AN ABSTRACT OF THE THESIS OF

Damon K. Williams for the Master of Science in Physical Science presented on May 15, 1999.

Title: Major Ion Concentration for Bear Den Creek, Fort Berthold Indian Reservation, North Dakota: 1969-1996

Abstract approved: ______________________

The analysis of major ion concentration is a practical method in the determination of the surface water quality. Plots of major ion concentration as a function of discharge have been analyzed for Bear Den Creek for the years between 1969 - 1996. The resulting data for Bear Den Creek, an ephemeral stream located on the Fort Berthold Indian Reservation, North Dakota, have established a baseline of naturally occurring major ion concentration with current conditions of low population and the primary landuse of ranching.

Comparison of alkalinity to hardness (A/H) ratios for Bear Den Creek have been analyzed to explore possible acidification of the surface water. Data from 1989-1996 have indicated that acidification is not a factor in the overall water quality of the Bear Den Creek drainage basin, which is consistent with the current conditions.

The results of the major ion concentration analysis have been compared with the North Dakota Class I stream standards, the most stringent of maximum allowable concentrations for Na^+, Cl^-, and SO_4^{2-}. The data compared unfavorably with the overall standards for the three ions, and is an indication Bear Den Creek does not meet the overall standards of a Class I stream.

This study also serves as part of the Fort Berthold Watershed Project, a joint effort of the Three Affiliated Tribes and Emporia State University. Funded through an Environmental Protection Agency Environmental Education Grant, the project goal is to build the environmental capacity of the Three Affiliated Tribes, Fort Berthold Indian

Reservation, regarding the importance of watershed management and to increase public access to watershed management.

MAJOR ION CONCENTRATION FOR BEAR DEN CREEK, FORT BERTHOLD INDIAN RESERVATION, NORTH DAKOTA: 1969-1996.

A Thesis

Presented to

The Division of Physical Sciences

EMPORIA STATE UNIVERSITY

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of the Requirements for the Degree

Master of Science

By

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I would also like to thank my parents for their support and encouragement. Special recognition to my father, Russell J. Williams, for his motivation and inspiration in completing this thesis and all my educational goals. *Mahalo.*

PREFACE

All units of this study are expressed in metric units, with the exception of discharge. Units of discharge are expressed in cubic feet per second or cfs. CFS is used here as it is a standard hydrologic unit for expressing discharge.

All aspects of this study utilized the Microsoft (MS) Office® Version 7 software package. This included MS Word (all text), MS Excel (all tables and plots), and MS Access (database).

Chapter 1

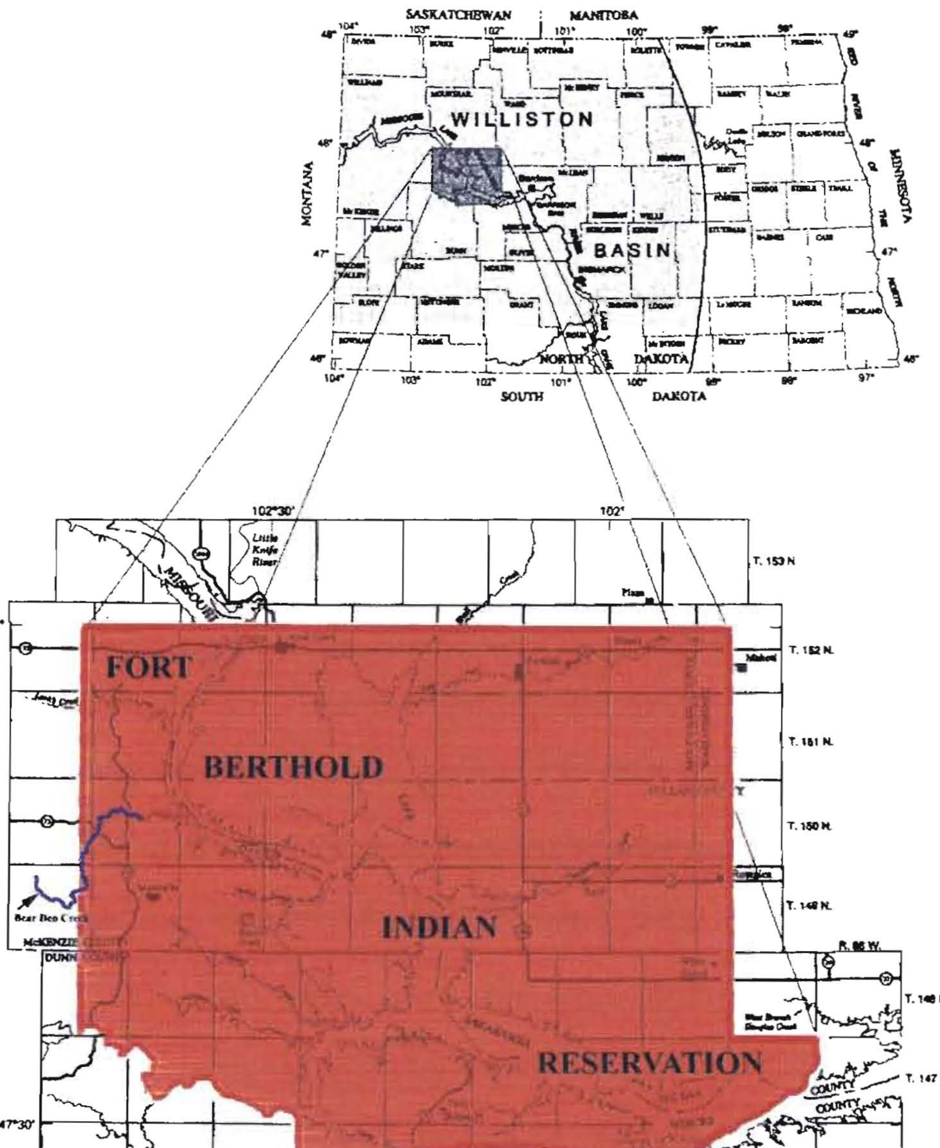
Introduction

The analysis of the chemical composition of water is a practical method in determining the overall quality of surface water. One aspect of the chemical composition of water is major ion concentration. Major ions are ions commonly found in all naturally occurring water bodies, with the exception of rainwater, in concentrations of > 1 mg/L (Schroeder, 1992). One method in determining water quality as related to major ion concentration is the comparison of concentration to discharge in a particular surface water body.

This study compares the major ion concentrations vs. discharge for Bear Den Creek. Bear Den Creek is a small, ephemeral stream on the lands of the Three Affiliated Tribes, Fort Berthold Indian Reservation, located in western North Dakota (Fig. 1). Bear Den Creek was chosen as the study site because of the large amount of water data collected by the United States Geological Survey (USGS) since June 1966. This study utilizes data from the United State Geological Survey between years 1969 to 1996 in order to establish a baseline of naturally occurring major ion concentration with the current rural population and landuse. The baseline will be useful to the Three Affiliated Tribes in evaluating changes in water quality with any future changes in land use or population. The Three Affiliated Tribes is currently investigating the possibility of oil exploration on the Reservation. The baseline may assist in the monitoring of this type of

Map 1. Fort Berthold Indian Reservation, North Dakota.
(Taken from Cates and Macek-Rowland, 1998)

The Fort Berthold Indian Reservation is highlighted in red. Bear Den Creek, located along the western boundary of the Reservation is highlighted in blue.



SASKATCHEWAN
MANITOBA
MONTANA
MINNESOTA
WILLISTON
BASIN
NORTH
DAKOTA
SOUTH
DAKOTA
102°30'
102°
48°
47°30'
FORT
BERTHOLD
INDIAN
RESERVATION
Bear Den Creek
T. 153 N.
T. 152 N.
T. 151 N.
T. 150 N.
T. 149 N.
T. 148 N.
T. 147 N.
T. 146 N.
R. 95 W.
R. 94 W.
R. 93 W.
R. 92 W.
R. 91 W.
R. 90 W.
R. 89 W.
R. 88 W.
R. 87 W.
R. 86 W.
0 1 2 3 4 5 10 MILES

activity and its effects on the major ion concentration and overall surface water quality on the Reservation.

Water chemistry of ground and surface water resources vary within the Bear Den Creek drainage basin. Ground water originates from the Sentinel Butte aquifer, an aquifer of Paleocene age underlying much of the Reservation. Waters of the Sentinel Butte aquifer vary from sodium bicarbonate type to calcium magnesium sodium sulfate type water (Cates and Macek-Rowland, 1998). Surface water of Bear Den Creek is of a sodium sulfate type. Sodium sulfate, in the form of the mineral mirabilite, is found in glacial deposits of areas in the northern Great Plains (Murphy, 1996). The sodium sulfate type water enters Bear Den Creek drainage basin by means of groundwater recharge.

Acidification of natural surface waters is also an important concern and may be used as an indicator of overall water quality. The data collected for the analysis of major ion concentration can also be used to ascertain if acidification of Bear Den Creek is occurring. The method used to indicate acidification is the analysis of the HCO_3^- / [Ca^{2+} + Mg^{2+}] or alkalinity to hardness (A/H) ratio (Schindler, 1988). If acidification is occurring, the hardness (Ca^{2+} + Mg^{2+}) of the surface water will increase as alkalinity (HCO_3^-) decreases resulting in a lower A/H ratio.

The Three Affiliated Tribes government of the Fort Berthold Indian Reservation, has begun its own sampling and monitoring program for surface water as the Tribes prepare to implement Tribal water quality standards. To assist the Tribes in its efforts, one goal of this project was to organize a database containing all water quality data recorded from Bear Den Creek, in combination with water quality data from six other streams located on the Fort Berthold Indian Reservation. This data has been entered into a Microsoft Access® database and will be on file with the Three Affiliated Tribes upon completion of this project. The database will consist of data, website access, and common queries to allow Tribal personnel and the general public access to surface water quality data.

This study was as part of the Fort Berthold Watershed Project, a joint effort of the Three Affiliated Tribes and Emporia State University. The project is funded through an Environmental Protection Agency Environmental Education Grant. The goal of the project is to build the Three Affiliated Tribes environmental capacity by educating tribal members regarding the importance of watershed management and to increase public access to watershed information. This is to be accomplished by the preparation of an accurate Reservation water quality database and the construction of an INTERNET website. The project has a dual focus: 1. to organize and summarize existing watershed information to increase accessibility, and 2. to inform elementary and secondary educators and the tribal community about the availability and use of watershed resource information. This paper partially fulfills the second goal of the grant.

Chapter 2

Methods and Materials

The United States Geological Survey (USGS) has operated a gaging station and sampling program on Bear Den Creek since June 1966. The data collected fall into two general categories; physical data (discharge, stream width, depth, temperature, etc.) and chemical composition (dissolved constituents). For the purposes of this study, only the major dissolved ion concentrations will be addressed.

Database

The USGS data used in the study of Bear Den Creek have been organized with water quality data from six other streams located on the Fort Berthold Indian Reservation in the form of a Microsoft Access® data base. It is hoped that the creation and use of this database will assist the Tribe in future efforts to monitor and regulate the surface waters of the Reservation.

Major Ions

Major dissolved ions are ions that are commonly found in all natural occurring water bodies, with the exception of rainwater at concentrations of > 1 mg/L. (Schroeder, 1992). There are three major sources for ions in water: rocks and soils of drainage basins, atmospheric deposition, and human activities. These sources are affected by five major factors: climate, geology, topography, biota, and time (Peters, 1984).

In the Bear Den Creek drainage basin, the principal source of major ion deposition is the rock and soil of the drainage basin. The Bear Den Creek drainage basin has a low population and the primary land use is ranching. These two conditions indicate the primary factors affecting major ion deposition of Bear Den Creek are climate and the geology of the area. The ions are introduced into ground and surface water by chemical, biological, and physical processes (weathering), which break down rock and soil, and release the ionic compounds present in minerals. The major dissolved ions include calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulfate (SO_4^{2-}), carbonate (CO_3^{-}), and bicarbonate (HCO_3^{-}). Brief descriptions of the ions and possible natural sources for each are discussed below.

Calcium, Ca^{2-}

Calcium ions, along with magnesium ions, contribute to the overall hardness of water. Hardness reflects the total Ca^{2+} and Mg^{2+} present within a sample. As the hardness increases, the sudsing ability of soaps and detergents decreases. The hardness of water is of commercial importance and only in extremely high concentrations do human health concerns arise. Some natural sources of Ca^{2+} include gypsum ($CaSO_4 * 2 H_2O$), limestone ($CaCO_3$), and dolomite ($CaMg (CO_3)_2$ (Hounslow, 1995).

Magnesium, Mg^{2+}

Magnesium ions as stated above contribute to the overall hardness of water. Sources of Mg^{2+} include olivine ($(Mg,Fe)_2SiO_4$), dolomite ($CaMg(CO_3)_2$), and mica ($K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$) (Hounslow, 1995).

Sodium, Na^{+}

Sodium ions are common in all natural waters. High concentrations of sodium are possible because it is naturally abundant and highly soluble. High sodium levels in water destined for human consumption are undesirable. A very high concentration of sodium can produce nausea and is considered an emetic - to induce vomiting (Kegley and Andrew, 1998), and also contributes to undesirable rust. Possible sources of sodium include halite (NaCl) and some sodic feldspars such as plagioclase - variety albite ($NaAlSi_3O_8$) (Hounslow, 1995).

Potassium, K^+

Potassium ions are also common in natural waters. Concentrations can be high, as it is naturally abundant and highly soluble. Common sources for potassium include feldspars, micas, and clays (Kegley et al., 1998).

Chloride, Cl^-

Chloride ions are common in all natural waters. Chloride plays an important role in the natural electrolytic balance or balance of essential ions in humans (Kegley et al., 1998). It is abundant in wastewater and may be used as an indicator for pollution sources. Sources of chloride include wastewater, hot springs, and mineral salts present in sedimentary rocks (Kegley et al.,1998).

Sulfate, SO_4^{2-}

Sulfate ions are common in low concentrations in all natural waters. Elevated concentrations may occur in wastewater from mining activities or where the mineral gypsum ($CaSO_4$) is naturally abundant. Sulfate is not toxic to humans and wildlife at naturally occurring concentrations of less than 1000 mg/L. A possible effect of SO_4^{2-} concentrations > 500 mg/L is a bitter taste (Kegley et al., 1998). Common sources for SO_4^{2-} include atmospheric deposition (H_2SO_4), pyrite (FeS_2), gypsum ($CaSO_4 * 2H_2O$) and anhydrite ($CaSO_4$) (Hounslow, 1995).

Bicarbonate, HCO_3^- and Carbonate, CO_3^{-2}

Bicarbonate and carbonate ions are common in all natural waters. Concentrations are typically low except in areas where carbonate minerals are abundant. The presence of these ions is of commercial concern because upon heating, HCO_3^- is converted to CO_3^{2-}. The CO_3^{2-} then combines with Ca^{2+} and Mg^{2+} to form calcium carbonate ($CaCO_3$), which encrusts the interior of pipes and restricts flows (Kegley et al., 1998).

