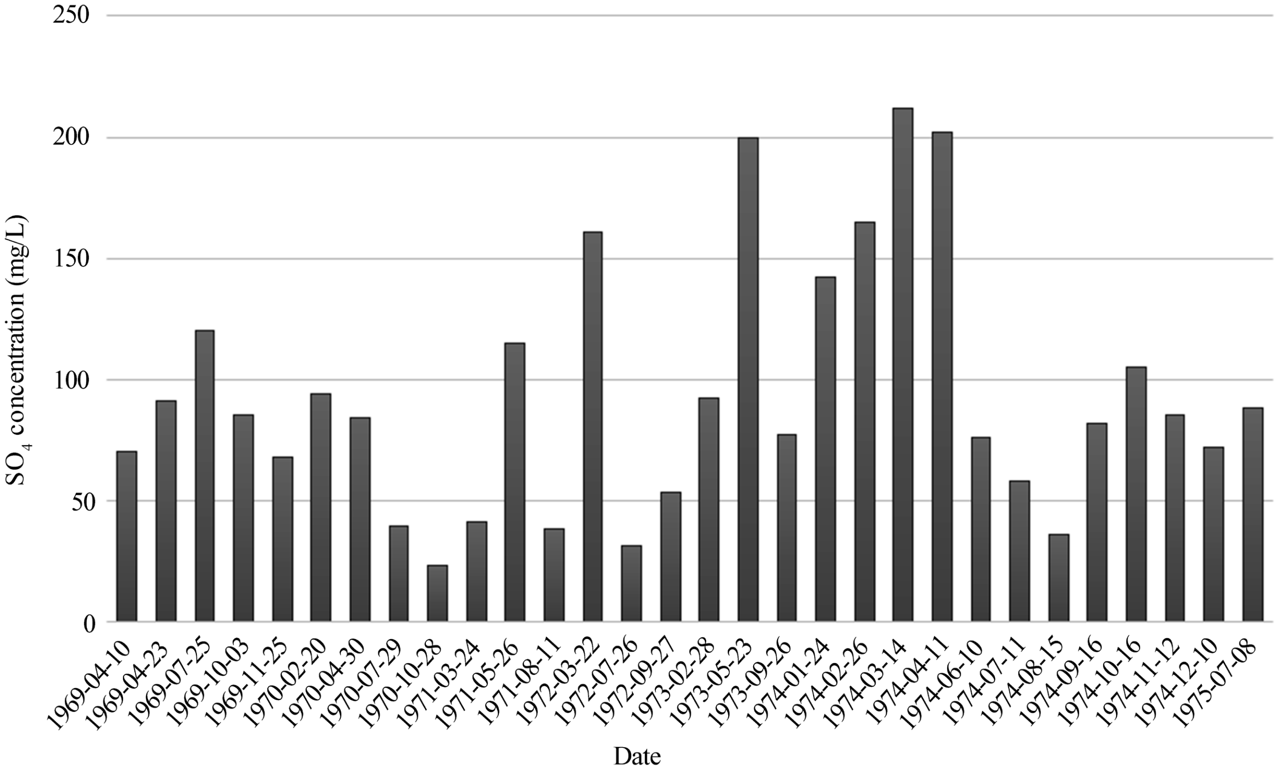


Figure 4. Range in SO_4 concentrations in the Platte River system at North Bend.

Ion exchange is typically one of the important geochemical processes responsible for the concentration of major ions in groundwater and surface water. According to Schoeller (1965, 1967), cation exchange between the groundwater or surface water and its host environment during residence or travel can be understood by studying the chloro-alkaline indices, CAI-1 = [(Cl − (Na + K)/Cl)] and CAI-2 = [Cl − (Na + K)]/(SO_4 + HCO_3 + CO_3) in meq/L. If Na and K ions in water are exchanged with Ca and Mg ions occurring in nearby sediment and rocks, the index value is positive (reverse cation exchange), whereas a negative value indicates aqueous Ca and Mg exchanged with Na and K in minerals and sediment (positive cation exchange) or chloro-alkaline disequilibrium (Handa, 1969; Sujatha & Reddy, 2003; Mohamed et al., 2022). (Home-based water softeners use the positive cation exchange process.) During this cation-exchange process, the host rocks or soils are the primary sources of dissolved solids in the water.

