Sources and Processes Affecting Dissolved Sulfate Concentrations in the Upper Sheyenne River

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Soil Maps Compiled by Rod Bassler

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INTRODUCTION

During the first operational year (2005) of the Devils Lake Outlet sulfate concentrations in the Sheyenne River at the Outlet reference gages were unexpectedly high. The purpose of this report is to review the sources and processes affecting sulfate concentrations in the upper Sheyenne River and to assess their relationship to the initial regulatory framework established for the Outlet and the assumptions governing that framework. The report content consists of: (1) a brief review of the standards established by the North Dakota Department of Health[1] and the findings of the Environmental Impact Statement[2], including those of HEC5-Q models used for initial assessment of water quality impact on downstream water quality at points of regulatory concern; (2) an assessment of historical sulfate data for the Sheyenne River in relation to model assumptions; (3) an evaluation of sources and processes affecting the distribution of sulfate in the upper Sheyenne River, including soil and ground-water contributions; and (4) an identification of data requirements needed to provide realistic and suitably conservative transfer functions for maintaining standards at the points of protection while operating the Outlet. The method used for this report is essentially that of data mining, employing existing river, ground water, soil, LANDSAT, ancillary data collected in the upper Sheyenne basin, and other information related to hydrologic processes, to provide a broad framework for more detailed assessment. It is our hope that evaluation of these data, much of it collected after initial assessments for the permitting process, will help to define critical issues for investigation in order to further refine the operational plan on a sound, factual basis.

REVIEW OF OPERATIONAL STANDARDS AND ASSUMPTIONS

"Effluent Limitations and Monitoring Requirements" for water chemistry in the Sheyenne River are constrained by four goals and standards[1]. These are:

(1) Sulfate: The Sheyenne River is classified as a Class 1A stream, which has a total sulfate standard of 450 mg/L.

(2) Sulfate: The EPA secondary drinking water standard is 250 mg/L. The first protection point with reference to this standard would be the water supply of Valley City. The secondary MCL is of negligible toxicological risk. But it is considered undesirable from the standpoint of taste.

(3) TDS: from D41 of the Final EIS[2], "The State of Minnesota's water quality rules have established 250 mg/L sulfate and 500 mg/L TDS as standards for the Red River of the North. It is desirable that minimal impact on this standard be incurred. The measuring point for this standard is the gage at Halstad, MN.

(4) TDS: The Canadian objective is 500 mg/L. It is desirable that minimal impact from outlet operation be incurred on this objective. The measuring point is Emerson, Manitoba.

(5) Significant degradation: According to Health Department standards, For Class 1 streams, which include both the Sheyenne River and the Red River of the North, a determination of "significant effect" would be if the ambient quality of any parameter were degraded by more than 15%, or that the available assimilative capacity were reduced by more than 15%, or that any pollutant load would be increased by 15%" (from D-41 of the draft EIS)[2]. Where variable measurements are common, it is unclear how the 15% standard would be applied; i.e. which times, or statistical aggregations of time would be applied.

The North Dakota State Health Department has weighted highly the sulfate secondary MCL at Valley City and the TDS objective at Halstad in considering operational constraints.

The permit sulfate constraint was to be applied as 300 mg/L. Two measuring points are designated for enforcement of this limit. The first is immediately upstream of the Outlet. The allowable release from the Outlet Q_o is determined as:

$$Q_o = \frac{Q_i(300 - C_i)}{(C_o - 300)} \qquad (1)$$

where C_o is the sulfate concentration in the Outlet water, C_i is the instream concentration just upstream of the Outlet (Condition 4 of the operational permit), and Q_i is the instream flow just upstream of the Outlet. In effect, this expresses a mixed total limit of 300 mg/L at the Outlet. The upstream monitoring point is at Flora, ND.

A second supplementary measuring point for sulfate is stipulated in Condition 4 of the operating permit, which states that the "7-day" average sulfate concentration measured in the samples from downstream monitoring location shall not exceed 300 mg/L. The downstream gage is at Bremen, ND.

(6) The U.S. Army Corps of Engineers Models

The control points for the HEC-5 and HEC5-Q models for the "upper" Sheyenne River begin at Peterson Coulee at the insertion point of the Devils Lake water. However, the first river control point having data is Warwick (EIS A-49 and Figure A4-1 on page A-38). All tributary loadings ... "with the exception of the Sheyenne River and Devils Lake Outlet, are computed using mean monthly constituent concentration for the tributary." (A-61). Fundamentally, the upper Sheyenne River from Peterson Coulee to Warwick was treated as a single tributary. "There were no defined tributaries between Peterson Coulee (the insertion point), and Warwick, and between Warwick and Cooperstown. "

> The USGS based their Sheyenne River headwaters water quality relationships on the Warwick water quality and flow records. Therefore, inflow quality between Peterson Coulee and Warwick was assumed *[to]* mimic the quality of the Sheyenne River headwaters developed by the USGS and was assigned a daily inflow quality type TT1. Incremental loading between Warwick and Cooperstown (Cooperstown local tributaries-TT123) was determined using a historic mass-balance relationship of flow and water quality records between Warwick and Cooperstown. Mean monthly flows were used to compute the mass balance for the reach." (A-65).[2]

Simulations of the upper Sheyenne River thus began at the proposed Outlet, and were based on gage water quality measurements at Warwick. Results of the simulations are thus based on a Warwick QW initial condition at the Outlet.