Sample Analysis

All samples were collected and data were complied by the USGS, although the Environmental Division of the Three Affiliated Tribes has begun cooperative sample collection with the USGS. Analysis of samples was done both in field and in the laboratory. Field data gathered included pH, air and water temperature, and discharge (by means of gaging station recording). All laboratory analysis was collected at the North Dakota State Department of Health in Bismarck, North Dakota.

Analysis Reliability

There are several statistical and quantitative methods to verify the accuracy of data collected during water sampling and analysis. These methods seek to ascertain and identify inconsistencies of analysis methods. For a major dissolved ion concentration, an ionic balance calculation may be performed. This calculation checks the accuracy of samples and is based on the premise that the solution analyzed is electrically neutral (Hounslow, 1998).

The ionic balance calculation compares the sum of cations (positively charged ions) and the sum of anions (negatively charged ions) within a sample. The sums of cations and anions must be equal and all ion concentrations must be in units of milliequivalents per liter (meq/L). The unit meq/L represents 1/1000 of an equivalent, where one equivalent represents the number of moles of cationic or anion charge (Hounslow, 1995). The general formula for the ionic balance follows:

$$\text{Ionic Balance} = (\sum C - \sum A) / (\sum C + \sum A) * 100 = (SC - SA) / (SC + SA) * 100$$

$\sum C$ = sum of cations $\sum A$ = sum of anions

The charge balance is expressed as a percentage. For data to be considered acceptable, the calculated percentage should be within + / - 5% of zero, where zero represents an equal amount of cations and anions present within the sample.

If the charge balance percentage is greater that 5%, then the following errors may have occurred (Hounslow, 1995):

1) The analysis is inaccurate.
2) Other constituents (ions) are present and were not used in charge balance calculation.
3) The water is very acidic and the H^+ ions were not included in analysis.

4) Organic ions are present in significant concentrations.

The meq/L conversion formula for each major ion is listed in Table 1.

For this study, an ionic balance was performed for selected data collected in between 1989 - 1996 (Table 2). Previous to 1989, bicarbonate and carbonate concentrations were not regularly included in the data collection of Bear Den Creek water samples. The data for the years of 1989 - 1996 fall within the 5% accepted range, with the exception of the 10/13/93 sample. A possible explanation for this discrepancy is the presence of a cation not accounted for in the ion balance calculation. Overall, the ion balance calculations indicate the data are accurate. Further study on other aspects of water quality of Bear Den Creek may require additional verification of data accuracy.

Table 1. Ion Conversion Unit Conversion.
Conversion table for milligram / Liter (mg/L) to milliequivalent / Liter (meq/L)

Species or Ion	Atomic or Molecular Weight (mg/L)	Valence or Charge	Conversion Formula
Calcium, Ca^{2+}	40.080	2	Meq/L = ([Ca^{2+}] mg/L * 2) / 40.080
Magnesium, Mg^{2+}	24.132	2	Meq/L = ([Mg^{2+}] mg/L * 2) / 24.312
Sodium, Na^{+}	22.991	1	Meq/L = ([Na^{+}] mg/L * 1) / 22.991
Potassium, K^{+}	39.102	1	Meq/L = ([K^{+}] mg/L * 1) / 39.102
Sulfate, SO_4^{2-}	35.453	-2	meq/L = ([SO_4^{2-}] mg/L * 2) / 96.060
Chloride, Cl^{-}	96.060	-1	meq/L = ([Cl^{-}] mg/L * 1) / 35.453
Bicarbonate, HCO_3^{-}	61.016	-1	meq/L = ([HCO_3^{-}] mg/L * 1) / 61.016
Carbonate, CO_3^{2-}	60.008	-2	meq/L = ([CO_3^{2-}] mg/L * 2) / 60.008

Table 2. Major Ion Balance Calculation.
Major Ion Concentration Data for Bear Den Creek,
Fort Berthold Indian Reservation, North Dakota.
Years: 05/08/89 - 08/07/96.
Sample Site: 06332515

Sample Date	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	Cl^{-} meq/L	SO_4^{2-} meq/L	HCO_3^{-} meq/L	CO_3^{2-} meq/L	Sum Cations	Sum Anions	Ion Balance percentage
05/09/89	2.50	2.63	24.79	0.19	0.08	17.07	10.24	0.80	30.11	28.20	3.28
06/14/89	0.80	2.06	27.40	0.15	0.05	16.03	11.52	3.20	30.41	30.80	-0.64
08/22/89	1.10	1.81	21.75	0.21	0.08	12.28	11.80	1.43	24.86	25.59	-1.44
10/25/89	1.35	2.14	28.27	0.16	0.06	15.82	15.00	1.20	31.92	32.08	-0.26
11/30/89	2.40	2.39	29.58	0.17	0.07	17.49	17.86	0.00	34.53	35.42	-1.28
03/05/90	2.00	2.39	26.53	0.11	0.23	14.78	15.41	0.00	31.02	30.42	0.98
04/17/90	1.80	2.14	22.62	0.15	0.10	11.24	12.19	1.60	26.70	25.14	3.01
05/03/90	2.20	2.88	35.67	0.28	0.28	24.98	11.19	1.20	41.02	37.66	4.27
08/02/90	1.30	0.78	10.44	0.19	0.12	6.45	5.72	0.40	12.70	12.70	0.04
11/26/90	2.30	2.55	32.62	0.15	0.24	19.36	18.19	1.20	37.62	38.99	-1.80
12/11/90	2.40	2.39	31.32	0.15	0.23	17.28	19.18	2.40	36.25	39.09	-3.76
03/11/91	1.70	1.65	15.66	0.21	0.10	10.83	8.93	0.40	19.21	20.26	-2.66
06/17/91	1.30	1.56	24.36	0.18	0.01	11.66	10.80	3.20	27.39	25.67	3.25
08/27/91	1.15	1.65	23.49	0.20	0.03	13.53	9.60	2.40	26.48	25.57	1.75
11/20/91	1.50	1.40	18.27	0.20	0.16	11.87	10.80	0.00	21.36	22.83	-3.32
12/10/91	2.35	2.22	29.14	0.15	0.45	16.66	18.19	0.00	33.86	35.30	-2.08
02/19/92	2.45	2.39	27.84	0.16	0.45	13.74	15.77	0.00	32.83	29.96	4.57
04/15/92	1.90	2.06	24.79	0.15	0.17	13.12	15.19	0.57	28.89	29.05	-0.26
06/02/92	0.90	2.30	30.01	0.15	1.81	15.20	14.80	2.40	33.36	34.20	-1.25
07/08/92	1.10	1.40	20.88	0.15	0.25	11.87	10.69	1.03	23.52	23.84	-0.67
10/06/92	1.45	2.22	28.27	0.16	0.08	13.53	17.37	1.13	32.10	32.12	-0.03
11/23/92	1.85	2.06	28.27	0.14	0.59	13.74	16.88	1.27	32.31	32.48	-0.26
05/05/93	1.75	2.30	28.71	0.18	0.08	16.86	16.16	1.83	32.94	34.94	-2.95
06/15/93	1.55	1.48	16.96	0.18	0.07	10.41	10.00	0.80	20.17	21.28	-2.67

Sample Date	Ca^{2+} meq/l	Mg^{2+} meq/l	Na^{+} meq/l	K^{+} meq/l	Cl^{-} meq/l	SO_4^{2-} meq/l	HCO_3^{-} meq/l	CO_3^{2-} meq/l	Sum Cations	Sum Anions	Ion Balance percentage
08/24/93	2.30	2.06	22.18	0.25	0.10	12.91	13.16	0.73	26.79	26.90	-0.21
10/08/93	1.60	2.14	21.75	0.19	0.10	14.78	13.28	1.27	25.67	29.42	-6.81
03/31/94	2.35	1.81	12.61	0.24	0.21	9.16	7.24	0.33	17.01	16.95	0.18
05/09/94	2.50	2.96	26.10	0.20	0.10	14.99	14.18	0.73	31.75	30.00	2.84
08/01/94	0.90	2.06	31.32	0.21	0.13	16.24	13.90	1.73	34.48	32.00	3.74
12/14/94	2.79	2.55	27.40	0.16	0.07	15.41	15.68	0.00	32.90	31.16	2.72
01/25/95	2.25	2.06	26.97	0.12	0.05	14.16	16.19	0.00	31.39	30.40	1.59
04/12/95	2.35	2.39	19.57	0.23	0.14	12.28	10.52	0.60	24.53	23.54	2.06
06/27/95	0.80	2.22	29.14	0.09	0.08	15.82	12.60	2.00	32.25	30.51	2.79
10/26/95	1.50	2.06	26.10	0.15	0.07	14.37	13.60	1.60	29.80	29.64	0.27
08/07/96	1.05	0.82	14.79	0.20	0.09	10.62	6.92	0.00	16.86	17.62	-2.20

Chapter 3

Physical Description and Previous Work

Physical Description

Bear Den Creek and its corresponding watershed are located along the western boundary of the Fort Berthold Indian Reservation, North Dakota (Fig. 1). The Reservation has a total area of approximately 5,000 km^2 in west central North Dakota. The main surface feature of the Reservation is the Lake Sakakawea reservoir. The reservoir was created in 1954 by the construction of the Garrison Dam; an impoundment of the Missouri River located southeast of the Reservation (Fig. 1).

The Reservation consists of two distinctive geomorphic regions, each developed on previously glaciated terrain. East of Lake Sakakawea is characterized as glaciated prairie, and land use is typically cropland. West of Lake Sakakawea is characterized as badlands. The land use is typically rangeland. The entire reservation is located within the Williston Basin, a structural sedimentary feature located on the western shelf of the Paleozoic North American craton (Peterson, 1988). The major structural features on the reservation include Nesson Anticline and the Antelope Anticline (Bluemle, 1978).

The general geology of the Bear Den Creek watershed consists of Tertiary bedrock units of the Sentinel Butte Member (Cates and Macek-Rowland, 1998). The lithology of the Sentinel Butte Member consists of clay, claystone, shale, sandstone, siltstone, and lignite (Table 3). Overlaying Sentinel Butte are Quaternary deposits consisting of glacial drift and alluvium. The surface layer is typically grayish brown silt

Table 3. Generalized Geologic Column of Near Surface Rocks, Fort Berthold Indian Reservation. (Modified from Cates and Macek-Rowland, 1998)

The Sentinel Butte member of the Fort Union formation represents the underlying bedrock of the Bear Den Creek drainage basin.

System	Series	Geologic Unit		Lithology	Maximum thickness (meters)
Quaternary	Holocene			Silt, sand, and gravel.	18
	Pleistocene			Till, silt, sand, and gravel.	137
Tertiary	Eocene	Golden Valley Formation		Sandstone, silt, clay, claystone, siltstone, and carbonaceous shale.	37
	Paleocene	Fort Union Formation	Sentinel Butte Member	Clay, claystone, shale, sandstone, siltstone, and lignite	130
			Tongue River Member	Clay, claystone, shale, sandstone, siltstone, and lignite	195
			Cannonball Member	Marine sandstone, clay, shale, and siltstone.	168
			Ludlow Member	Continental siltstone, sandstone, shale, clay, and lignite.	
Cretaceous		Hell Creek Formation		Siltstone, sandstone, shale, claystone, and lignite.	107
		Fox Hills Sandstone		Sandstone, shale, and siltstone.	114
		Pierre Shale		Shale.	700

loam with an approximate thickness of 10 cm. The subsoil is silt loam to a depth of 1.50 meters (Scharr, 1982).

Hydrologic Description

The drainage basin of Bear Den Creek has an approximate area of 300 km^2, of which 88 km^2 lies within the Fort Berthold Reservation. The stream is ephemeral. Upstream flow is from north to south and downstream flows southwest to northeast (Fig. 2). The USGS has operated the long-term gaging station and sampling program on Bear Den Creek since June 1966.

The stream is 50 km long with an average stream slope of 31.40 m per km. The mean basin elevation is 706 m above sea level (Cates, 1998). As stated above, stream data have been collected on Bear Den Creek beginning in June 1966 by the United States Geological Survey (USGS, 1966-1996). All sampling was conducted by the USGS. Analysis was performed by the North Dakota State Department of Health.

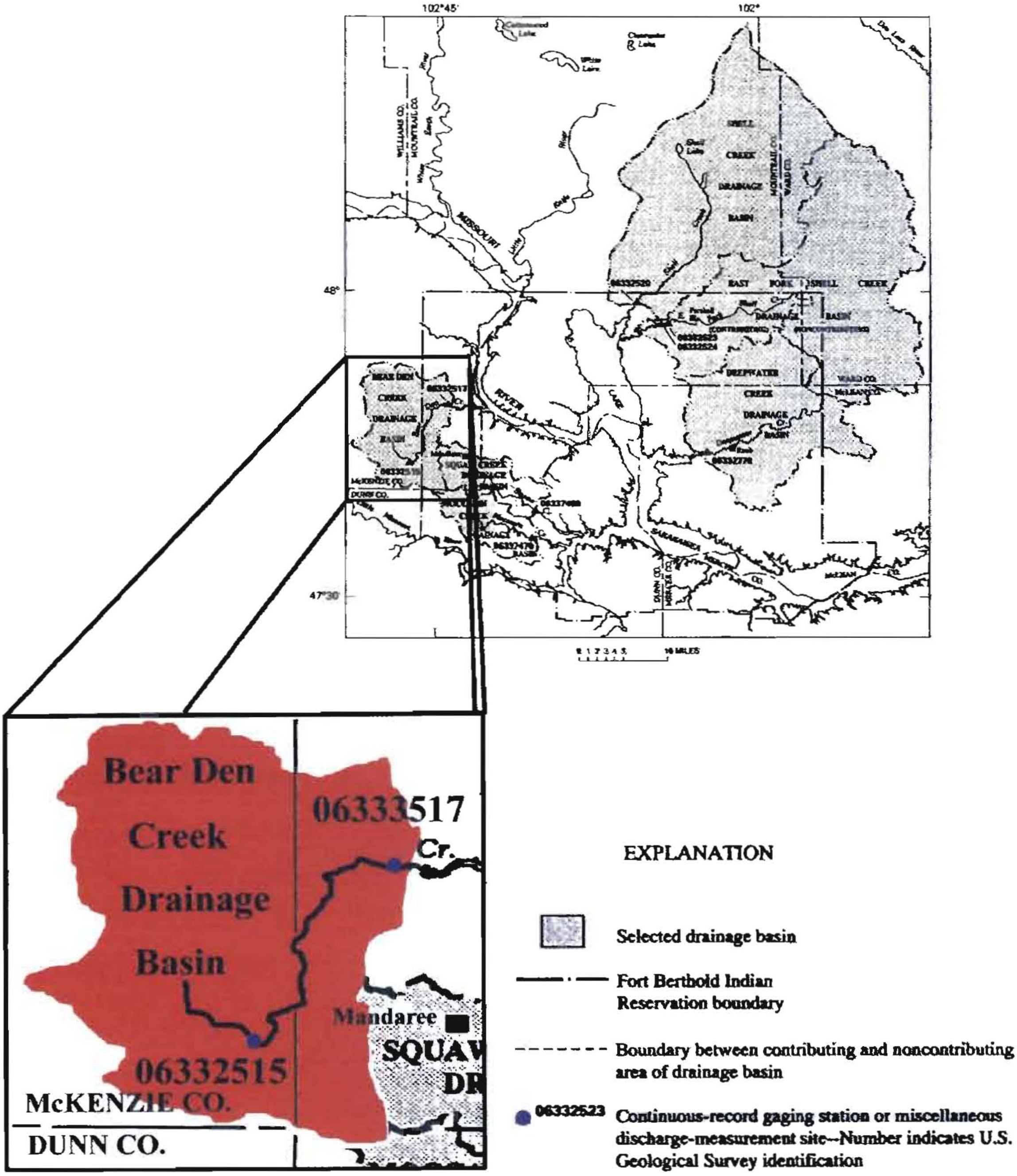
Previous Work

The geology and hydrology of the reservation were first investigated by Dingham and Gordon (1954), as part of a larger study. This investigation was conducted before creation of the Lake Sakakawea reservoir and reflects a total reservation area of approximately 1295 km^2 less than the current area of the Reservation. This study was the first study to incorporate lands encompassed by the Reservation boundaries.