Most of the computed CAI-1 and CAI-2 values for the three Platte River systems water samples evaluated for this study are negative, revealing that chloro-alkaline disequilibrium and positive cation exchange conditions predominate for the Platte River systems throughout Nebraska. However, several Platte River sampling stations recorded more than two positive values, revealing reverse cation exchange reactions. The South Platte River at Big Springs yielded five positive CAI values (5% occurrence), three positive results for the 26 water samples (12%) collected at Louisville, and the Platte River station at Plattsmouth provided 11 positive values, accounting for 44% of the 25 samples collected at this site. The high percentage of positive CAI values for the Plattsmouth sample site suggests a significant Ca and possibly Mg exchangeable content in soil, sediment, or rocks near the mouth of the Platte River.

Several agricultural sources contribute significant levels of SO_4 to the South Platte River discharge, with lesser impacts on the Platte River system (e.g., median 222 mg/L at Alda) and the North Platte discharges. Sulfur is the fourth major nutrient needed by crops. SO_4-S fertilizers dissolve quickly; consequently, SO_4 is readily available to growing crops (ScienceDirect, 2020). A Master of Science thesis from the University of Nebraska-Lincoln in 1962 ("Sulfur Fertilization for Corn Production on Thurman Loamy Sand") strongly suggests that sulfur fertilizer (encompassing SO_4) applications to corn were underway by 1960 in Nebraska, including the Platte River watershed. Due to its mobility, sulfate can also be leached below the root zone by significant rain on permeable (sandy) soils. An additional agricultural source of SO_4 is animal manure; it can provide sulfur along with other plant nutrients to surface water and groundwater (Sulphur Institute, 2024). Additional agricultural and environmental sources of SO_4 and S encompass: soil organic matter, soil minerals, atmospheric deposition, and irrigation water (Jeschke et al., 2017).

Groundwater near an irrigation canal in Frontier County (south side of Platte River) has experienced notable increases in SO_4, Na, Cl, and SC since the advent of irrigation. SC increased by almost 62%; Na increased from 19-49 mg/L; Cl increased from 4.2-21 mg/L; and SO_4 rose from 21-150 mg/L (a 6.1× increase). The authors imply that these increases in SO_4, Na, Cl, and SC levels are attributable to irrigated agriculture (Goeke et al., 1992). Consequently, it seems probable that appreciable SO_4 concentrations recorded at numerous Platte River systems stations are attributable, at least in part, to modern agricultural practices.

Numerous South Platte River water samples hypothetically exceeded the

USEPA Secondary (aesthetic quality) Maximum Contaminant Levels (SMCL) for TDS and SO_4 in drinking water supplies—500 and 250 mg/L, respectively (USEPA, 2019; Atkinson, 2018) (**Table 2**). The Big Springs and North Platte stations recorded the most exceedances for TDS, 95 and 93, respectively, and for SO_4, these stations recorded 95 and 47 exceedances, respectively. The SMCL of 250 mg/L for Cl was only exceeded twice, once each at the Platte River Louisville and Plattsmouth stations, respectively.

Table 2. Exceedances of USEPA secondary drinking water standards for SO_4 and TDS.

Sampling station	TDS exceedance	SO_4 exceedance	Cl exceedance
N. Platte at Henry	11	—	—
N. Platte at Mitchell	20	1	—
N. Platte at Minatare	20	2	—
N. Platte at Bayard	20	3	—
N. Patte at Bridgeport	21	2	—
N. Platte at Lisco	20	—	—
N. Platte at Lewellen	16	2	—
S. Platte at Big Springs	95	95	—
S. Platte at Ogallala	10	10	—
N. Platte at Keystone	3	3	—
S. Platte at Paxton	26	26	—
N. Platte at Sutherland	1	1	—
S. Platte at Hershey	12	12	—
N. Platte at North Platte	1	1	—
S. Platte at North Platte	93	47	—
Platte R. at Brady	5	—	—
Platte R. at Lexington	53	1	—
Platte R. at Odessa	23	4	—
Platte R. at Kearney E	4	1	—
Platte R. at Alda	8	2	—
Platte R. at Grand Island	24	4	—
Platte R. at Chapman	7	1	—
Platte R. at Silver Creek	9	2	—
Platte R. at Duncan	22	1	—
Platte R. at Columbus	11	1	—
Platte R. at Schuyler	5	—	—
Platte R. at North Bend	3	—	—
Platte R. at Valley	2	—	—
Platte R. at Ashland	—	—	—
Platte R. at Louisville	4	—	1
Platte R. at Plattsmouth	7	—	1