SOURCES AND PROCESSES AFFECTING SULFATE IN THE UPPER SHEYENNE RIVER

A common assumption of surface-water quality for North Dakota streams fed by ground water has been that base flows comprised of mineralized ground-water seepage are generally higher in salts, and in the northern Great Plains frequently higher in sulfate. Conversely, larger flows caused by storm-waters are usually assumed to be fresher, coming mainly from surface runoff not affected by prolonged contact with salts. In most cases, with respect to sulfate in North Dakota, the surface of soils is well leached of salts in recharge zones, or may contain more calcium bicarbonate, with sulfates more deeply leached in the soil profile on slightly evaporative soils. In the 1980s this viewpoint began to change. As stated by Bevan and Germann[3], "It is now commonly accepted that in many catchments the magnitude and shape of the storm hydrograph is dominantly controlled by subsurface flows." They cite several research papers in which hydrograph separation techniques based on the chemical characteristics of rain, soil, and ground water "suggest that pre-storm water may make up a significant proportion of the hydrograph peak." As the method suggests, a corollary of the subsurface effect on hydrograph peaks is a change in water chemistry that reflects the effects of the ground-water source.

High Stream-Bank Water-Table Effects on Hydrograph Components

Several physical mechanisms account for the previous difficulties in predicting hydrographs. These include: (1) "Displacement" of old water at the base of a hill-slope by new rainwater infiltrating upslope, causing a "rapid, wavelike transmission of the pressure changes at the boundary of the saturated zone" (Bevan and Germann[3]); (2) Transmission of increased air pressure under an infiltration wetting front. This mechanism would need a large-scale continuous wetting front with few large pores. (3) A very rapid filling of soil pores, and therefore a large increase in pressure head can occur during storms when the water table is near (within a few feet) of land surface. This is caused by the shape of the soil-water capillary characteristic curve and is called the Weiringermeer Effect (Gillham[5]). (4) Seepage (Q) to a stream or drainageway, as

modeled using a Depuit-Forchheimer approximation of flow to a line sink (eq. 8.1.18, Bear[6]),

$$Q = \frac{K}{2L}\left(h_L^2 - h_o^2\right) \qquad (2)$$

where K is the hydraulic conductivity, is strongly affected by pore-water head, increasing by the square of the head differential.

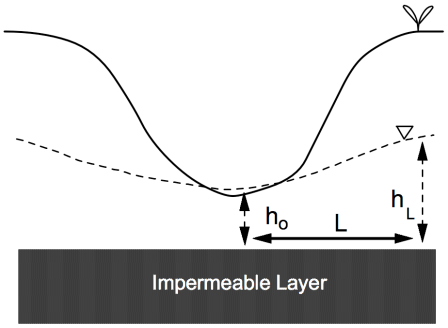


Figure 1. Depuit-Forchheimer parameters. (Fig. revised 1/4/16)

All of these, and particularly mechanisms (3) and (4) mean that in wet years, or even more during wet climate periods where water tables are near land surface, precipitation can cause large surges of near-surface ground water into streams.

Soil Sulfate Sources

The second major influence on surface-water chemistry during storm runoff is the chemical composition of porewater adjacent to surface-water bodies which serves as the direct source of the hydraulic surges discussed above. Sulfur is ubiquitous in many bedrock formations of the northern Great Plains, and in the high-organic Cretaceous shales forming the local bedrock surface it is commonly present in the form of pyrite. Pyrite in glacial till and sands and gravels from weathered shale oxidizes when exposed to air and forms sulfate. Most of eastern North Dakota has a ready supply of mineral sulfur in the parent materials of its soils, and when oxidizing conditions occur, particularly during droughts when water tables are low, sulfate is formed and added to the soil solution. During wet cycles when water tables are high these move upward in the soil profile under evaporative force and precipitate within the soil profile as calcium, magnesium or sodium

salts. The closer the water table is to land surface, and the more local evaporation governs the system, the more and nearer the surface one finds sulfatic salts. Where water tables are deep and decoupled from evapotranspiration, and where local recharge is dominant, salts are flushed and remain deep below the land surface.

Some of the soil taxa which may indicate the presence of sulfate include:

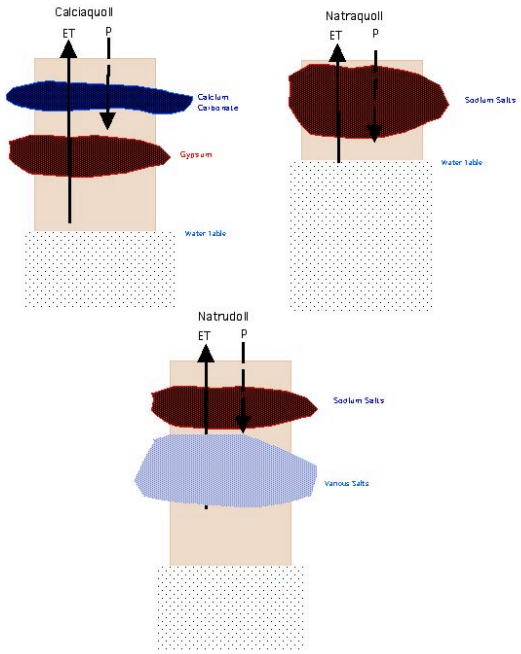


Figure 2. Schematic of salt placement in area soils.
Natriboroll taxa have been reclassified as Natrudolls.

(1) Natriboroll - these soils contain high clay content (argillic horizon) and high sodium (a natric horizon) and frequently sulfate in North Dakota below the topsoil. The sodium and sulfate are weathered from soil parent materials.