The USGS, in cooperation with the North Dakota Water Commission and the North Geological Survey, have conducted a three-part reconnaissance ground-water study for each county within the Fort Berthold Indian Reservation boundaries. Included in this

Map 2. Bear Den Creek Drainage Basin, Fort Berthold Indian Reservation, North Dakota (Modified from Cates and Macek-Rowland, 1998).

The Bear Den Creek drainage basin is highlighted in red.


102°45'
102°
48°
47°30'
MISSOURI
RIVER
Bear Den
Creek
Drainage
Basin
06333517
Cr.
Mandaree
SQUAW
DR
06332515
McKENZIE CO.
DUNN CO.
EXPLANATION
Selected drainage basin
Fort Berthold Indian Reservation boundary
Boundary between contributing and noncontributing area of drainage basin
06332523 Continuous-record gaging station or miscellaneous discharge-measurement site--Number indicates U.S. Geological Survey identification

report was data on water resources of the Reservation (Pettyjohn 1976; Armstrong, 1973, 1985; Croft, 1970, 1985a; Klausing, 1971,1976). This study updated the hydrologic data gathered by Dingham and Gordon (1954). It also provided a greater detailed ground and surface water study of the area encompassed by the Reservation boundaries.

A report on the specific water resources of the Fort Berthold Indian Reservation was conducted by the USGS, with cooperation of the Three Affiliated Tribes (Cates et al., 1998). The report gave a summary of all surface and ground water resources specific to the area within the Reservation. This is of importance to the Tribe, as the Tribe begins to establish its own water quality-monitoring program.

Chapter 4

Data Analysis and Discussion

The study of major ion concentration may be undertaken by analyzing recorded ion concentrations and observing changes in concentration with discharge over a period of time. This is accomplished graphically by plotting data and observing general trends that may exist. This technique has been applied to Bear Den Creek data and is included with discussion below.

The data for Bear Den Creek were collected at USGS Site 06332515 (Fig. 2). Beginning in June 1966, discharge and water quality data have been collected for Bear Den Creek by the USGS as part of the National Hydrologic Benchmark Network (USGS, 1966-1996). This network consists of 53 sites in small drainage basins located throughout the United States. The purpose of the network is to provide consistent data on hydrology and water quality in undeveloped watersheds, for comparison with drainage basins where human activity is present (Macek-Rowland and Lent, 1996).

Major ion concentrations are given in milliequivilents / Liter (meq/L) and are compared to corresponding discharge, given in LOG Discharge units. LOG Discharge is used here to simplify graphical plotting of data. The use of LOG values allows the entire range of discharge levels to be plotted in a smaller area for ease of observing trends.

Plots of major ion concentrations may be used to determine the primary factor that contributes to overall concentration: time or discharge. If concentration varies as a function of time then a linear trend would develop showing increases or decreases. This would be represented by a positive (upward) or negative (downward) arrangement of data points. If discharge was the primary factor controlling concentration a different trend would occur as concentration varied seasonally or annually. This would be represented by a "scattering" or random arrangement of data points. Plots of Bear Den Creek data has produced graphs showing a random scattering of data points indicating that the major ion concentration is a function of discharge. Figures showing the trends are found below as the data of the major ions is presented.

Data Analysis

Calcium, Ca^{2+}

The plot of Ca^{2+} data indicates that Ca^{2+} concentration bears a relationship to climate and discharge (Fig. 3). A sharp increase in Ca^{2+} is observed as LOG Discharge increases from approximately -1.00 to -0.50 (0.10 to 0.25 cfs). This increase in Ca^{2+} ion concentration may be due to the effects of increased photosynthetic activity as sunlight is made available to plants and algae as ice cover of Bear Den Creek melts during spring thaw. The increased photosynthetic activity causes an increase in pH and the precipitation of $CaCO_3$, increasing the available Ca^{2+} ions (Schroeder, 1992). This trend of increasing concentration continues until LOG Discharge approaches 0.00 (1.00 cfs). After LOG Discharge passes 0.00 (1.00 cfs), Ca^{2+} concentration decreases presumably due to dilution.

Magnesium, Mg^{2+}

The plot of Mg^{2+} data indicates that Mg^{2+} concentration is also related to discharge. There is a large cluster of Mg^{2+} data at LOG Discharge of -1.00 to -0.50 (0.10 to 0.25 cfs). In this LOG Discharge range, Mg^{2+} concentration has an approximate

Figure 3. Ca^{2+} Concentration vs. LOG Discharge for Bear Den Creek, 1969-1990.
Ca^{2+} data for dates 04/22/69 - 08/07/96.
Sample site: USGS Site 06332515.

Figure 3.

Ca^{2+} Concentration vs LOG Discharge for Bear Den Creek, 1969-1996

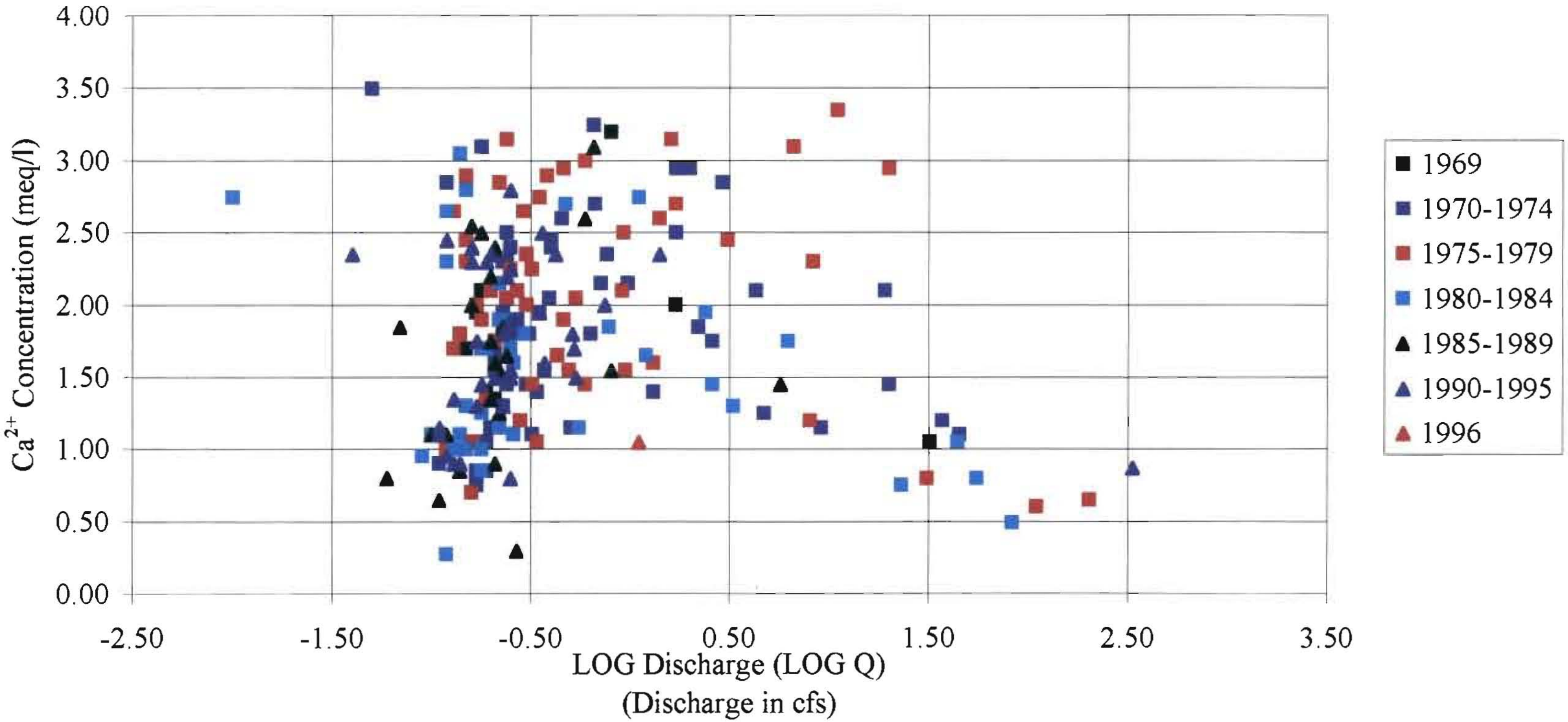
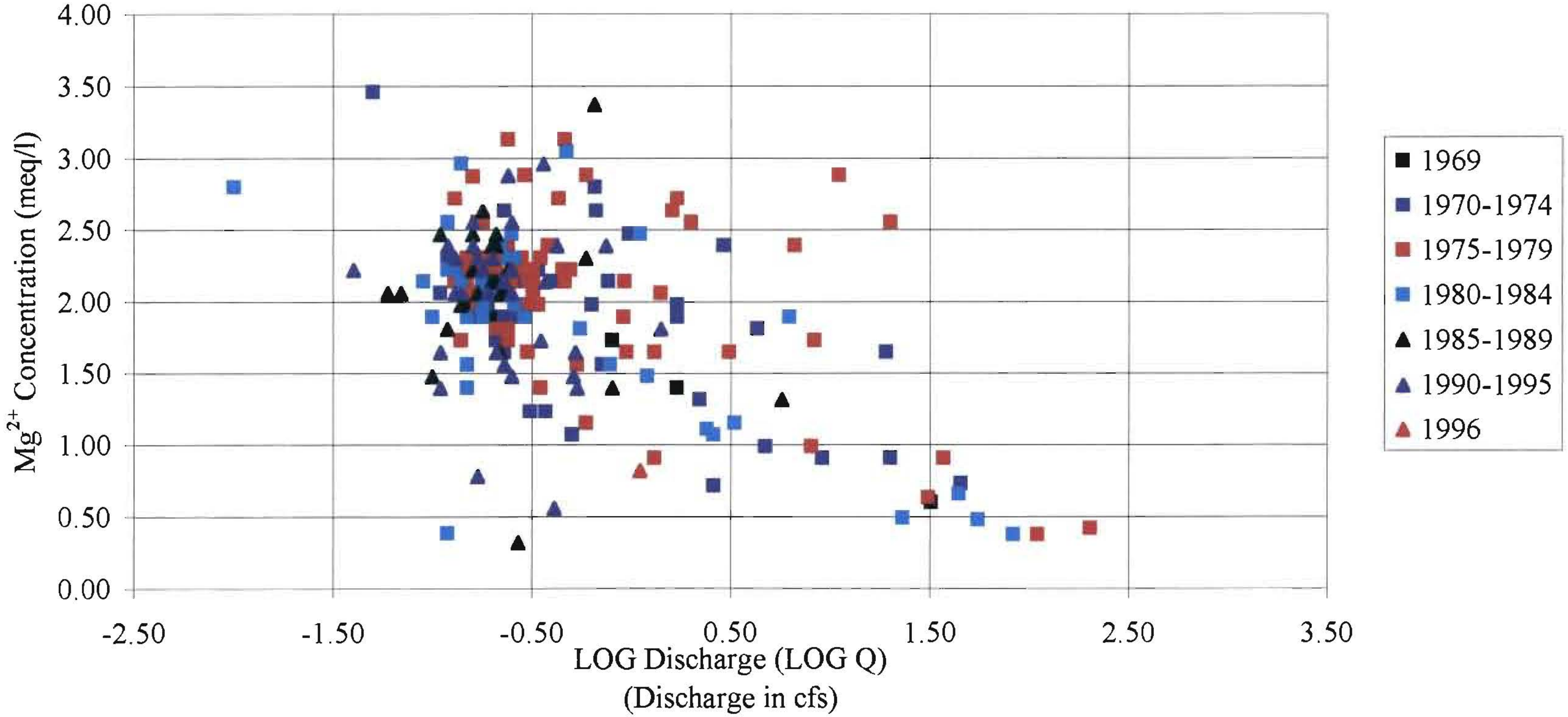


Figure 4. Mg^{2+} Concentration vs. LOG Discharge for Bear Den Creek, 1969-1996.
Mg^{2+} data for 04/22/69 - 08/07/96.
Sample site: USGS Site 06332515
Outliers not shown: 08/16/79 (18.92 meq/l), 04/14/83 (9.79 meq/l)

Figure 4.
Mg^{2+} Concentration vs LOG Discharge for Bear Den Creek, 1969-1996



range of 1.50 to 2.50 meq/L (18.25 to 30.40 mg/L) (Fig. 4), indicating that conditions were not appropriate to allow Mg^{2+} to precipitate from solution. As discharge increases Mg^{2+} concentration also declines.

Sodium, Na^{+}

The plot of Na^{+} data indicates the presence of a decreasing linear relationship of Na^{+} to increasing discharge (Fig. 5). The initial trend of increasing concentration as discharge increases from LOG Discharge –1.00 to –0.50, as seen with Ca^{2+} and Mg^{2+}, is not evident here. The greatest concentration of data is located in the range of LOG Discharge -1.00 to -0.50 (0.10 to 0.25 cfs), with Na^{+} concentrations of approximately 24.00 to 36.00 meq/L (550 to 830 mg/L). As discharge increases above 0.25 cfs, Na^{+} concentration continues to decrease. The plot of Na^{+} is similar to the plot of SO_4^{2-} as the likely source of the two ions is sodium sulfate (Na_2SO_4) (Murphy, 1996).

Potassium, K^{+}

The plot of K^{+} data does not indicate a trend similar to Ca^{2+}, Mg^{2+}, or Na^{+} (Fig.6). There is a large concentration of data points at LOG Discharge values of -1.00 to -0.50 (0.10 to 0.25 cfs), with a concentration range of 0.12 to 0.28 meq/L (4.70 to 11.00 mg/L). The average K^{+} concentration is 0.20 meq/L (7.82 mg/L). As discharge increases above this point, K^{+} concentration appears to stabilize near the average of 0.20 meq/L.