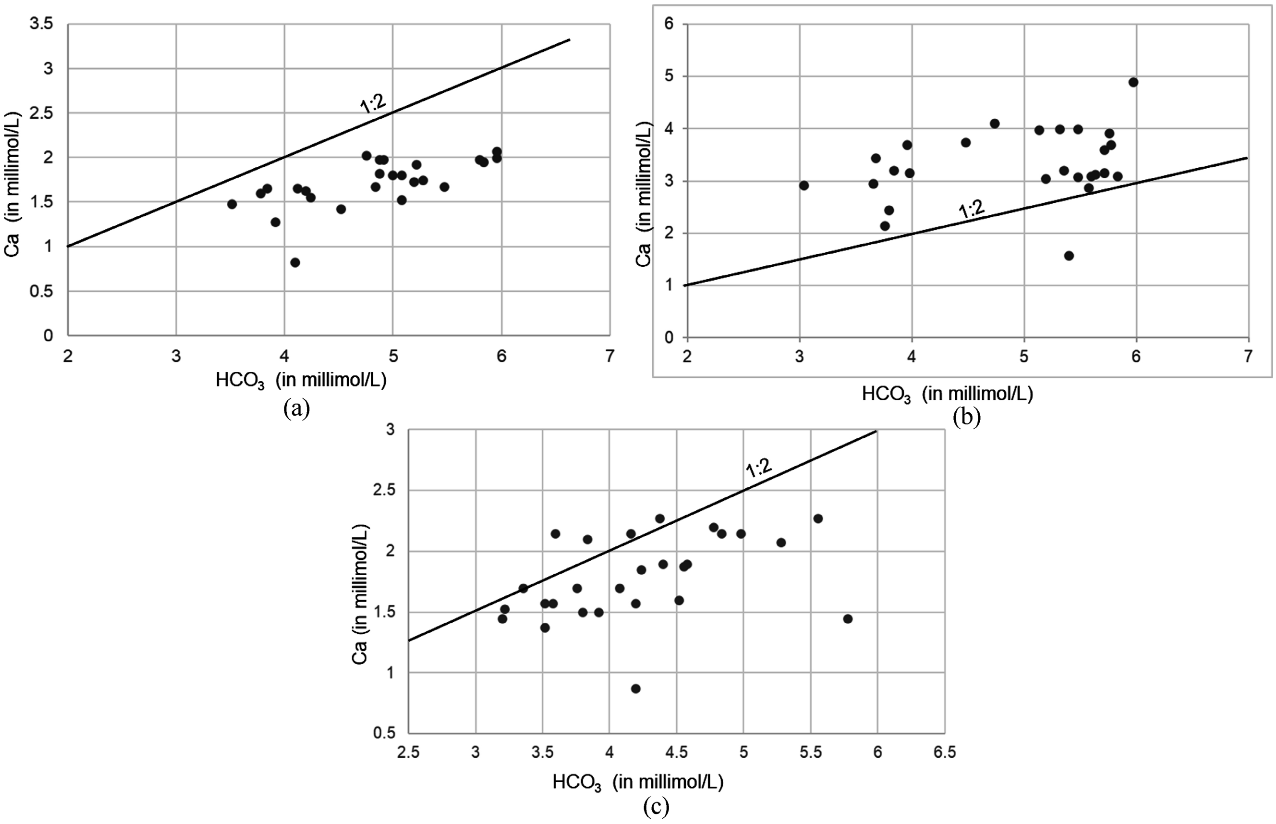
Numerous South Platte River samples yielded mineralization to the brackish level of ≥ 1000 mg/L TDS (Freeze & Cherry, 1979). At the Big Springs station, 87 samples yielded brackish levels. For the next downstream station, Ogallala, all 10 analyses exceeded 1000 mg/L. Downstream at Paxton, 11 samples were classified as brackish. Farther downgradient at the North Platte sampling site, 19 samples exceeded the 1000 mg/L TDS level.

The three Platte River systems flow sampled and analyzed for this study fall into four hydrochemical facies: North Platte samples occur in the Ca-HCO_3 and Na-HCO_3 facies (**Table 1**); South Platte flow falls into the Ca-SO_4 and Na-SO_4 facies; and the Platte River system discharge is captured by all four hydrochemical facies. This is prima facie evidence that the Platte River system discharge is a geochemical mixture of the North Platte and South Platte River systems discharges.