(2) Calciaquoll - these soils have relatively high water tables with slightly more evaporative discharge than local recharge. This hydrologic regime causes deposition and retention of less soluble calcium carbonate in the upper soil profile, with frequent presence of gypsum (containing sulfate) in the lower soil profile.

(3) Natraquoll - these soils have high water tables and high sodium (a natric horizon) and frequently high sulfate in their upper horizons.

Maps of soil great groups affecting sulfate concentrations along the Sheyenne River are appended and include (1) a map key, and (2) four maps identifying soil taxa from west of Harvey to Cooperstown as identified on the map key.

Salt placement in these soils can change with climate regime and consequent changes in the predominant water table. For example, one of the environmental concerns listed in the EIS is that higher flows and salinity from the Devils Lake Outlet waters will cause higher water tables adjacent to the Sheyenne River downstream of the Outlet, and result in evaporative concentration of salts near land surface. This is also a concern of landowners along the Outlet channel itself, and is the reason that the SWC has undertaken soil salinity measurements using VERIS. In a recent USDA-NRCS annual focus meeting held in Bismarck, soil conservationists from North Dakota and South Dakota discussed large-scale salinization of surface soil that has resulted from the wet climate of the 1990s. High water tables can cause topsoil salinization within a relatively short period of time.

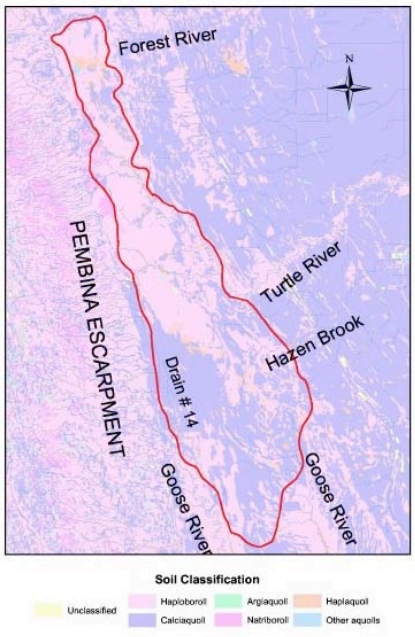


Figure 3. Illustration of saline salt placement along drainageways of the Pembina Escarpment.

High water tables can affect salinization of streams through: (1) base flows at the streambank and banks of tributaries; (2) drainageways, which comprise ephemeral tributaries of the streams; and (3) formation and integration of saline wetlands with drainageways to the river. Mechanisms for contributions at streambanks were discussed above. An example of porewater effects on water chemistry of drainageways can be seen in the Pembina Escarpment, draining to the Elk Valley aquifer in Grand Forks County, which has been intensively monitored. Drainageways in the Pembina Escarpment have been incised through the upper portions of the Pierre Shale and through glacial till soils formed from weathering of that shale. The soils are high in sulfate and are classified as Natriborolls. Their distribution along the drainageways is shown (as pink) on the left side of the soil map above. The distribution of salinity as reflected by specific conductance in the drainageways is shown on Figure 4.

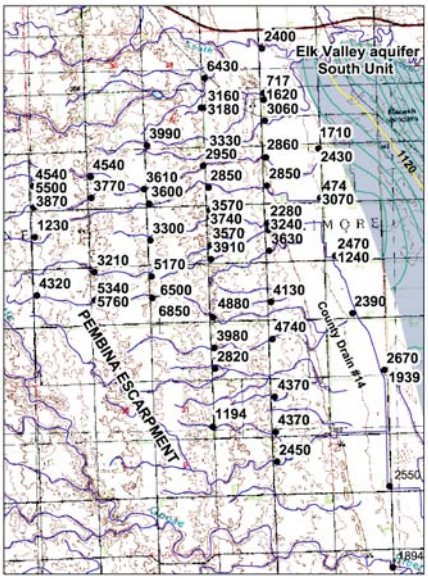


Figure 4. Specific conductance (EC) in drainageways of the Pembina Escarpment.

Specific conductance values approach 6,000 µS/cm in the upper reaches, and gradually decrease to 3,000 to 4,000 µS/cm in the middle reaches, and 1,000 to 2,000 µS/cm in the lower reaches. The decrease is caused by addition of surface water runoff and less

prevalence of saline soils (Natriborolls on the previous figure) downstream on the drainageways. A relationship for sulfate vs. EC near the Pembina Escarpment is shown on Figure 5. The range of sulfate concentrations represented would be about 3,000 mg/L for the 6,000 μS/cm EC value, and about 670 mg/L for the 2,000 mg/L EC value.

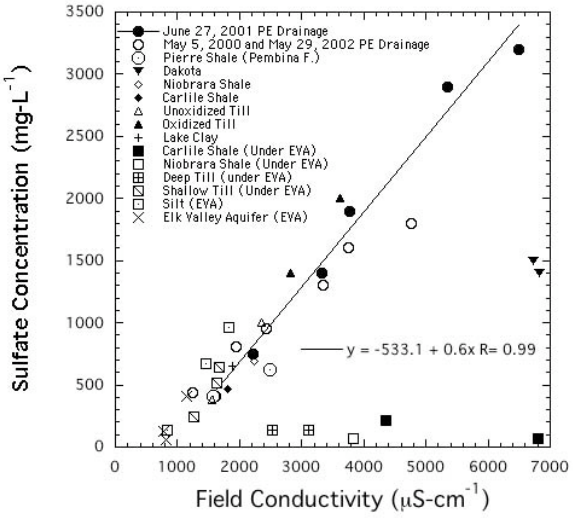


Figure 5. Relationship between sulfate concentration and EC in eastern ND.