Sulfate - SO_4^{2-}

The plot of SO_4^{2-} data shows a linear relationship of SO_4^{2-} concentration to discharge (Fig. 7). The plot of SO_4^{2-} is similar to the Na+ plot as the likely source of the two ions is sodium sulfate (Na_2SO_4) (Murphy, 1996). The greatest concentration of SO_4^{2-}

Figure 5. Na^+ Concentration vs. LOG Discharge for Bear Den Creek, 1969-1996.
Na^+ data for dates 04/22/69 - 08/07/96.
Sample site: USGS Site 06332515

The linear trend indicated by the Na^+ plot corresponds to the plot of SO_4^{2-}. This is likely due to the presence of sodium sulfate (Na_2SO_4) in the Bear Den Creek drainage basin.

Figure 5.

Na^+ Concentration vs LOG Discharge for Bear Den Creek, 1969-1996

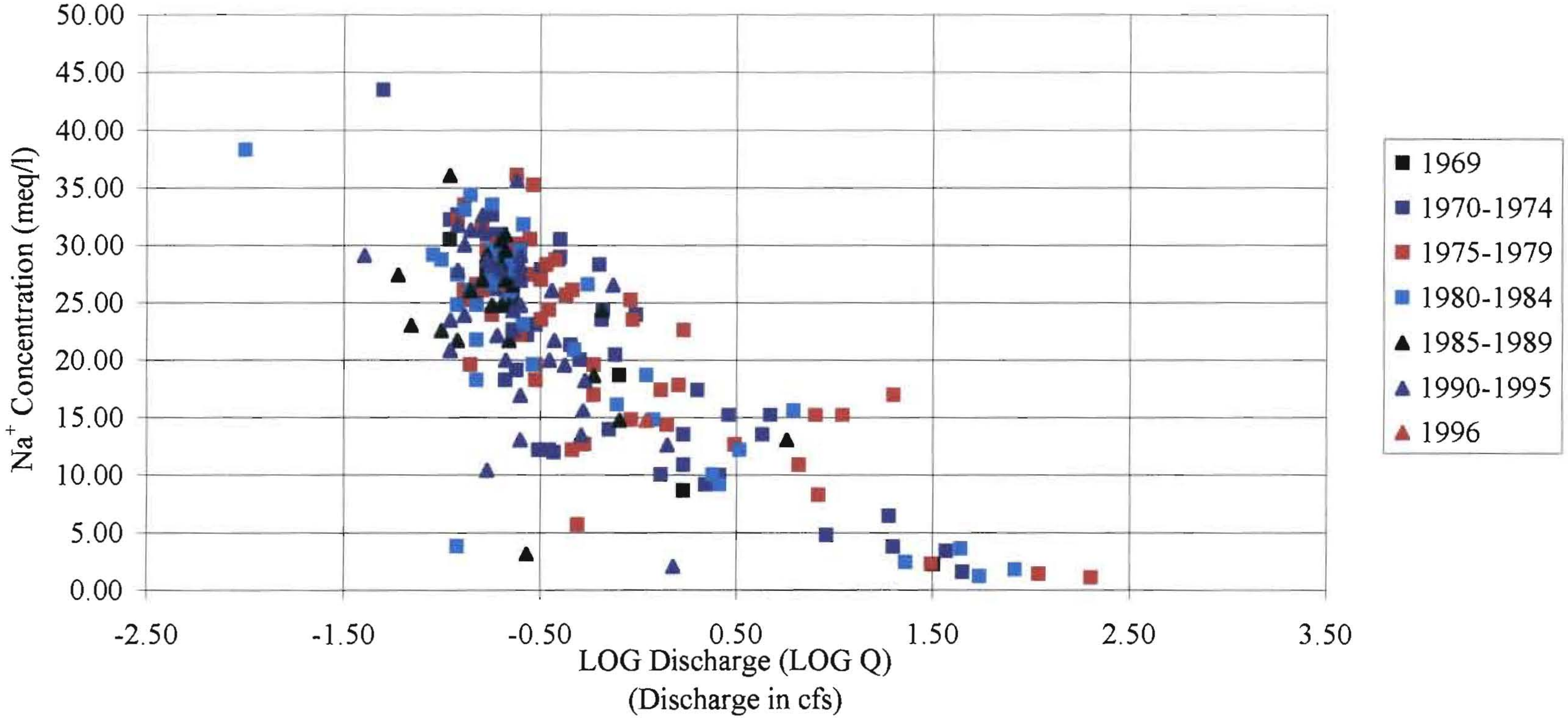


Figure 6. K^+ Concentration vs. LOG Discharge for Bear Den Creek, 1969-1996.
K^+ data for dates 04/22/69 - 08/07/96.
Sample site: USGS Site 06332515

Figure 6.

K^+ Concentration vs LOG Discharge for Bear Den Creek, 1969-1996

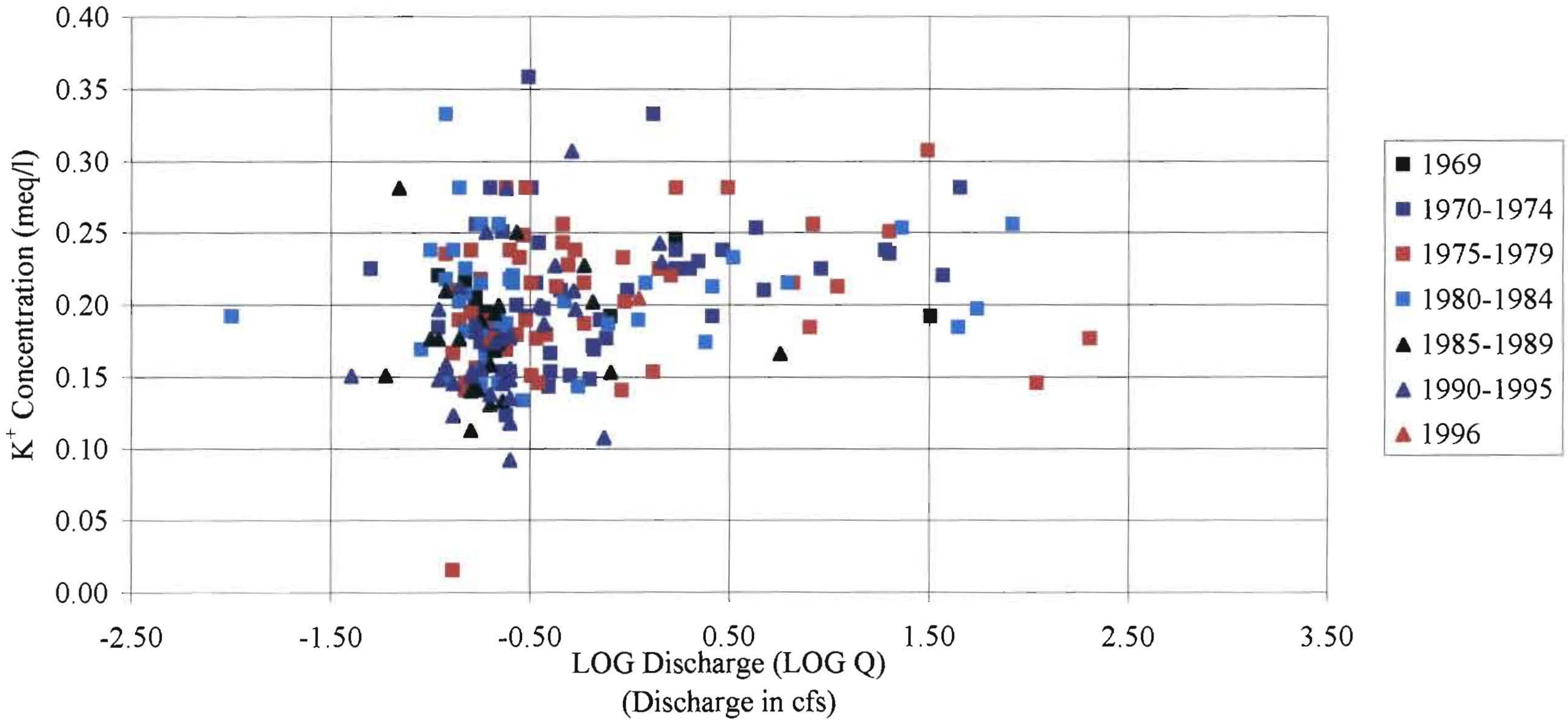
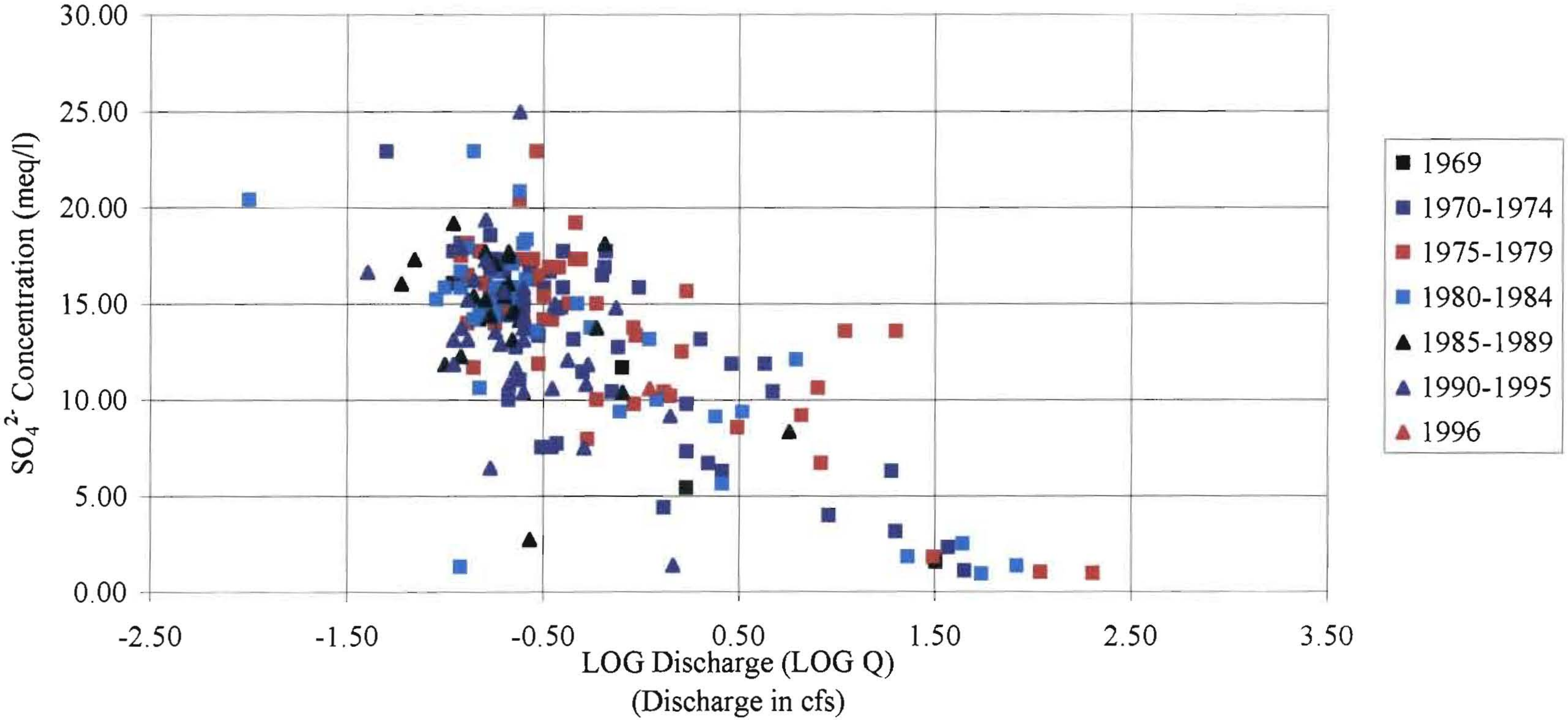


Figure 7. SO_4^{2-} Concentration vs. LOG Discharge for Bear Den Creek, 1969-1996.
SO_4^{2-} data for dates 04/22/69 - 08/07/90.
Sample site: USGS Site 06332515.
Outlier not shown: 04/14/83 (64.75 meq/l).

The linear trend indicated by the SO_4^{2-} plot corresponds to the plot of Na^+. This is due to the presence of sodium sulfate (Na_2SO_4) in the Bear Den Creek drainage basin.

Figure 7.

SO_4^{2-} Concentration vs LOG Discharge for Bear Den Creek, 1969-1996



occurs in a range of LOG Discharge of -1.00 to -0.50 (0.10 to 0.25 cfs), with an SO_4^{2-} concentration between 10.00 - 19.00 meq/L (960 to 1825 mg/L). As discharge increases from this point, SO_4^{2-} concentration decreases.

Chloride, Cl^-

The plot of Cl^- data indicates the presence of a trend similar to Ca^{2+} and Mg^{2+} (Fig.8). There is an initial small increase of Cl^- concentration from 0.05 to 0.20 meq/L (1.75 to 7.10 mg/L) as LOG Discharge increases from -1.00 to -0.50 (0.10 to 0.25 cfs). As LOG Discharge increases beyond 0.00 (1.00 cfs), the data indicates that Cl^- concentration begins to decrease due to dilution.

Bicarbonate & Carbonate

Data collected for HCO_3^- and CO_3^{2-} originate from USGS Site 06333515 (Fig. 2). Only data collected for years 1989 - 1996 are plotted for comparison of concentration to discharge because data collected before 1989 does not specifically analyze for HCO_3^- and CO_3^{2-}. The HCO_3^- and CO_3^{2} data for years 1989 -1996 have undergone an ion balance calculation and have been determined accurate for analysis (Table 2).

Bicarbonate, HCO_3^-

The plot of HCO_3^- data collected from 1989 to 1996 indicates a subtle downward trend of decreasing HCO_3^- concentration as discharge increases (Fig. 9). The greatest cluster of data points occurs at LOG Discharge –1.00 to –0.50 (0.10 to 0.25 cfs) with HCO_3^- concentrations of 19.18 to 10.00 meq/L (610 to 1170 mg/L). As discharge increases above 0.25 cfs, HCO_3^- concentration decreases.

Figure 8. Cl^- Concentration vs. LOG Discharge for Bear Den Creek, 1969-1996.
Cl^- data for dates 04/22/69 - 08/07/90.
Sample site: USGS Site 06332515.
Outliers not shown: 04/26/71 (1.16 meq/l), 06/12/78 (1.35 meq/l),
06/02/88 (5.08 meq/l)

Figure 8.