The SI values for calcite, dolomite, and gypsum were calculated using Visual MINTEQ (VM). All VM-computed values for gypsum are negative, documenting unsaturated (dissolving) conditions. For the five South Platte sampling stations, a total of 83 sample analyses were evaluated, yielding all small positive SI values for calcite and dolomite. Median calcite values ranged from 0.78 for the sampling station at North Platte to a high of 1.03 for the Big Springs station. Median supersaturated SI values for dolomite ranged from 1.17 at Hershey to 1.59 at the Ogallala station. For a representative group of North Platte and Platte River systems sampling stations and tributary sampling stations (N. Platte at Henry, Platte at Plattsmouth, Wood R. at Kearney, and at Grand Island) with n = 65, 59 sample analyses (91%) yielded positive calcite SI values with medians ranging from 0.13 at the Wood River (Grand Island station) to a median of 0.65 at Wood River (Kearney station). For dolomite, 44 analyses (68%) yielded positive SI values, with medians ranging from 0.26 for the Wood River Grand Island station to 0.99 for the Wood River station at Kearney. These low SI values comprise a line of evidence for the near thermodynamic equilibrium of the surface waters of the Platte River watershed with slight supersaturated conditions for calcite and dolomite in many locations and undersaturated (dissolving) conditions for gypsum at all sampling stations.

To investigate the primary and possibly secondary processes that affect calcium concentrations, the binary plots 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). 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, which is observed in hard rock formations with an increase in salinity. Hence, calcium's origin 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 North Platte River system, the Mitchell station yields a low (< 0.5) Ca:HCO_3

ratio (data points below the 1:2 equiline) (**Figure 5(a)**). This may be attributable to ion exchange and/or HCO_3 enrichment associated with silicate (feldspar) weathering. The Paxton sampling station, representing the South Platte system, reveals a positive Ca:HCO_3 value (all data points above the Ca:HCO_3 equiline, > 0.5 ratio) (**Figure 5(b)**) suggesting reverse ion exchange and/or possibly weathering of gypsum. The relatively high SO_4 content for the sampling stations along the South Platte lends credibility to the hypothesis of gypsum/anhydrite dissolution. The plot of Ca versus HCO_3 for the Platte River system at Duncan depicts near equilibrium conditions marked by a distribution skewed to the low Ca:HCO_3 ratio (**Figure 5(c)**) possibly caused by ion exchange and/or dissolution of HCO_3 sourced from feldspar(s).



(a)

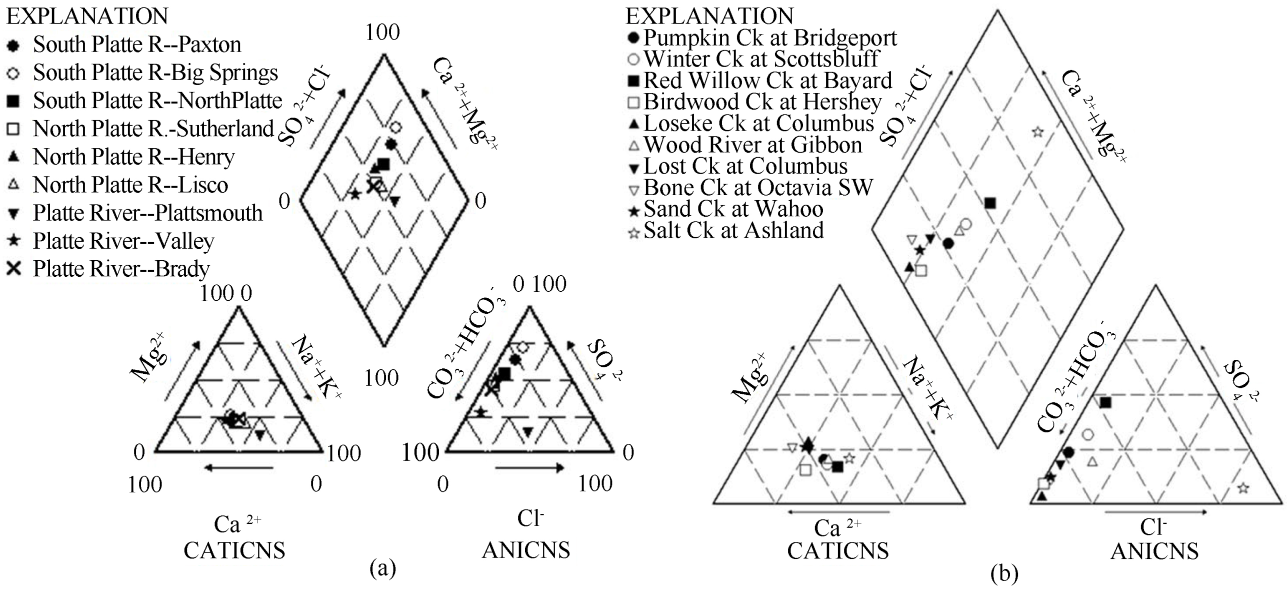
(b)