Figure 6 illustrates how drainageways, like those of the Escarpment, would affect runoff to a major stream. When the water table is low and below the bottom of the drainageway, runoff waters following a major storm would be largely unaffected by salinity of the underlying materials (A). The salinity of water flowing in the drainageways would consist primarily of fresh waters from direct runoff and saline seepage waters from the soils neighboring the channel. However, when water tables are higher, the drainageways form a system of highly saline pools (B,C). When smaller storms having sufficient runoff to cause flow in the drainageways to occur, surface runoff mixes with the saline pools and transports them downstream to the receiving water body (D,E). In addition, where bordering soils are saline, initial high water tables and saturation with rainfall will cause direct border flux of salts into the drainageway, according to hydraulic mechanisms described above.

A local example of drainageway retention is in the Devils Lake Outlet itself. The lower reaches of the Outlet channel were excavated through soils that were primarily of the Calciaquoll taxa, which often has sulfate as gypsum in the lower soil profile. The elevation of the channel bottom and water levels in the channel are both well below land surface.

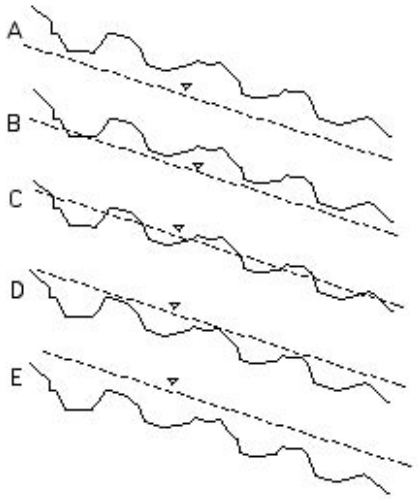


Figure 6. Water-table effects on soil salinity in drainageways as discussed in the text. A illustrates a low water-table scenario; B, C and D increasingly elevated water tables; and E storm-flow conditions.

Norman Prochnow, a registered Soil Classifier employed by Western Plains Consulting (WPC), examined soil series and salinity adjacent to the channel, and offered the opinion that in some locations where the Outlet channel elevation is low in relation to land surface, desalinization of soils along the channel would be more likely than salinization. The channel would serve as a line sink, draining adjacent lands. Sulfate concentrations in static water during the Devils Lake Channel operating hiatus are shown on Fig. 7. Sulfate in the channel increased from about 700 mg/L to more than 3,000 mg/L over a period of two months of nearly static water. Unless the water depth in the channel was very small, a four-fold increase in salinity from evaporative concentration during that time would be implausible. The Outlet channel is gaining sulfate from drainage of

adjacent sulfatic subsoils. This would be expected along natural drainageways as well. Similar processes in the streambank and drainageways would be expected in the Sheyenne River when flowing through saline areas in a wet climate.

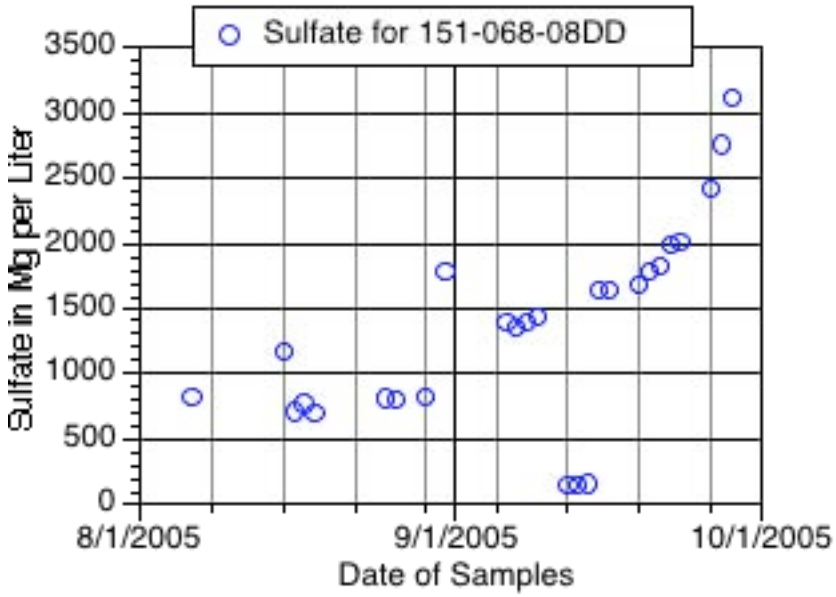


Figure 7. Effects of soil drainage from a Calciaquoll soil into the channel of the Devils Lake Outlet.

Soil classifications, and saturation-extract EC and sulfate data from WPC are on Table 1. Half of the sites (12 out of 25) had sulfate concentrations greater than 1,500 μS/cm. Of these eight (66%) were Calciaquolls, one was a Natraquoll, and three (25%) were Hapludolls. Steinwand and Richardson[7] cited evidence of gypsum precipitation at approximately 4,000 μS/cm for soils in Nelson County. Six of the sites had subsoils (1 to 3 feet) with EC greater than 4,000 μS/cm. Five of these six were Calciaquolls. The other was the Natraquoll. Using a transfer function for sulfate vs. EC from subsoil data (Fig. 8), topsoils would have gypsum on five sites, four of them Calciaquolls and the other a Natraquoll. Because gypsum in Calciaquolls is normally below the calcic horizon, the evidence of shallow gypsum indicates a recent high water-table regime with strong evaporative influence. It also indicates that soils have been naturally salinizing, most likely since the wet climatic shift experienced since 1993.