Cl^- Concentration vs LOG Discharge for Bear Den Creek, 1969-1996

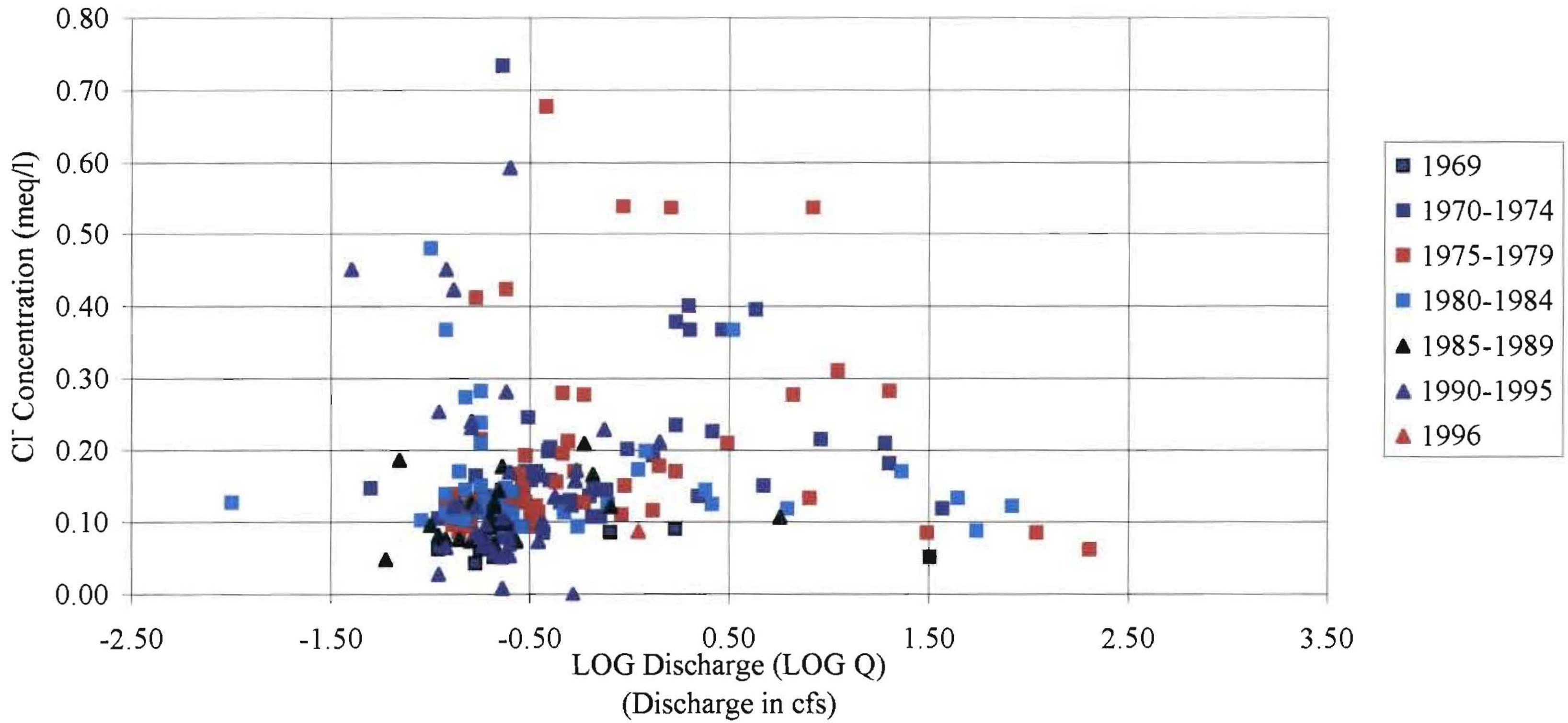


Figure 9. HCO_3^- Concentration vs. LOG Discharge for Bear Den Creek, 1989-1995.
HCO_3^- data for dates 05/09/89 - 10/26/95.
Sample site: USGS Site 06332515

Figure 9.
HCO_3^- Concentration vs. LOG Discharge for Bear Den Creek, 1989-1996

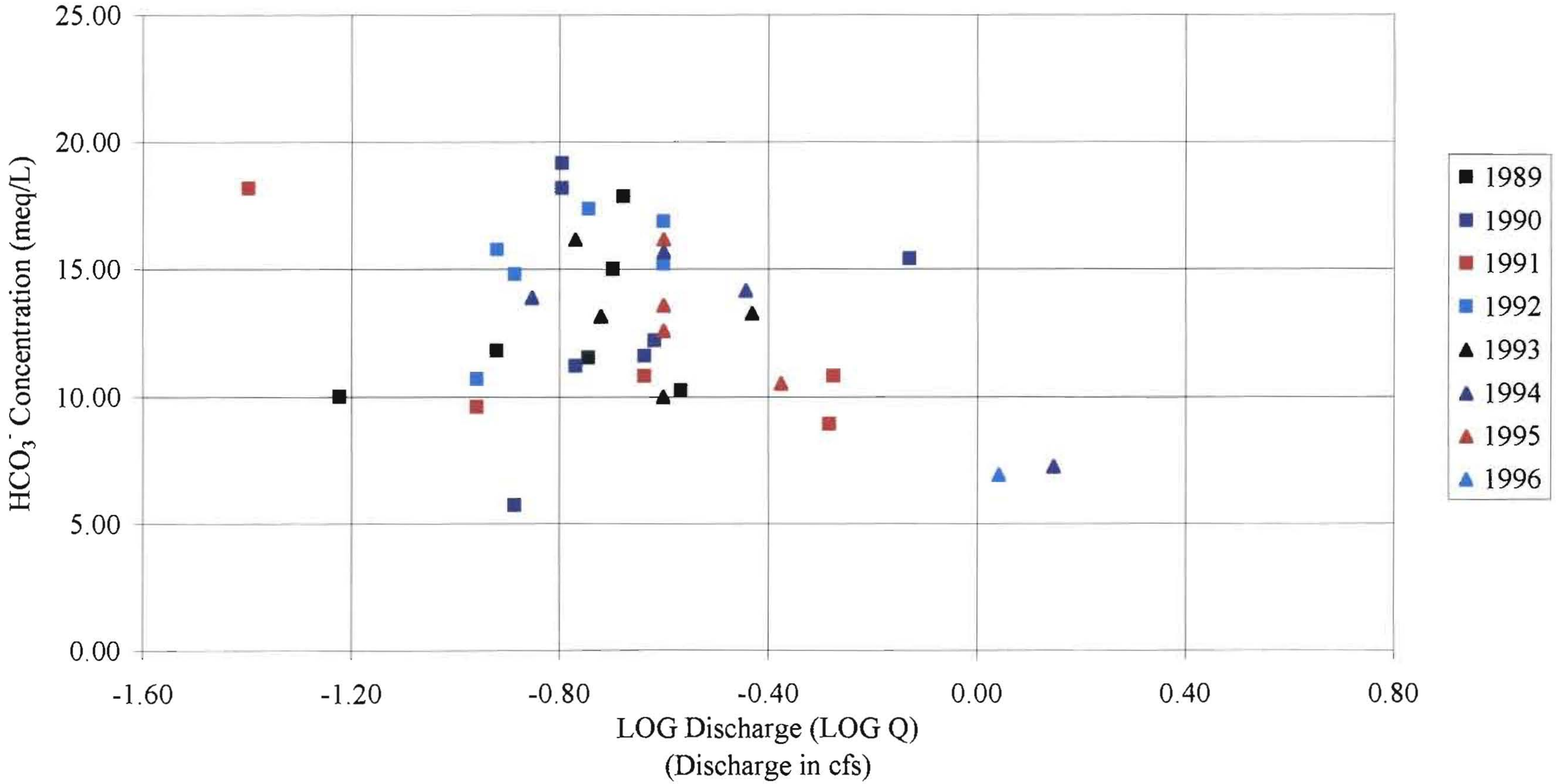
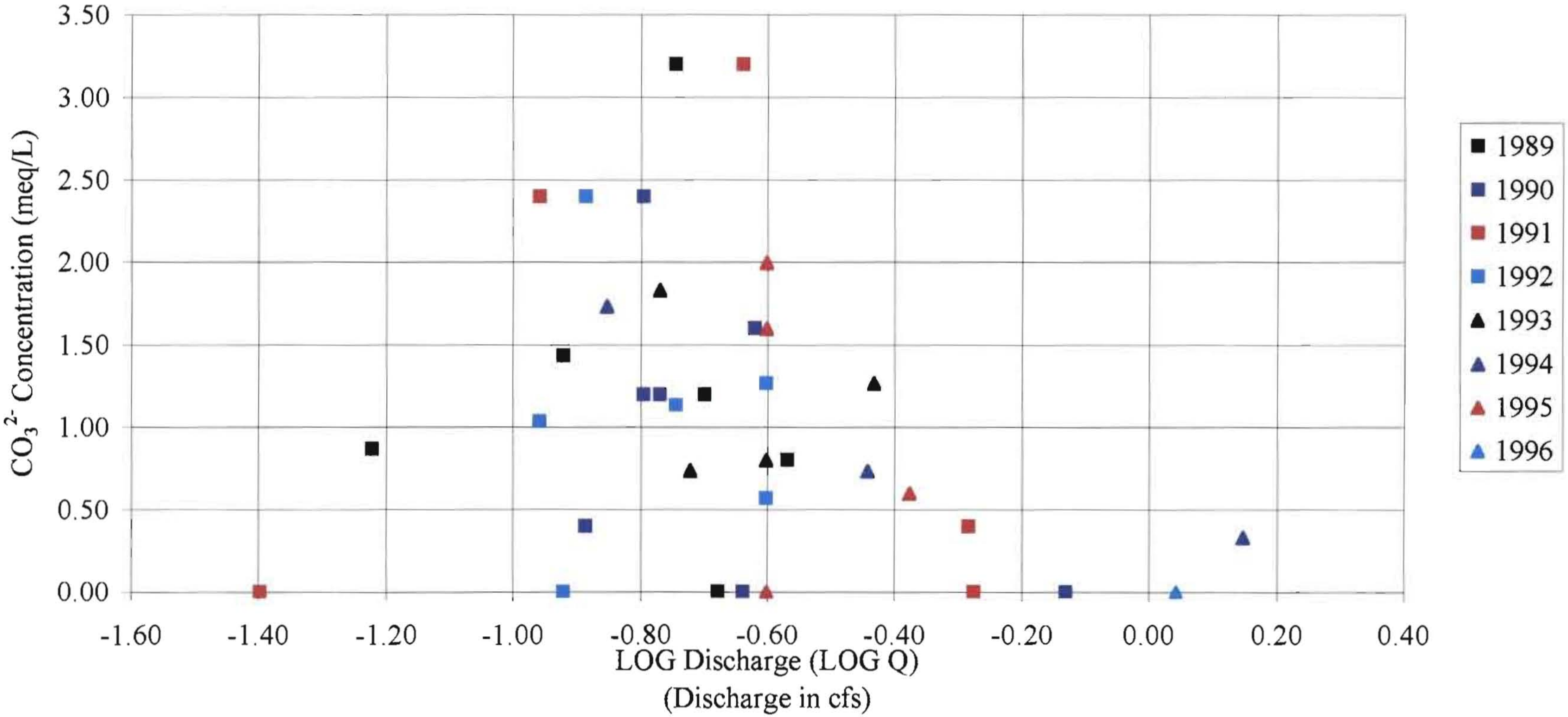


Figure 10. CO_3^{2-} Concentration vs. LOG Discharge for Bear Den Creek, 1990-1995.

CO_3^{2-} data for dates 05/09/89 - 10/26/95.

Sample site: USGS Site 06332515

Figure 10.
CO_3^{2-} Concentration vs. LOG Discharge for Bear Den Creek, 1989-1996



Carbonate, CO_3^{2-}

The plot of CO_3^{2-} data collected from 1989 to 1996 indicates a trend of decreasing CO_3^{2-} concentration with increasing discharge, although the lack of data hampers this interpretation (Fig. 10). In this data set, there are eight occurrences of CO_3^{2-} concentrations at 0.00 meq/L. There are three possible explanations for this: CO_3^{2-} is below the detectable limit of the laboratory technique used, human error in analysis or sampling, or the inclusion of CO_3^{2-} in the hardness analysis data.

Discussion

The study of Bear Den Creek has four objectives to which this study addresses. The principal focus of the four objectives address aspects in the realm of water quality.

1. Delineation of changes in major ion concentration vs. discharge over time.
2. Analysis of alkalinity to hardness ratios (HCO_3^- / [Ca^{2+} + Mg^{2+}]) versus time and discharge, to determine if acidification is occurring in the Bear Den Creek drainage basin.
3. Comparison of results to existing North Dakota and proposed Three Affiliated Tribes water quality standards in order to determine suitability or quality of Bear Den Creek waters.
4. The establishment of a baseline for major ion concentration to assist in the establishment of future secondary water quality standards and monitoring programs for the Three Affiliated Tribes.

The four areas of comparison within this study, discussed below, are of great importance to the Tribe. The establishment of water quality standards and regulations, and monitoring programs is vital to the establishment of a baseline to assist in the future development of Tribal environmental programs.

Changes in major ion concentration

The plots of major ion concentration vs. discharge over the years 1969 to 1996 indicates that major ion concentration has not varied on Bear Den Creek significantly during this time. Minor variations within the plotted data indicate that changes in ion concentration of Na^{+} and SO_4^{2-} are a function of discharge and are related primarily to annual precipitation, geology of the drainage basin, and seasonal changes in runoff (Peters, 1984). Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, HCO_3^{-}, and CO_3^{2-} plots indicate that discharge, along with climate and biological activity are factors in overall concentrations present in Bear Den Creek (Peters, 1984).

The amount of annual precipitation directly affects weathering rates and therefore major ion deposition. Streams in arid regions tend to have higher SO_4^{2-} and Cl^{-} concentrations than HCO_3^{-} (Clarke, 1924). The data for Bear Den Creek agree with this tendency (Fig. 11,13, and 15). The lower HCO_3^{-} concentration is attributed to the lack of carbonic acid. Carbonic acid is produced by the hydrolysis of CO_2, the addition of HCO_3^{-} and CO_3^{2-} into solution (Clarke, 1924). Western North Dakota is semi-arid receiving 33.00 – 41.00 cm precipitation per year, which fall primarily as rain during the months of April to September (Jensen, no date). In arid and semi-arid regions, chemical precipitation of Ca^{2+} and CO_3^{2-} as $CaCO_3$ reduces the amount of CO_3^{2-} in solution and results in higher SO_4^{2-} and Cl^{-} concentrations (Clarke, 1924).

The seasonal variation of precipitation in western North Dakota also affects the major ion deposition as a function of runoff (precipitation minus evapotranspiration). Much of the precipitation received in the Bear Den Creek drainage basin is in the form of rain, primarily in early spring storms (Jensen, no date). As runoff increases, the effect of increased major ion deposition is not evident as dilution occurs simultaneously. As the amount of runoff increases past 7.6 cm / year, the increase in major ions is small and overall total dissolved solid yield, becomes constant (Peters, 1984).