(c)

Figure 5. Binary Ca:HCO_3 diagrams for the Platte River watershed at: (a) Mitchell; (b) Paxton; and (c) Duncan.

The aqueous geochemistry of nine representative North Platte, South Platte, and Platte River sample analyses is displayed on a Piper trilinear diagram (**Figure 6(a)**). Three data points represent each of the three Platte River systems. Referencing the cation triangle, eight analyses plot in the *no dominant type* subtriangle; only the data point for the Platte River at Plattsmouth lies in the *Na type* subtriangle. The data points in the anion triangle are more spread out with five located in the *no dominant type* subtriangle. Three data analyses reside in the SO_4 *type* subtriangle, and one lies in the HCO_3 *type* subtriangle (Platte River at Valley).

Interestingly, in the diamond portion of the Piper diagram, the three data points for the South Platte stations—Big Springs, Paxton, and North Platte—are in this downstream order and in the order of decreasing SO_4 concentrations.



(a) (b)

Figure 6. Piper trilinear diagram illustrating geochemistry of representative sample analyses for: (a) nine Platte River sampling stations; and (b) 10 tributary sampling stations.

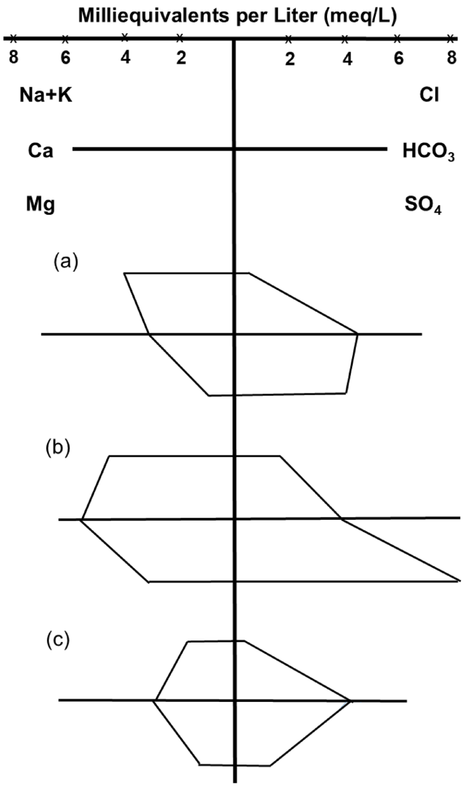


Figure 7. Stiff diagrams illustrating the geochemistry of samples collected on July 23, 1974, at: (a) North Platte at Lisco; (b) South Platte River at Paxton; and (c) Platte River at Valley.

Referencing the Piper diagram for the Platte River tributaries (**Figure 6(b)**), eight of the 10 data points occur in the no dominant type subtriangle for cations. The remaining two analyses (Birdwood Creek and Wood River at Gibbon) fall in the Ca type subtriangle. Eight data points reside in the HCO_3 type subtriangle of the anions triangle. The Red Willow Creek sample plots in the no dominant type anion. The Salt Creek analysis is high in Cl and consequently occurs in the Cl type subtriangle. The primary difference between the Piper diagrams for the Platte River systems and its tributaries is the number of samples falling in the HCO_3 type subtriangle—two for the tributaries and eight for the Platte River systems. All three of the South Platte River samples plot in the SO_4 type anion subtriangle because of notable SO_4 concentrations.