Table 1. Soil classification, EC and Sulfate for topsoil (0 to 1 foot), and subsoil (1 to 3 foot) depths for 25 sample sites adjacent to the Devils Lake Outlet. * Toposoil sulfate is estimated using a transfer function (Fig. 8) determined from the subsoil depths samples.

Sample Number	Soil Series	Soil Classification	Sample Depth (ft.)	Conductivity (mS/cm)	Sulfate (mg/l) Calculated*	Sample Depth (feet.)	Conductivity (mS/cm)	Sulfate (mg/l)
S-1	Buse	fine loamy, mixed, superactive, frigid, Typic Calciudolls	0-1	590	0.0	1-3	500	44.4
S-2	Langhei	fine loamy, mixed, superactive, frigid, Typic Eutrudepts	0-1	760	82.7	1-3	820	37
S-3	Svea	fine loamy, mixed, superactive, frigid, Pachic Hapludolls	0-1	3940	2203.0	1-3	4,320	2760
S-4	Hamerly	fine loamy, mixed, superactive, frigid, Aeric Calciaquolls	0-1	7000	4622.0	1-3	9,120	6940
S-5	Barnes	fine loamy, mixed, superactive, frigid, Calcic Hapludolls	0-1	790		1-3	3,870	2920
S-6	Ferney	fine, smectitic, frigid, Leptic Natrudolls	0-1	11,800	9164.9	1-3	10,200	7280
S-7	Renshaw	fine loamy over sandy or sandy skeletal, mixed, superactice, frigid, Calcic Hapludolls	0-1	450	0.0	1-3	980	21.4
S-8	Tonka	fine, smectitic, frigid, Argiaquic Argialbolls	0-1	990	222.6	1-3	410	31.5
S-9	Fordville	fine loamy over sandy or sandy skeletal, mixed, superactive, frigid, Pachic Hapludolls	0-1	1,130	308.8	1-3	1,050	22.8
S-10	Fordville	fine loamy over sandy or sandy skeletal, mixed, superactive, frigid, Pachic Hapludolls	0-1	400	0.0	1-3	380	61.6
S-11	Spottswood	fine loamy over sandy or sandy skeletal, mixed, superactive, frigid, Aquic Hapludolls	0-1	1,070	271.7	1-3	1,470	150
S-12	Fram	coarse loamy, mixed, superactive, frigid Aeric Calciaquolls	0-1	2,160	966.7	1-3	1,430	415
S-13	Vallers	fine loamy, mixed, superactive, frigid, Typic Calciaquolls	0-1	4,610	2700.9	1-3	3,140	1760
S-14	Vallers	fine loamy, mixed, superactive, frigid, Typic Calciaquolls	0-1	2,150	960.1	1-3	1,430	530
S-15	Hamerly	fine loamy, mixed, superactive, frigid, Aeric Calciaquolls	0-1	9,320	6703.6	1-3	8,630	6400
S-16	Divide	fine loamy over sandy and sandy skeletal, mixed, superactive, frigid, Aeric Calciaquolls	0-1	1,320	427.0	1-3	780	131
S-17	Heimdal	coarse loamy, mixed, superactive, frigid, Calcic Hapludolls	0-1	420	0.0	1-3	600	52.8
S-18	Fram	coarse loamy, mixed, superactive, frigid Aeric Calciaquolls	0-1	3,580	1942.8	1-3	4,130	1860
S-19	Divide	fine loamy over sandy and sandy skeletal, mixed, superactive, frigid, Aeric Calciaquolls	0-1	6,680	4351.7	1-3	5,750	3180
S-20	Fram	coarse loamy, mixed, superactive, frigid Aeric Calciaquolls	0-1	1,600	603.8	1-3	910	291
S-21	Fram	coarse loamy, mixed, superactive, frigid Aeric Calciaquolls	0-1	9,060	6459.7	1-3	10,500	7300
S-22	Emrick	coarse loamy, mixed, superactive, frigid, Pachic Hapludolls	0-1	4,300	2468.3	1-3	6,280	4200
S-23	Fordville	fine loamy over sandy or sandy skeletal, mixed, superactive, frigid, Pachic Hapludolls	0-1	710	52.5	1-3	1,340	33.2
S-24	Ojata	fine silty, mixed, superactive, frigid, Aeric Calciaquolls	0-1	16,400	14376.1	1-3	15,800	13700
S-25	Emrick	coarse loamy, mixed, superactive, frigid, Pachic Hapludolls	0-1	1,050	259.4	1-3	4,520	2540

The soil seepage source of high sulfate in surface-water bodies (natural and man-made) is further demonstrated by the relationship between the sulfate component of soil porewater and the sulfate concentrations measured in the Outlet in 2005 (Fig. 8). EC and sulfate from 25 subsoil saturation extract measurements are sufficiently highly correlated to form a predictive model. These, in turn, are highly predictive of sulfate vs. EC

measured in the Devils Lake Outlet channel and presented in Fig. 7. These demonstrate the effect of porewater seepage on Outlet channel waters. The Outlet soil seepage scenario also provides a man-made and controlled model for the river salinization processes described above: i.e. upward movement of sulfatic salts through high water table conditions, and subsequent sulfate mobilization and seepage to surface waters, enhanced by high water tables and their effects on storm response.