Human activity is also an influence on ion concentration in streams. Direct human influences can include quarrying and agricultural operations by the disturbance and break down of rock and soils. Both quarrying and cultivation increases the surface area of materials susceptible to weathering (Peters, 1984). Other human activities that have been responsible for increasing major ion concentration into other areas include combustion of fossil fuels, sewage and wastewater disposal, urban runoff, and industrial releases (Peters 1984). The data from Bear Den Creek and landuse of the surrounding area (i.e.: agriculture – ranching) indicate that the effects of human activity on major ion concentration are little to none at this time. If land use changes however, possible changes in major ion concentration may occur.

<u>Alkalinity to Hardness Ratios</u>

The data used for the major ion concentration analysis of Bear Den Creek are also useful to determine if acidification of stream waters is occurring. This is accomplished by plotting values of alkalinity (HCO_3^-) to hardness ($Ca^{2+} + Mg^{2+}$), known as (A/H) ratios ($HCO_3^- / [Ca^{2+} + Mg^{2+}]$) (Schindler, 1988). The A/H ratio compares the alkalinity of the water, represented by bicarbonate (HCO_3^-) and the hardness of the water, represented by the sum of calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations. As acidification of a stream occurs, Ca^{2+} and Mg^{2+} concentrations increase and HCO_3^- concentrations decrease as the acid neutralizes the bicarbonate present (Schindler, 1988). Acidification of streams is indicated by the lowering of the A/H ratio.

The A/H ratio of Bear Den Creek is compared with changes in discharge and over time. Data used for this analysis was collected from 1990 to 1996. The samples collected for this time period contain the necessary data (Ca^{2+}, Mg^{2+}, and HCO_3^-) for this analysis (Appendix A & B).

The plot of the A/H ratio (HCO_3^- / [Ca^{2+} + Mg^{2+}]) does not indicate a discernible trend as related to increasing discharge (Fig. 11). The majority of data points are concentrated between LOG Discharges of -0.96 to -0.13 (0.11 to 0.74 cfs). As discharge increases above –0.13, there is no noticeable trend, indicating that the A/H ratio is not affected by varying discharge within this small range of data. Insufficient data at LOG Discharge > 0.00 (1.00 cfs) hinders analysis of this ratio.

The plot of the A/H ratio (HCO_3^- / [Ca^{2+} + Mg^{2+}]) does not indicate a discernible trend as related to time (Fig. 12). In 1991 and 1993, there is a lower A/H ratio observed in early part of these years. This indicates slight acidification and may be due to melting of the accumulated snow cover in early spring producing a “spring acid shock”. This slight acidification is not present in all of the data. In 1992 and 1994, the data indicates a slight increase in the A/H ratio during the early part of the year. This may be caused by a

Figure 11. Ratio: HCO_3^- / (Ca^{2+} + Mg^{2+}) vs. LOG Discharge
for Bear Den Creek, 1990-1995.
HCO_3^-, Ca^{2+}, and Mg^{2+} data for dates 11/26/90 - 10/20/95.
Sample site: USGS Site 06332515.

Figure 11.

Ratio: ($HCO_3^- / [Ca^{2+} + Mg^{2+}]$) vs. LOG Discharge for Bear Den Creek, 1990-1995

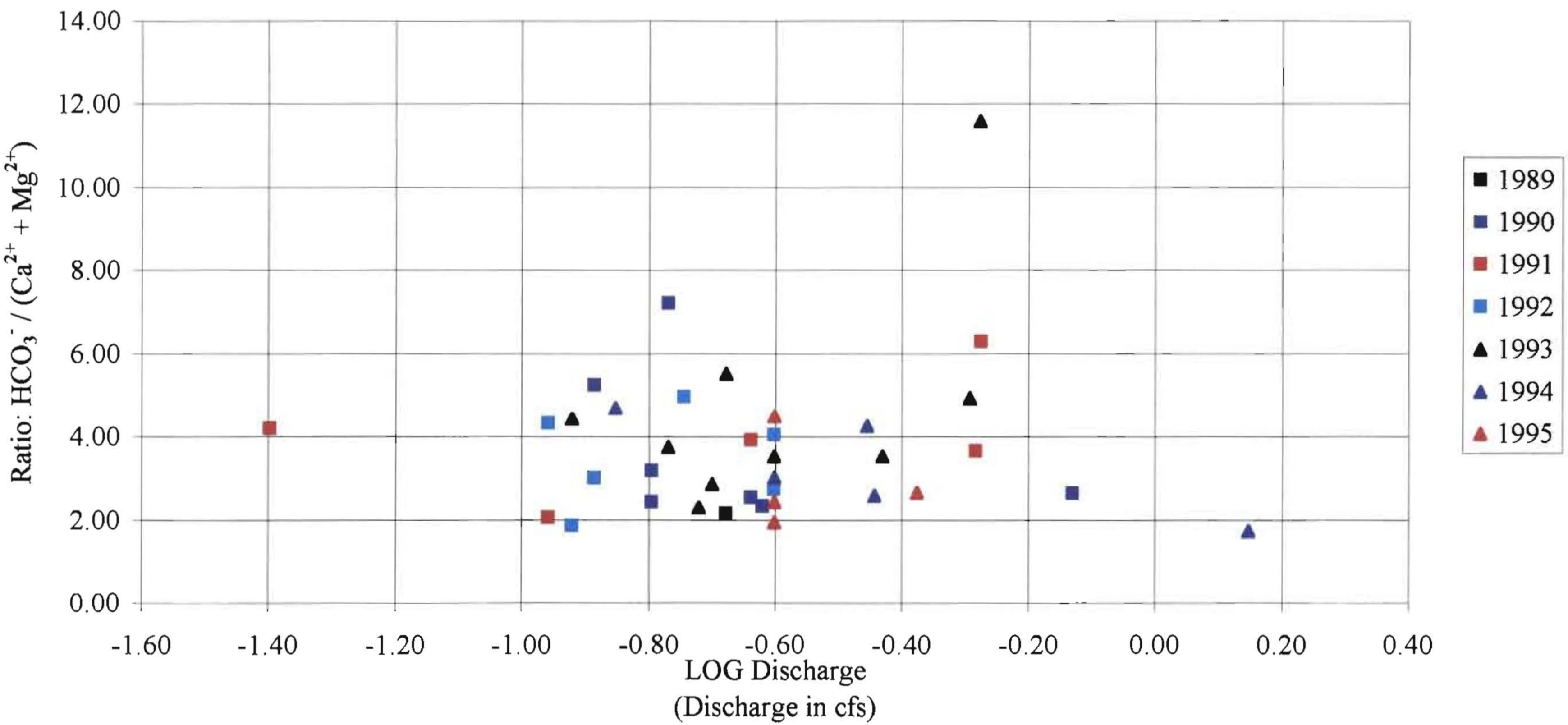
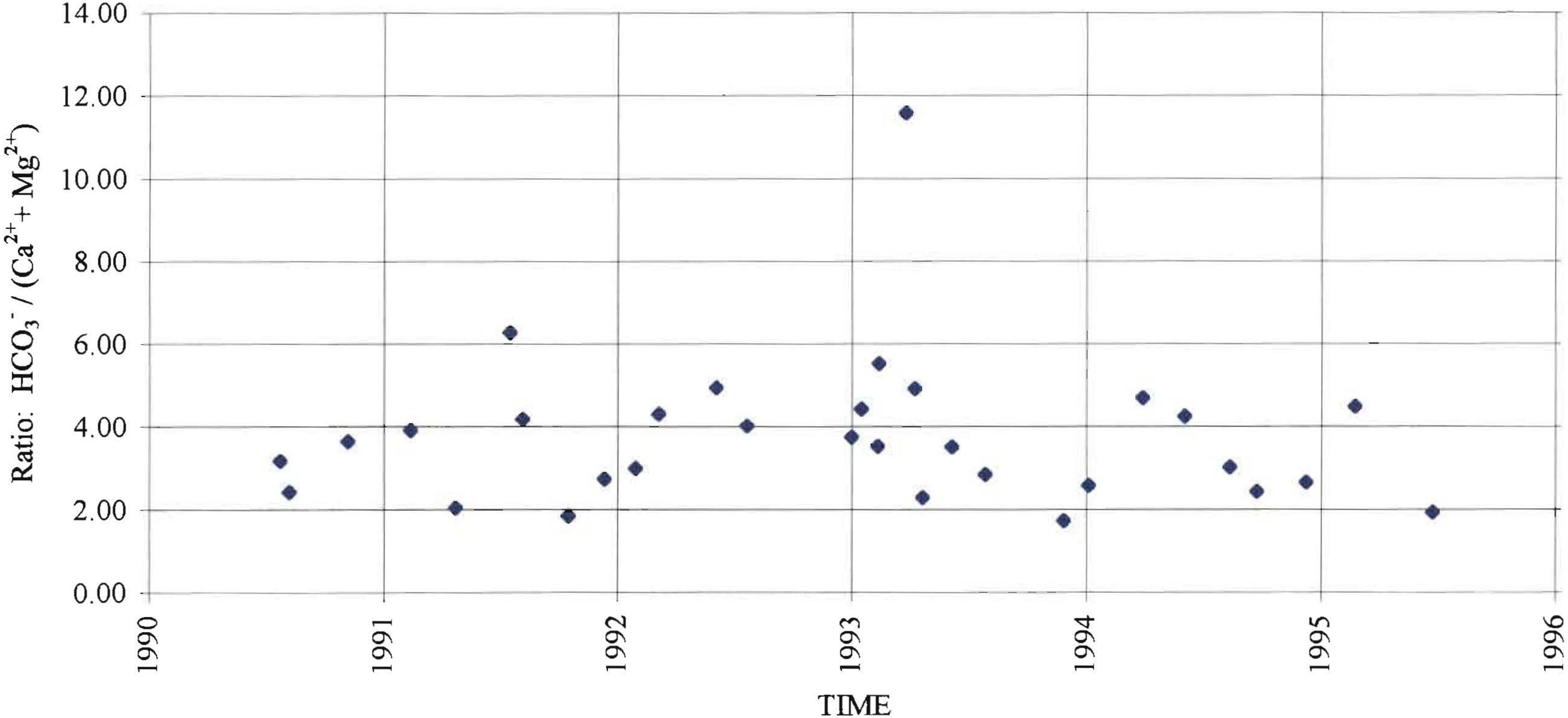


Figure 12. Ratio: $HCO_3^- / (Ca^{2+} + Mg^{2+})$ vs. TIME for Bear Den Creek, 1990-1995.
HCO_3^-, Ca^{2+}, and Mg^{2+} data for dates 11/26/90 - 10/20/95.
Sample site: USGS Site 06332515

Figure 12.
Ratio: (HCO_3^- / [Ca^{2+} + Mg^{2+}]) vs Time for Bear Den Creek, 1990-1995



decreased amount of runoff that did not discernibly affect the buffering capacity or HCO_3^- of the waters sampled.

The two plots of the A/H ratio indicate that acidification of Bear Den Creek is not occurring in any measurable way. The lack of a large human population and industrial activity in the surrounding area may explain this.

Comparison to Existing Water Standards

There are two types of water quality standards: primary and secondary. Primary standards regulate human health concerns while secondary standards address concerns of industrial or commercial use (Schroeder, 1992). Water quality standards represent the maximum allowable levels for various dissolved constituents. The maximum concentrations allowable vary with the stream classification. Stream classification results from the typical use waters from a surface water body are to be applied.

In order to apply the most stringent standard possible, Bear Den Creek results are compared to Class I stream standards. A Class I stream is defined by the State of North Dakota as "such to permit the propagation or life, or both, of resident fish species, and other aquatic biota...after treatment..., the treated water shall meet the bacteriological, physical, and chemical requirements of the department for municipal use" (ND § 33-16-02). The application of Class I stream standards allows a future determination of utilization of waters from Bear Den Creek for municipal use and for other uses such as industrial and commercial, where less stringent standards may be applied.

The Three Affiliated Tribes have not adopted primary or secondary water quality standards. In 1998, the Tribe directed the formulation of a set of water quality standards and has presented for approval to the Three Affiliated Tribes Business Council, the governing body of the Reservation. The major ion concentration data of this report is compared to both the proposed Tribal standards and the current North Dakota water quality standards (ND § 33-16-02).

The proposed Tribal standards and the North Dakota standards are similar in the maximum standard for chlorine (Cl^-). The proposed Tribal standards do not address the majority of secondary standards, including the major ions. The focus of the proposed Tribal standards is primary water quality. The North Dakota water quality standards also do not address maximum concentrations of all major ions. Only specific standards are present for Na^+, Cl^-, and SO_4^{2-} concentration in surface waters (ND § 33-16-02). Data for the standard comparison is taken from 1989 –1996. Only this set of data is used for comparison with the water quality standards, as it is has undergone an ion balance calculation and has been found accurate for analysis (Table 2).

The North Dakota Class I standard states the maximum allowable concentration for Na^+ is 50% of total cations present in meq/L (ND § 33-16-02). The concentration of Na^+ in Bear Den Creek is 85.79% of the total cations present for each sample. For the years of 1989 –1996, each sample exceeded the allowable Na^+ maximum by an average of 35.79% (Table 4). The presence of high Na^+ concentration may be due to the presence of sodium sulfate (Na_2SO_4) in the Bear Den Creek drainage basin (Murphy, 1998). Clearly, the waters of each sample from Bear Den do not meet the standard for Na^+ established for Class I Streams.

The Class I standard states the maximum allowable concentration for total Cl^- is

100 mg/L (2.82 meq/L) (ND § 33-16-02). The concentration for Cl^- in Bear Den Creek is 7.09 mg/L (0.20 meq/L) (Table 4). For the years of 1989 –1996, no sample from Bear Den Creek exceeded the maximum concentrations for a Class I stream. The waters from Bear Den Creek do meet the standard for Cl^- concentration established for Class I streams.

The Class I standard states the maximum allowable concentration for total SO_4^{2-} is 250 mg/L (2.60 meq/L) (ND § 33-16-02). The concentration for SO_4^{2-} in Bear Den Creek is 1363.01 mg/L (14.19 meq/L) (Table 4). For the years of 1989 – 1996, each sample from Bear Den Creek exceeded the maximum SO_4^{2-} standard by an average of 1113.01 mg/L (11.59 meq/L). The high SO_4^{2-} concentrations may be due to the presence of sodium sulfate (Na_2SO_4) in the Bear Den Creek drainage basin (Murphy, 1996). Clearly, the waters from each sample from Bear Den Creek exceeded the standard for SO_4^{2-} concentration established for Class I streams.

Overall, the concentrations of Na^+, Cl^-, and SO_4^{2-} found in Bear Den Creek do not meet the maximum allowable standard for a Class I stream. Any future use of waters from Bear Den Creek for human consumption will require additional treatment in order to lower the high major ion concentrations naturally present. The other major ion concentrations (Ca^{2+}, Mg^{2+}, K^+, HCO_3^-, and CO_3^{2-}) must also be considered and additional standards created for future use of waters from Bear Den Creek.