The Stiff diagram illustrates three Platte River systems analyses—one representative each for the North Platte, the South Platte, and the Platte River. The North Platte analysis, Lisco sampling station (**Figure 7(a)**), possessing the Na-HCO_3 hydrochemical facies, also carries a high SO_4 content—196 mg/L. The South Platte sample, Paxton station (**Figure 7(b)**), is dominated by SO_4, consequently a Ca-SO_4 hydrochemical facies. The Platte River sample, Valley station (**Figure 7(c)**), is the Ca-HCO_3 hydrochemical facies, commonly occurring at this point on the Platte River system.

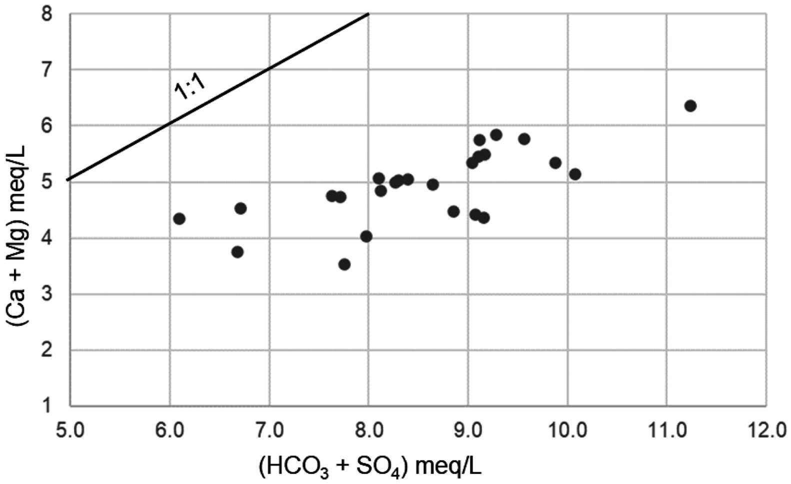


Figure 8. Binary diagram of (Ca + Mg) versus (HCO_3 + SO_4) (in meq/L) for the North Platte River Mitchell station.

Silicate (feldspar) rock weathering plays a key role in determining the major ion chemistry of groundwater (especially in igneous aquifers) 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 groundwater in accordance with Dehnavi et al., (2011) [Equation (1)]:

$$\begin{aligned}&2NaAlSi_3O_8\,(\text{albite}) + 2H_2CO_3 + 9H_2O\\&\Rightarrow Al_2Si_2O_5\,(OH)_4 + 2Na + 4H_4SiO_4 + 2HCO_3^-\end{aligned} \tag{1}$$

Numerous 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, or ion exchange is a second potential geochemical process.

Scatter diagrams of (Ca + Mg) versus (HCO_3 + SO_4) for all Platte River (North, South, and Platte systems) sampling stations plot below the 1:1 equiline, encompassing the Platte River at Mitchell (**Figure 8**). These study-area geochemical scatter diagrams 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 Platte River watershed 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 Platte River watershed.

Table 3. Ten plausible models generated by NETPATH to simulate the significant decrease of SO_4 concentrations downgradient along the South Platte River.

Model no.	Calcite	Dolomite	Gypsum	Albite	NaCl	CO_2 (g)	Dilution factor
1	1.113	—	−1.284	—	−0.362	1.211	2.35
2	0.971	0.112	−1.042	—	—	1.582	2.54
3	1.113	—	−1.071	−0.362	—	1.211	2.35
4	1.575	−0.361	−2.071	—	−1.542	—	1.74
5	1.575	−0.361	−2.071	−1.542	—	—	1.74
6	0.359	0.589	—	—	1.561	3.184	3.34
7	0.359	0.589	—	1.561	—	3.184	3.34
8	—	0.563	0.616	—	2.476	4.122	3.82
9	2.127	−0.875	−2.938	—	−2.967	−1.233	—
10	2.127	−0.875	−2.938	−2.967	—	−1.233	—

Negative number indicates amount of mineral precipitating; positive number indicates amount of mineral dissolving. For carbon dioxide gas, negative number indicates degassing; positive number indicates carbon dioxide gas being dissolved. Mineral mass transfers are in millimoles per liter (mmol/L). Conversion of mmol/L to mg/L is obtained by multiplying by the gram formula weight—mass transfer not simulated.