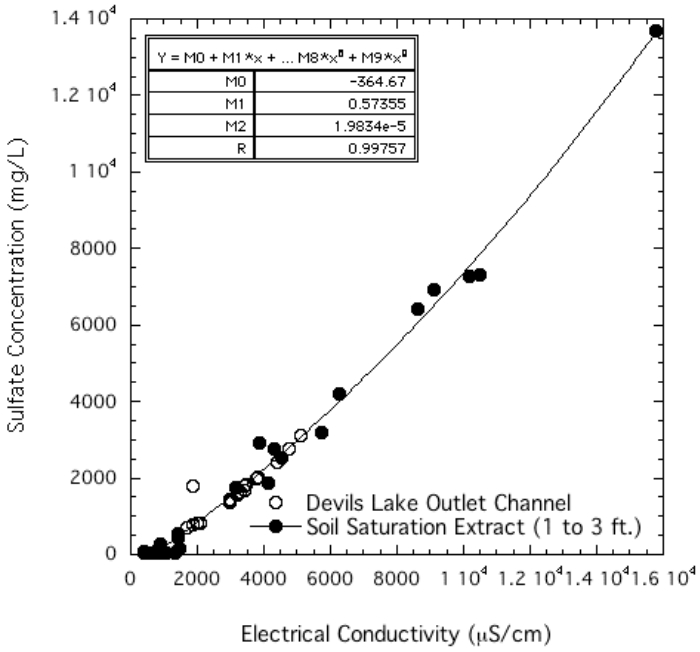
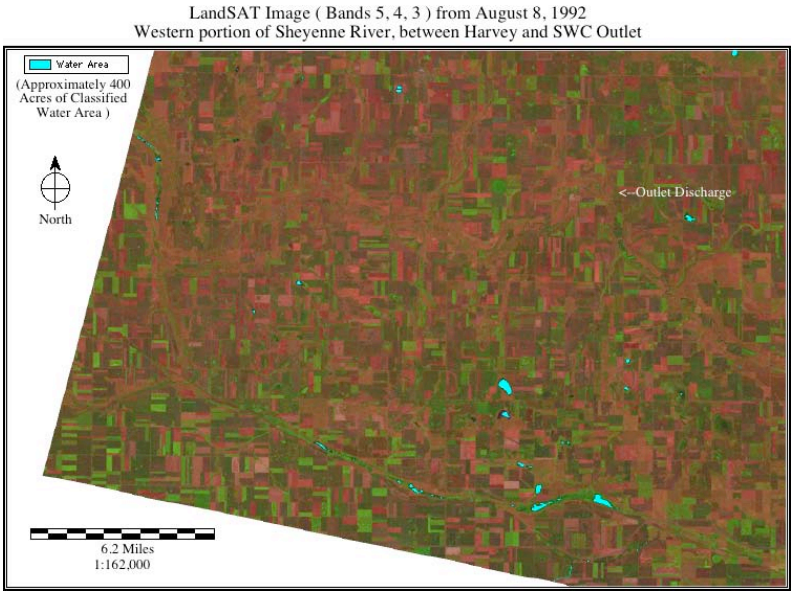


Figure 8. Sulfate vs. EC for soil saturation extracts from 25 subsoil samples collected near the Devils Lake Outlet channel.

Surface-Water Integration During Wet Climatic Periods

The third mechanism is formation and overtopping of wetlands, followed by expansion of wetlands and their integration with the drainage system to the Sheyenne River. This process is well known in the Devils Lake Basin as illustrated by difference of estimated wetland surface prior to wet conditions in 1992 and 1995 (Fig. 9), and in 1999 and 2005 (Fig. 10). Wetland surface area increased more than an order of magnitude, from about 400 square miles to between 5,000 and 6,000 square miles. The rising wetlands are associated with and reflect high water tables in neighboring soils which cause salt placement near land surface as well as evaporative concentration within the

wetland. As wetlands continue to expand they overtop and eventually integrate with drainageways and river tributaries, introducing high TDS water.



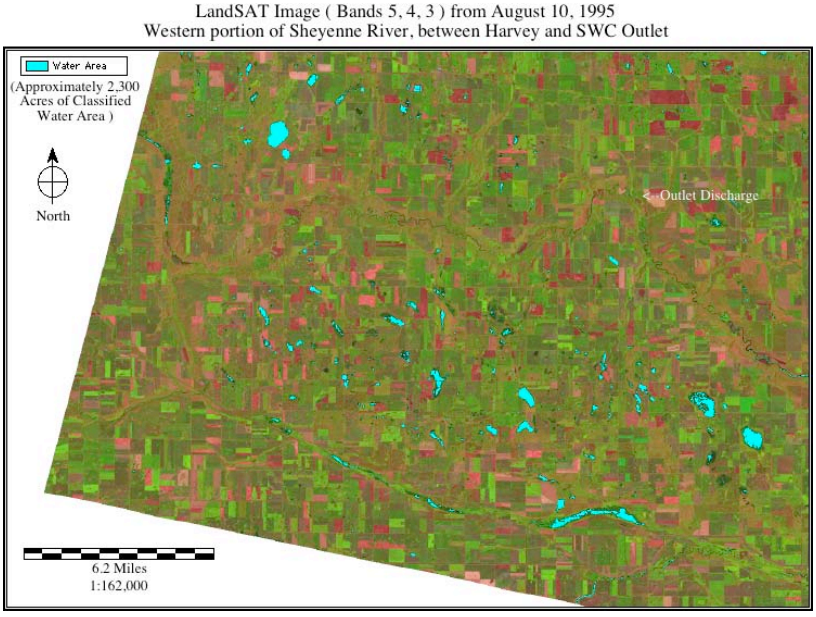


Figure 9. LANDSAT assessment of surface-water area between Harvey and the Devils Lake Outlet in 1992 and 1995.