Establishment of major ion concentration baseline and database

A baseline of naturally occurring major ion concentration for Bear Den Creek has been established. As the population increases and future development on the Reservation is considered, the baseline will be invaluable for monitoring changes in water quality. The

Table 4. Water Quality Standard Comparison
Bear Den Creek, Fort Berthold Indian Reservation, North Dakota
1989 -1996 major ion concentration data
Sample Site: USGS Site 06332515

Na^+, Cl^-, and SO_4^{2-} concentrations compared with North Dakota Class I Stream water quality standards: Na^+ (50% of cations in meq/L), Cl^- (100 mg/L (2.82 meq/L)), SO_4^{2-} (250 mg/L (2.60 meq/L)). The proposed Three Affiliated Tribes water quality standard cite only Cl^- maximum concentration and are the same as the North Dakota Class I stream standard.

Sample Date	Na^+ meq/L	Sum Cations	+/- of Na^+ Standard (Standard: 50% of total cations)	Cl^- meq/L	+/- of Cl^- Standard (Standard: 2.82 meq/L)	SO_4^{2-} meq/L	+/- of SO_4^{2-} Standard (Standard: 2.60 meq/L)
05/09/89	24.79	30.11	32.34	0.08	-2.74	17.07	14.47
06/14/89	27.40	30.41	40.11	0.05	-2.77	16.03	13.43
08/22/89	21.75	24.86	37.46	0.08	-2.74	12.28	9.68
10/25/89	28.27	31.92	38.58	0.06	-2.76	15.82	13.22
11/30/89	29.58	34.53	35.66	0.07	-2.75	17.49	14.89
03/05/90	26.53	31.02	35.53	0.23	-2.59	14.78	12.18
04/17/90	22.62	26.70	34.71	0.10	-2.72	11.24	8.64
05/03/90	35.67	41.02	36.94	0.28	-2.54	24.98	22.38
08/02/90	10.44	12.70	32.17	0.12	-2.70	6.45	3.85
11/26/90	32.62	37.62	36.72	0.24	-2.58	19.36	16.76
12/11/90	31.32	36.25	36.39	0.23	-2.59	17.28	14.68
03/11/91	15.66	19.21	31.51	0.10	-2.72	10.83	8.23
06/17/91	24.36	27.39	38.91	0.01	-2.81	11.66	9.06
08/27/91	23.49	26.48	38.71	0.03	-2.79	13.53	10.93
11/20/91	18.27	21.36	35.52	0.16	-2.66	11.87	9.27
12/10/91	29.14	33.86	36.07	0.45	-2.37	16.66	14.06
02/19/92	27.84	32.83	34.80	0.45	-2.37	13.74	11.14
04/15/92	24.79	28.89	35.81	0.17	-2.65	13.12	10.52
06/02/92	30.01	33.36	39.97	1.81	-1.01	15.20	12.60
07/08/92	20.88	23.52	38.76	0.25	-2.57	11.87	9.27
10/06/92	28.27	32.10	38.09	0.08	-2.74	13.53	10.93
11/23/92	28.27	32.31	37.50	0.59	-2.23	13.74	11.14
05/05/93	28.71	32.94	37.15	0.08	-2.74	16.86	14.26
06/15/93	16.96	20.17	34.10	0.07	-2.75	10.41	7.81

Sample Date	Na^+ meq/L	Sum Cations	+/- of Na^+ Standard (Standard: 50% of total cations)	Cl^- meq/L	+/- of Cl^- Standard (Standard: 2.82 meq/L)	SO_4^{2-} meq/L	+/- of SO_4^{2-} Standard (Standard: 2.60 meq/L)
08/24/93	22.18	26.79	32.82	0.10	-2.72	12.91	10.31
10/08/93	21.75	25.67	34.72	0.10	-2.72	14.78	12.18
03/31/94	12.61	17.01	24.15	0.21	-2.61	9.16	6.56
05/09/94	26.10	31.75	32.19	0.10	-2.72	14.99	12.39
08/01/94	31.32	34.48	40.82	0.13	-2.69	16.24	13.64
12/14/94	27.40	32.90	33.28	0.07	-2.75	15.41	12.81
01/25/95	26.97	31.39	35.92	0.05	-2.77	14.16	11.56
04/12/95	19.57	24.53	29.79	0.14	-2.68	12.28	9.68
06/27/95	29.14	32.25	40.35	0.08	-2.74	15.82	13.22
10/26/95	26.10	29.80	37.58	0.07	-2.75	14.37	11.77
08/07/96	14.79	16.86	37.69	0.09	-2.73	10.62	8.02

Tribe is currently investigating the potential for petroleum resources on the Reservation. The lack of an established water quality standards and surface water quality monitoring may hinder future efforts to regulate and maintain acceptable surface water quality on the Reservation.

The water quality data collected by the USGS for Bear Den Creek is now electronically filed along with data from six other streams located on the Fort Berthold Indian Reservation. The database currently holds all the data collected by the USGS between the years of 1966 to 1996. The database may be expanded and modified to meet the expanding needs of the Tribe as it establishes and maintains its surface water quality program.

Future Study

A possible area of future study on the Bear Den Creek drainage basin involve current landuse within the drainage basin. The current primary landuse within the Bear Den Creek drainage basin is ranching. The effects of cattle production and associated runoff may play a larger role in the determination of overall water quality of Bear Den Creek. The data collected by the USGS does contain analysis of possible chemical identifiers of this activity. Future study on this data would provide an analysis of the role cattle production has on the water quality of Bear Den Creek

Chapter 5

Conclusion

This study of the major ion concentration of Bear Den Creek, Fort Berthold Indian Reservation, North Dakota has plotted concentration as a function of discharge for the years between 1969 to 1996. This has established a baseline of naturally occurring major ion concentration of Bear Den Creek. The baseline will be useful to the Three Affiliated Tribes government of the Fort Berthold Indian Reservation as it establishes and maintains Tribal water quality standards and monitoring programs.

The role of possible acidification of the Bear Den Creek drainage basin has been explored by the analysis of alkalinity to hardness (A/H) ratios (Schindler, 1992). A trend of lower A/H ratios over time is an indicator of acidification of surface water bodies. The analysis of alkalinity (HCO_3^-) and hardness ($Ca^{2+} + Mg^{2+}$) data for the years between 1989 to 1996 has shown that acidification is not a factor in the overall water quality of Bear Den Creek. The result is consistent with current low population and the primary landuse of ranching that is present in the surrounding area of the Bear Den Creek drainage basin.

Comparison of major ion concentration data for Bear Den Creek and the State of North Dakota Class I stream standard has been addressed in this study. The Class I Stream classification is the most stringent water quality standard applied to streams by the State of North Dakota. A Class I stream is defined by the State of North Dakota as "such to permit the propagation or life, or both, of resident fish species, and other aquatic biota...after treatment..., the treated water shall meet the bacteriological, physical, and chemical requirements of the department for municipal use" (ND § 33-16-02).

Current North Dakota Class I stream standards identify maximum concentrations for Na^+ (50% of total cations), Cl^- (100 mg/L or 2.82 meq/L), and SO_4^{2-} (250 mg/L or 2.60 meq/L) (ND § 33-16-02). For the years between 1969 to 1996, the data for Bear Den Creek indicates concentrations of: Na^+ (85% of total cations), Cl^- (7.09 mg/L or 0.20 meq/L), and SO_4^{2-} (1363.01 mg/L or 14.19 meq/L) (Table 4). The presence of sodium sulfate in the Bear Den Creek drainage basin is a likely cause of the poor Na^+ and SO_4^{2-} standard comparison (Murphy, 1996). Clearly, the overall concentrations of the three ions indicate waters of Bear Den Creek do not meet the standards of a Class I stream.

This study of major ion concentration of Bear Den Creek was done in conjunction with the Fort Berthold Watershed Project, a joint effort of the Three Affiliated Tribes and Emporia State University. The project is funded through an Environmental Protection Agency Environmental Education Grant. The goal of the project is to build the environmental capacity of the Three Affiliated Tribes by educating tribal members regarding the importance of watershed management and to increase public access to watershed management.

One method used to accomplish this task was the electronic filing of USGS collected data from Bear Den Creek, along with data from six other streams located on the Fort Berthold Indian Reservation. The database currently holds all the data collected by the USGS between the years of 1966 to 1996. The database, used in the major ion concentration analysis of this paper, may be expanded and modified to meet the expanding needs of the Tribe as it establishes and maintains its surface water quality program.

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Appendix A.

Major Ion Concentration and LOG Discharge Data

(Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-})

Bear Den Creek, Fort Berthold Indian Reservation, North Dakota

Years: 04/10/69 – 08/07/96

Sample Site: USGS Site 06332515

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
04/10/69	1.51	1.05	0.60	2.22	0.19	1.52	0.05
05/05/69	-0.10	3.19	1.73	18.70	0.19	11.66	0.08
05/25/69	-0.77	1.95	2.30	27.84	0.20	17.07	0.04
06/02/69	-0.72	1.40	2.30	29.36	0.19	16.66	0.06
07/16/69	0.23	2.00	1.40	8.61	0.25	5.41	0.09
08/18/69	-0.82	1.70	1.97	25.58	0.21	14.16	0.10
09/15/69	-0.96	1.10	2.06	30.45	0.22	16.03	0.06
10/13/69	-0.68	1.35	1.89	28.88	0.17	15.20	0.05
11/12/69	-0.74	2.10	2.06	28.49	0.14	14.57	0.06
01/12/70	-1.30	3.49	3.46	43.50	0.23	22.90	0.15
04/14/70	0.41	1.75	0.72	9.96	0.19	6.25	0.23
05/14/70	1.28	2.10	1.65	6.44	0.24	6.25	0.21
06/17/70	1.30	1.45	0.90	3.74	0.24	3.12	0.18
07/20/70	-0.43	1.55	1.23	11.92	0.20	7.70	0.08
08/20/70	-0.72	1.05	1.97	26.18	0.17	15.41	0.08
09/21/70	-0.64	1.30	1.89	29.36	0.15	15.41	0.08
10/19/70	-0.64	1.95	2.06	25.66	0.17	14.78	0.14
11/17/70	-0.40	2.40	2.14	28.92	0.17	15.82	0.20
12/08/70	-0.92	2.84	2.30	32.62	0.15	18.11	0.13
03/19/71	1.65	1.10	0.73	1.57	0.28	1.08	0.85
04/26/71	0.23	2.50	1.89	10.87	0.23	7.29	1.16
05/17/71	-0.64	2.30	2.63	26.31	0.25	15.62	0.73
06/21/71	0.63	2.10	1.81	13.48	0.25	11.87	0.39
07/20/71	-0.68	1.55	1.73	18.27	0.17	9.99	0.11
08/30/71	-0.96	0.90	2.06	32.19	0.18	17.70	0.10
09/27/71	-0.64	1.85	1.65	22.62	0.15	12.70	0.05
10/26/71	-0.15	2.15	1.56	13.92	0.19	10.41	0.11
11/30/71	-0.19	3.24	2.80	23.49	0.17	16.86	0.11
03/01/72	-0.51	1.80	1.23	12.18	0.36	7.50	0.25
03/30/72	0.34	1.85	1.32	9.13	0.23	6.66	0.14
04/25/72	0.23	2.94	1.97	13.48	0.24	9.79	0.23
05/31/72	0.46	2.84	2.39	15.22	0.24	11.87	0.37
06/28/72	-0.01	2.15	2.47	23.92	0.21	15.82	0.20
07/26/72	-0.47	1.40	2.22	28.27	0.21	16.66	0.17
08/29/72	-0.70	1.15	2.14	30.88	0.28	16.66	0.11
09/27/72	-0.30	1.15	1.07	20.01	0.15	11.45	0.13

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
10/31/72	-0.41	2.05	2.14	28.71	0.14	14.78	0.20
11/28/72	-0.40	2.45	2.39	30.45	0.15	17.70	0.16
03/13/73	0.96	1.15	0.90	4.78	0.23	3.96	0.21
04/05/73	-0.12	2.35	2.14	20.44	0.18	12.70	0.14
05/03/73	-0.18	2.69	2.63	24.36	0.17	17.70	0.14
05/30/73	-0.20	1.80	1.97	28.27	0.15	16.45	0.14
06/26/73	-0.57	1.90	2.14	22.18	0.20	16.66	0.14
07/31/73	-0.72	0.85	2.06	28.71	0.18	15.62	0.14
08/28/73	-0.77	0.85	1.89	29.58	0.19	15.62	0.11
09/25/73	0.67	1.25	0.99	15.22	0.21	10.41	0.15
11/01/73	-0.60	1.80	1.89	26.97	0.18	14.57	0.09
11/27/73	-0.60	2.40	2.30	29.14	0.15	14.99	0.10
01/03/74	-0.62	2.50	2.06	27.84	0.12	15.62	0.08
02/07/74	-0.62	2.30	1.73	19.14	0.28	11.03	0.12
02/26/74	0.11	1.40	0.90	10.00	0.33	4.37	0.19
03/27/74	-0.46	1.95	1.40	12.18	0.24	7.50	0.16
04/09/74	1.57	1.20	0.90	3.35	0.22	2.29	0.12
05/08/74	-0.35	2.59	2.22	21.31	0.21	13.12	0.13
06/11/74	0.30	2.94	2.55	17.40	0.23	13.12	0.37
07/09/74	-0.49	1.10	2.14	27.84	0.28	15.82	0.16
08/06/74	-0.77	0.75	1.97	30.88	0.26	18.53	0.16
09/10/74	-0.52	1.45	1.97	23.05	0.19	13.33	0.17
10/08/74	-0.62	1.45	1.81	27.40	0.19	14.57	0.09
10/29/74	-0.68	1.65	1.81	26.10	0.18	14.37	0.10
12/09/74	-0.74	3.09	2.55	32.62	0.17	17.28	0.14
03/18/75	1.49	0.80	0.63	2.26	0.31	1.79	0.08
04/18/75	2.31	0.65	0.42	1.09	0.18	0.96	0.06
05/06/75	0.82	3.09	2.39	10.87	0.21	9.16	0.28
06/09/75	0.90	1.20	0.99	15.22	0.18	10.62	0.13
07/07/75	1.30	2.94	2.55	16.96	0.25	13.53	0.28
08/11/75	-0.52	2.35	2.14	19.57	0.28	16.45	0.19
09/08/75	-0.89	1.70	2.14	25.23	0.02	13.95	0.14
10/06/75	-0.82	2.45	2.30	26.53	0.21	17.70	0.11
11/10/75	-0.66	2.84	2.30	26.10	0.19	15.82	0.12
12/08/75	-0.42	2.89	2.39	28.71	0.18	16.86	0.68
01/12/76	-0.82	2.89	2.22	26.10	0.15	14.57	0.09