NETPATH models and quantifies chemical reactions that are consistent with the initial geochemical data along a flow path. For a set of minerals or gas phases hypothesized to be the reactive phases in the system, NETPATH calculates the mass transfers in every possible combination of the selected phases that account for the observed changes in the selected chemical compositions observed along the flow path. The six ubiquitous minerals and gas phase selected for Platte River watershed modeling are enumerated in **Table 3** including calcite and CO_2 (g).

To investigate potential geochemical interactions that may contribute to the observed significant decrease in SO_4 content in South Platte flow from Big Springs to slightly beyond the last monitoring station along the South Platte (North Platte station), NETPATH modeling was performed. The chosen phases are: calcite, gypsum, CO_2 (g), NaCl, dolomite, and albite (a common Na plagioclase feldspar). Two model environments were simulated—one allowing dilution and evaporation and another not allowing dilution or evaporation. Eight models simulating variable dilution (models one through eight) and two simulating no dilution conditions (models nine-ten) were retained (**Table 3**). For most of the models, calcite is dissolving and gypsum is precipitating. For three models (six-eight), CO_2 is dissolving at significant concentrations (3.2-4.1 mmol/L). The author posits that models one through five are probably the most realistic because dilution (inflow) is highly plausible in this downgradient model setting but not above a 3.0 dilution factor. Geochemical modeling rarely leads to unique solutions (Parkhurst & Plummer, 1993); consequently, these modeling results should be interpreted judiciously.

5. Conclusion

This study presents an analysis and interpretation of the extensive legacy (1968-1975) major ion and related water-chemistry data for the Platte River watershed in Nebraska, encompassing 22 tributaries. The Platte River watershed comprises three river systems: the North Platte, the South Platte, and the Platte River. Each of the three river systems possesses a singular geochemistry; the South Platte has yielded significant SO_4 levels ranging from 92-1100 mg/L with a median of 476 mg/L, and the median TDS content is 1022 mg/L. Across stations, delta SO_4 concentrations in the South Platte range from 135 mg/L downstream at North Platte to 972 mg/L upstream at Big Springs. For the North Platte River system, the median SO_4 equals 101 mg/L, and the median TDS is 410 mg/L. Median SO_4 and TDS values are 160 and 482 mg/L, respectively, for the Platte River system. For most North Platte and Platte River stations, the range (delta) in SO_4 concentration for individual stations is at least 100 mg/L, and at the Platte River's North Bend station it reaches 189 mg/L. Probable sources of the high and variable SO_4 in South Platte and Platte River discharges encompass: agricultural sources (fertilizer, irrigation water, livestock manure) and soil organic matter and SO_4 minerals, e.g., gypsum, anhydrite.

The three Platte River system discharges sampled and analyzed for this study fall into four hydrochemical facies: North Platte samples occur in the Ca-HCO_3 and Na-HCO_3 facies; South Platte flow falls into the Ca-SO_4 and Na-SO_4 facies; and the Platte River system discharge is captured by all four hydrochemical facies. This provides clear evidence that the Platte River system discharge is a hydrochemical mixture of the North Platte and South Platte River discharges.

Two binary graphical methods suggest that the predominant geochemical process throughout much of the Platte River system is the dissolution of silicate minerals (feldspars). Additionally, in the South Platte River, the dissolution of gypsum and anhydrite is likely a major geochemical weathering process, resulting in SO_4 concentrations reaching 1100 mg/L.

Hydrogeochemical modeling indicates that the SIs for calcite and dolomite for the Platte River systems and their tributaries are typically low positive values (~0.1 - 2.0), suggesting mildly 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 of the Platte River systems and their tributaries.

NETPATH computer modeling suggests that the significantly declining SO_4 concentrations along the South Platte from near the Nebraska-Wyoming border (Deuel County) to its confluence with the North Platte River near North Platte are principally dilution (surface and groundwater recharge), gypsum precipitation, and calcite and CO_2 (g) dissolution.

The extensive STORET database for major cations and anions, TDS, and contaminants (e.g., nitrate, trace metals) encompasses a sound historical hydrochemical baseline for the expansive Platte River watershed. This valuable database can inform current and near-term water resource investigations and management to encompass nonpoint source pollution.

The significant SO_4 levels (up to 1100 mg/L) in the South Platte River flow during the study period merit a recommended follow-on study to identify current SO_4 concentrations, and if these river concentrations remain high, recommend designing and performing a study to identify and evaluate all appreciable SO_4 sources to South Platte River discharge.

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

There is no conflict of interest.

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