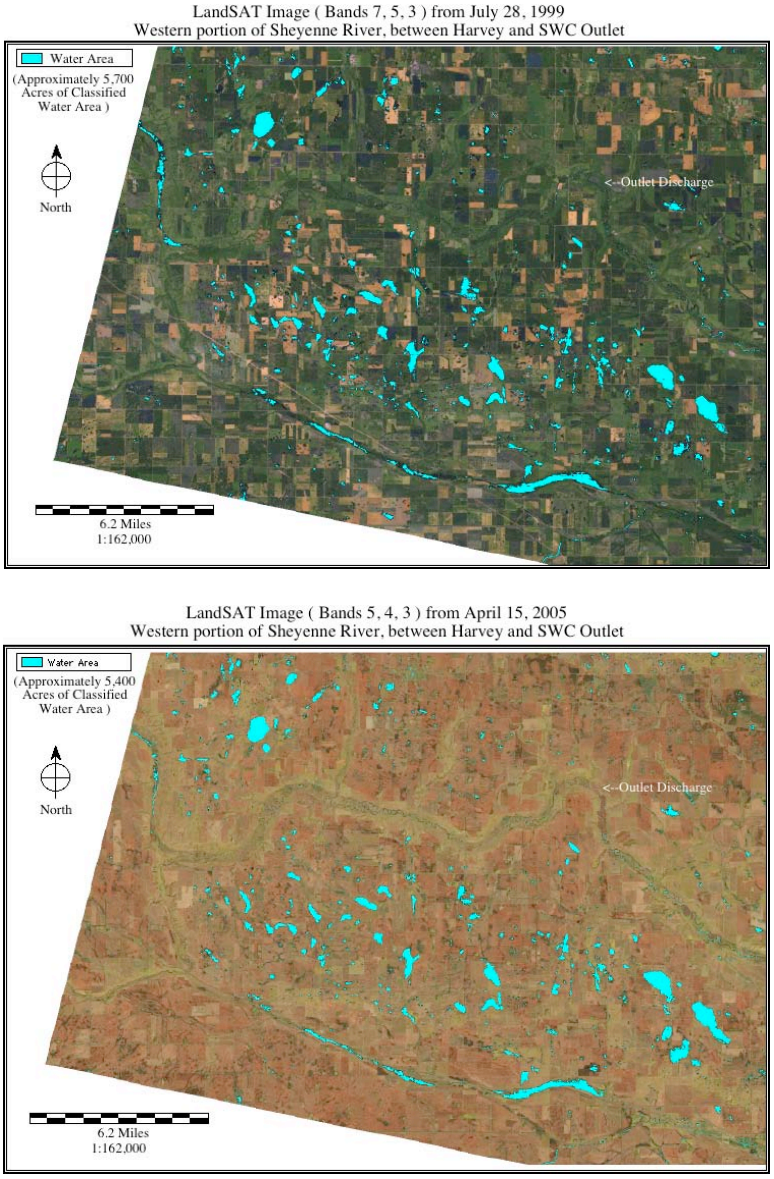


Figure 10. LANDSAT assessment of surface-water area between Harvey and the Devils Lake Outlet 1999 and 2005.

Effects of Climatic Moisture Patterns on Sheyenne River Salinity

Effects of climatic patterns with respect to precipitation on water quality in the Sheyenne River are discussed in detail in Appendix A. These can be generally described as follows: For a year having wet summer conditions following several years having drier summer conditions, dissolved salts (from proxy EC measurements) decrease with increasing discharge (1993 data, Appendix A, Fig. A-3). The larger the rainfall events, the fresher the water. Large rainfall in this case infiltrates freely into the dry soil, carrying salts deeper, and runoff from large storms is comprised mainly of surface runoff. For a moderately dry year following a climatic period sufficiently wet to elevate the water table, EC increases with increasing discharge (1994, Appendix A, Fig. A-3), indicating that more discharge to the river following storms is coming from soil and bank seepage, and possibly from higher salt concentrations near the soil surface caused by evaporation from shallower water tables. The EC vs. CFS relationship tends to gradually level off over several drier years (1995-1998).

For two very wet years (1999 and 2000) following the drier years, EC again decreases with increasing precipitation, as in 1993 (Appendix A, Fig. A-3a). For subsequent drier years (2002 through 2004), the EC vs. CFS relationship again shifted to a pattern of increasing salts with increasing flows. This pattern has been longer and more sustained than in the previous cycle beginning in 1993. This may have been caused by an initially higher water table remaining from the influence of the previous 1993 cycle (Fig. A-1 in Appendix A). It was also likely influenced by two back-to-back years of large general summer precipitation in the upper basin (Figures A-1 and A-3a in Appendix A).

In summary, the overall recurring pattern seems to be: larger runoff events produce fresher water as long as the water table is low. Once the water-table elevation is elevated the system is primed for a higher proportion of water from saline sources, and larger summer storms produce more saline water in the river. Increases in salinity at higher flows may diminish after as few as one or two drier years. Summer precipitation in the Upper Sheyenne River Basin was large in 2005, and from previous patterns, high salt content with larger rainfall events would appear to be a good possibility in 2006.

SULFATE DYNAMICS IN THE UPPER SHEYENNE RIVER BASIN

The HEC5-Q models for simulation of downstream water quality assumed that the upper Sheyenne River, upstream of Warwick, had a water chemistry similar to Warwick. It was also based on water quality data from the Sheyenne River prior to 2000. There is an additional gaging station near Harvey, ND. The Outlet is approximately equidistant in river miles from the Harvey and Warwick gages (Fig. 11).