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
02/09/76	0.23	2.69	2.71	22.62	0.28	15.62	0.17
03/08/76	-0.28	2.05	1.56	12.61	0.24	7.91	0.17
04/12/76	0.15	2.59	2.06	14.35	0.23	10.20	0.18
05/03/76	-0.23	2.99	2.88	19.57	0.21	14.99	0.28
06/01/76	-0.37	1.65	2.71	25.66	0.21	14.99	0.16
06/28/76	-0.49	1.45	2.06	26.97	0.21	15.41	0.11
08/02/76	-0.80	1.05	2.06	31.32	0.24	16.03	0.10
08/30/76	-0.92	1.00	2.22	32.19	0.24	17.49	0.12
10/04/76	-0.72	1.35	2.30	30.01	0.19	15.41	0.11
11/01/76	-0.68	1.75	2.22	26.53	0.17	14.78	0.10
12/06/76	-0.89	2.64	2.71	33.49	0.17	18.11	0.10
03/07/77	-0.04	2.10	1.89	25.23	0.14	13.74	0.11
04/11/77	0.11	1.60	1.65	17.40	0.15	10.41	0.12
05/09/77	-0.70	2.10	2.22	27.84	0.18	15.82	0.11
06/16/77	-0.89	1.70	2.14	26.10	0.21	16.45	0.10
07/11/77	-0.23	1.45	1.15	16.96	0.19	9.99	0.13
08/08/77	-0.85	1.80	1.73	19.57	0.19	11.66	0.08
09/12/77	-0.03	1.55	1.65	23.49	0.20	13.33	0.15
10/10/77	-0.52	2.00	1.65	18.27	0.19	11.87	0.13
11/07/77	-0.49	2.25	2.22	23.49	0.15	14.16	0.09
12/05/77	-0.46	2.74	2.30	24.36	0.15	14.16	0.11
01/09/78	-0.82	2.30	2.14	26.53	0.14	14.37	0.11
04/10/78	0.92	2.30	1.73	8.26	0.26	6.66	0.54
05/01/78	0.20	3.14	2.63	17.83	0.22	12.49	0.54
06/12/78	-0.04	2.50	2.14	14.79	0.23	9.79	1.35
07/10/78	0.49	2.45	1.65	12.61	0.28	8.54	0.21
08/07/78	-0.74	1.90	2.22	23.92	0.22	13.95	0.21
09/11/78	-0.34	1.90	2.14	26.10	0.26	17.28	0.19
10/09/78	-0.60	2.25	2.14	22.18	0.24	14.16	0.14
11/06/78	-0.57	2.10	2.22	27.40	0.18	16.24	0.13
12/11/78	-0.62	3.14	3.13	36.10	0.28	20.40	0.42
01/10/79	-0.54	2.64	2.88	35.23	0.25	22.90	0.15
04/18/79	2.04	0.60	0.38	1.39	0.15	1.02	0.08
05/07/79	1.04	3.34	2.88	15.22	0.21	13.53	0.31
06/11/79	-0.34	2.94	3.13	12.18	0.24	19.15	0.28
07/09/79	-0.31	1.55	2.22	5.65	0.23	17.28	0.21

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
08/06/79	-0.80	0.70	18.92	26.10	0.19	14.37	0.13
09/11/79	-0.47	1.05	1.97	28.27	0.18	16.86	0.12
10/08/79	-0.55	1.20	2.30	30.45	0.23	17.28	0.17
11/12/79	-0.62	2.05	2.39	30.01	0.17	17.28	0.12
12/10/79	-0.77	2.00	2.55	29.58	0.16	15.82	1.27
01/14/80	-2.00	2.74	2.80	38.28	0.19	20.40	0.13
03/31/80	0.79	1.75	1.89	15.66	0.21	12.08	0.12
05/12/80	-0.60	1.70	2.47	29.58	0.22	18.11	0.11
06/09/80	-0.59	1.10	2.30	31.75	0.21	18.32	0.14
07/14/80	-0.89	1.00	2.22	33.06	0.24	17.91	0.11
08/11/80	-0.74	1.00	2.14	33.49	0.26	16.66	0.15
09/08/80	-1.00	1.10	1.89	28.71	0.24	15.82	0.48
10/13/80	-0.74	1.25	1.97	29.58	0.21	14.57	0.11
11/10/80	-0.66	1.90	2.06	27.84	0.26	17.07	0.14
12/08/80	-0.85	3.04	2.96	34.36	0.28	22.90	0.17
01/19/81	-0.92	2.64	2.55	27.40	0.15	15.82	0.11
03/09/81	-0.11	1.85	1.56	16.09	0.19	9.37	0.12
04/12/81	-0.54	1.80	1.89	19.57	0.13	13.53	0.09
05/11/81	-0.74	1.25	1.89	28.71	0.15	15.82	0.24
06/08/81	-0.62	1.90	2.30	27.40	0.19	20.82	0.15
07/13/81	-0.59	1.60	1.97	23.05	0.22	16.24	0.11
08/10/81	-0.82	2.79	1.56	21.75	0.18	14.37	0.10
09/14/81	-0.82	1.00	1.89	24.79	0.21	14.57	0.27
11/09/81	-0.74	1.70	2.06	27.40	0.14	14.99	0.28
04/06/82	0.41	1.45	1.07	9.13	0.21	5.62	0.12
04/14/82	1.64	1.05	0.66	3.57	0.18	2.50	0.13
05/14/82	0.04	2.74	2.47	18.70	0.19	13.12	0.17
06/14/82	-0.33	2.69	3.04	20.88	0.20	14.99	0.11
07/19/82	-0.66	1.15	2.14	25.23	0.19	15.20	0.09
08/23/82	-0.74	0.85	1.89	26.53	0.18	14.37	0.21
09/13/82	-1.05	0.95	2.14	29.14	0.17	15.20	0.10
10/12/82	0.52	1.30	1.15	12.18	0.23	9.37	0.37
02/14/83	1.92	0.49	0.38	1.78	0.26	1.33	0.12
03/14/83	1.74	0.80	0.48	1.17	0.20	0.94	0.09
04/11/83	0.38	1.95	9.79	10.00	0.17	64.75	0.14
07/11/83	-0.92	2.30	2.22	24.79	0.22	16.66	0.14

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
08/29/83	-0.85	1.10	2.14	26.10	0.20	14.16	0.10
10/11/83	-0.72	1.70	2.14	26.97	0.16	15.82	0.13
02/28/84	0.08	1.65	1.48	14.79	0.21	9.99	0.20
03/22/84	1.36	0.75	0.49	2.44	0.25	1.81	0.17
06/15/84	-0.26	1.15	1.81	26.53	0.14	13.74	0.09
08/14/84	-0.82	1.30	1.40	18.27	0.23	10.62	0.14
10/02/84	-0.92	0.27	0.39	3.83	0.33	1.31	0.37
11/05/84	-0.66	2.15	2.39	28.27	0.15	15.82	0.12
03/25/85	0.76	1.45	1.32	13.05	0.17	8.33	0.11
06/06/85	-0.62	1.65	2.22	24.79	0.15	14.16	0.10
08/08/85	-1.00	1.10	1.48	22.62	0.18	11.87	0.10
10/21/85	-0.10	1.55	1.40	14.79	0.15	10.41	0.12
12/09/85	-0.70	2.20	2.39	30.45	0.13	15.82	0.11
06/18/86	-0.66	1.25	2.06	24.79	0.17	14.57	0.14
12/01/86	-0.19	3.09	3.37	24.36	0.20	18.11	0.17
01/05/87	-0.80	2.54	2.22	26.97	0.11	15.20	0.13
02/18/87	-0.23	2.59	2.30	18.70	0.23	13.74	0.21
05/15/87	-0.68	1.60	2.47	26.97	0.19	16.03	0.12
07/31/87	-0.66	1.55	1.65	21.75	0.20	13.12	0.10
09/09/87	-0.85	0.85	1.97	26.10	0.18	15.41	0.08
10/20/87	-0.77	1.30	2.06	29.14	0.14	14.37	0.08
11/24/87	-0.70	1.75	2.14	24.79	0.13	15.41	0.09
03/09/88	-1.15	1.85	2.06	23.05	0.28	17.28	0.19
04/20/88	-0.64	1.85	2.06	26.53	0.13	14.57	0.18
06/02/88	-0.68	0.90	2.14	30.88	0.17	17.70	5.08
08/06/88	-0.96	0.65	2.47	36.10	0.18	19.15	0.08
11/22/88	-0.80	2.00	2.47	32.62	0.14	17.70	0.07
05/09/89	-0.57	0.29	0.32	3.18	0.25	2.71	0.07
06/14/89	-0.74	2.50	2.63	24.79	0.19	17.07	0.08
08/01/89	-1.22	0.80	2.06	27.40	0.15	16.03	0.05
08/22/89	-0.92	1.10	1.81	21.75	0.21	12.28	0.08
10/25/89	-0.70	1.35	2.14	28.27	0.16	15.82	0.06
11/30/89	-0.68	2.40	2.39	29.58	0.17	17.49	0.07
03/05/90	-0.13	2.00	2.39	26.53	0.11	14.78	0.23
04/17/90	-0.64	1.80	2.14	22.62	0.15	11.24	0.10
05/03/90	-0.62	2.20	2.88	35.67	0.28	24.98	0.28

Sample Date	LOG Discharge	Ca^{2+} meq/L	Mg^{2+} meq/L	Na^{+} meq/L	K^{+} meq/L	SO_4^{2-} meq/L	Cl^{-} meq/L
08/02/90	-0.77	1.30	0.78	10.44	0.19	6.45	0.12
08/27/90	-0.89	1.35	2.06	23.92	0.12	13.12	0.12
11/26/90	-0.80	2.30	2.55	32.62	0.15	19.36	0.24
12/11/90	-0.80	2.40	2.39	31.32	0.15	17.28	0.23
03/11/91	-0.28	1.70	1.65	15.66	0.21	10.83	0.00
06/17/91	-0.64	1.30	1.56	24.36	0.18	11.66	0.01
08/27/91	-0.96	1.15	1.65	23.49	0.20	13.12	0.03
11/20/91	-0.28	1.50	1.40	18.27	0.20	11.87	0.16
12/10/91	-1.40	2.35	2.22	29.14	0.15	16.66	0.45
02/19/92	-0.92	2.45	2.39	27.84	0.16	13.74	0.45
04/15/92	-0.60	1.90	2.06	24.79	0.15	13.12	0.17
06/02/92	-0.89	0.90	2.30	30.01	0.15	15.20	0.42
07/08/92	-0.96	1.10	1.40	20.88	0.15	11.87	0.25
10/06/92	-0.74	1.45	2.22	28.27	0.16	13.53	0.08
11/23/92	-0.60	1.85	2.06	28.27	0.14	13.74	0.59
05/05/93	-0.77	1.75	2.30	28.71	0.18	16.86	0.08
05/20/93	-0.92	0.95	2.39	31.75	0.16	17.91	0.06
06/15/93	-0.60	1.55	1.48	16.96	0.18	10.41	0.07
06/16/93	-0.68	1.50	1.65	20.01	0.17	10.83	0.06
07/28/93	-0.39	0.90	0.56	2.09	0.23	1.39	0.17
08/11/93	-0.29	1.80	1.48	13.48	0.31	7.50	0.12
08/24/93	-0.72	2.30	2.06	22.18	0.25	12.91	0.10
10/08/93	-0.43	1.60	2.14	21.75	0.19	14.78	0.10
11/29/93	-0.70	2.35	2.30	27.84	0.14	15.62	0.06
03/31/94	0.15	2.35	1.81	12.61	0.24	9.16	0.21
05/09/94	-0.44	2.50	2.96	26.10	0.20	14.99	0.10
08/01/94	-0.85	0.90	2.06	31.32	0.21	16.24	0.13
10/05/94	-0.46	1.95	1.73	20.01	0.20	10.62	0.07
12/14/94	-0.60	2.79	2.55	27.40	0.16	15.41	0.07
01/25/95	-0.60	2.25	2.06	26.97	0.12	14.16	0.05
04/12/95	-0.38	2.35	2.39	19.57	0.23	12.08	0.14
06/27/95	-0.60	0.80	2.22	29.14	0.09	15.82	0.08
10/26/95	-0.60	1.50	2.06	13.05	0.15	14.37	0.07
08/07/96	0.04	1.05	0.82	14.79	0.20	10.62	0.09

Appendix B.
Major Ion Concentration and LOG Discharge Data.
(HCO_3^- & CO_3^{2-})
Bear Den Creek, Fort Berthold Indian Reservation, North Dakota.
Years: 05/09/89 - 08/07/96
Sample Site: USGS Site 06332515

Sample Date	LOG Discharge	HCO_3^- meq/L	CO_3^{2-} meq/L
05/09/89	-0.57	10.24	0.80
06/14/89	-0.74	11.52	3.20
08/01/89	-1.22	9.98	0.87
08/22/89	-0.92	11.80	1.43
10/25/89	-0.70	15.00	1.20
11/30/89	-0.68	17.86	0.00
03/05/90	-0.13	15.41	0.00
04/17/90	-0.64	11.60	0.00
05/03/90	-0.62	12.19	1.60
08/02/90	-0.77	11.19	1.20
08/27/90	-0.89	5.72	0.40
11/26/90	-0.80	18.19	1.20
12/11/90	-0.80	19.18	2.40
03/11/91	-0.28	8.93	0.40
06/17/91	-0.64	10.80	3.20
08/27/91	-0.96	9.60	2.40
11/20/91	-0.28	10.80	0.00
12/10/91	-1.40	18.19	0.00
02/19/92	-0.92	15.77	0.00
04/15/92	-0.60	15.19	0.57
06/02/92	-0.89	14.80	2.40
07/08/92	-0.96	10.69	1.03
10/06/92	-0.74	17.37	1.13
11/23/92	-0.60	16.88	1.27
05/05/93	-0.77	16.16	1.83
06/15/93	-0.60	10.00	0.80
08/24/93	-0.72	13.16	0.73
10/08/93	-0.43	13.28	1.27
03/31/94	0.15	7.24	0.33
05/09/94	-0.44	14.18	0.73
08/01/94	-0.85	13.90	1.73
12/14/94	-0.60	15.68	0.00
01/25/95	-0.60	16.19	0.00
04/12/95	-0.38	10.52	0.60
06/27/95	-0.60	12.60	2.00
10/26/95	-0.60	13.60	1.60
08/07/96	0.04	6.92	0.00

I, Damon K. Williams, Hereby submit this thesis/report to Emporia State University as partial fulfillment of the requirements for an advanced degree. I agree that the Library of the University may make it available to use in accordance with its regulations governing materials of this type. I further agree that quoting, photocopying, or other reproduction of this document is allowed for private study, scholarship (including teaching) and research purposes of a nonprofit nature. No copying which involves potential financial gain will be allowed without written permission of the author.

Signature of Author

5/14/99

Date

Major Ion Concentration for Bear Den Creek, Fort Berthold Indian Reservation, North Dakota: 1969-1996

Title of Thesis

Signature of Graduate Office Staff

May 14, 1999

Date Received