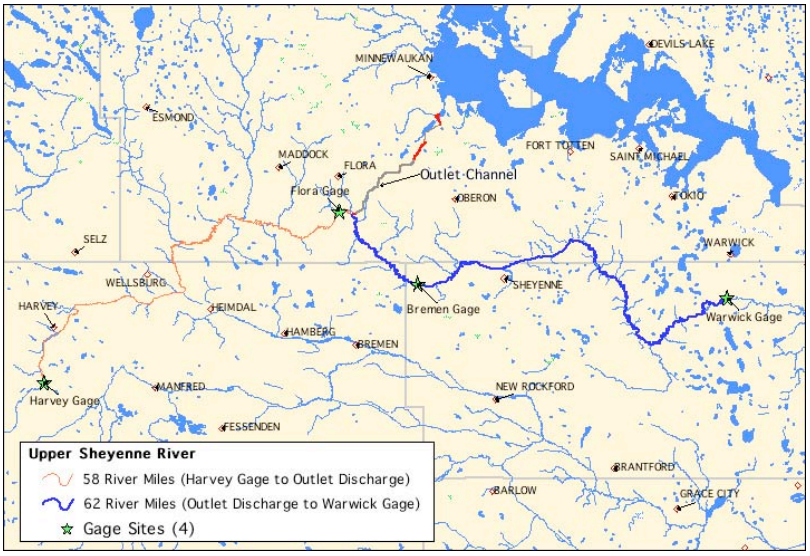


Figure 11. Map of gage locations, and illustration of river miles between Harvey, Flora and Warwick Gages.

Spatial and Temporal Variation of Sulfate at Gages of the Upper Sheyenne River Basin

The chemical composition of hydrographs for the period of record at both Harvey and Warwick (Fig. 12) indicate that there are substantial differences in sulfate concentrations in the upper Sheyenne River. Hydrographs indicate that minimum concentrations are frequently similar. Differences are mainly in the maximum concentrations. It also appears that sulfate concentrations from 2000-2005 generally increase at both sites compared with the 1990s.

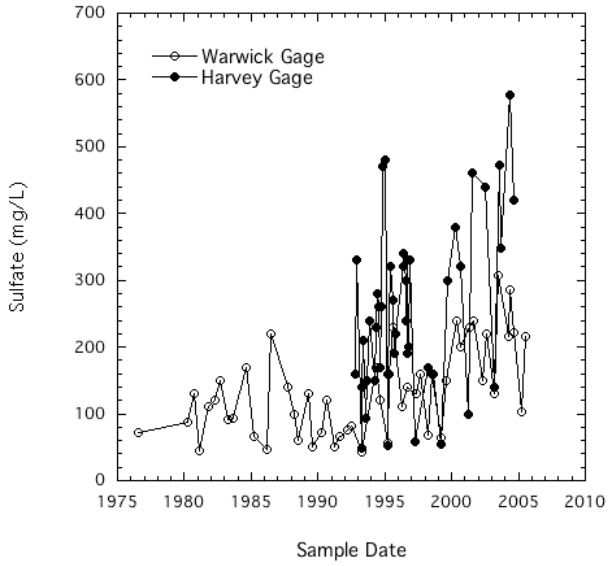


Figure 12. Record of sulfate concentrations measured in water samples from the Harvey and Warwick gages.

Paired comparisons of Harvey and Warwick data would require event-based sampling, with consideration of flow times between the gages. Existing USGS data are insufficient for such comparisons. Water samples for each year generally consist of a single sample at high flow and one at low flow, with some additional samples. These data are sufficient only for a bulk comparison. There are additional Health Department data for Warwick, but because the USGS data are approximately comparable in intra-annual sample frequency and time, only the USGS data are used for the analysis of variance. Results of analysis of variance (Table 2) for mean sulfate concentrations at Harvey and at Warwick from: (1) July 1992 through winter 1999, and (2) spring 2000 through fall 2005 indicate that mean sulfate concentrations at Harvey and Warwick for both time periods differed at greater than 99% confidence using a Bonferroni test (BSD). They also differed from themselves between climatic periods at 90% confidence (Warwick) and > 99.9 % confidence (BSD- Harvey). Annual mean concentrations for all treatments are shown below. Inclusion of the Health Department data slightly altered the means (not shown), but did not alter the ANOVA separation.

From 1992 through 1999, mean sulfate at the concentration at the Warwick gage (W1) was 53% that of the Harvey gage (H1). From 2000 through 2005 the sulfate at the

concentration at the Warwick gage (W2) was 57% that of the Harvey gage (H2). The upward shift at both gages was thus consistent.

Table 2. Summary of statistical means for sulfate concentrations (mg/L) at: (H1) Harvey before 2000, (H2) Harvey after 2000, (W1) Warwick before 2000, and (W2) Warwick after 2000.

Summary of **sulfate**
For categories in **treatment**
No Selector
84 total cases of which 6 are missing

Group	Count	Mean	MidRange	StdDev	PopStdv	Min	Max	Range	StdErr
H1	36	223.250	264	105.342	103.868	48	480	432	17.5570
H2	13	369.462	355	164.600	158.143	100	610	510	45.6519
W1	16	118.625	136	53.1851	51.4962	42	230	188	13.2963
W2	13	212.308	205.500	56.8747	54.6434	104	307	203	15.7742

Comparison of the post-2000 upward shift at Warwick (W2) with the 1990s data (W1) indicates a 56% increase following 2000; comparison of post-2000 upward shift at Harvey (H2) with the 1990s data (H1) indicates a 60% increase following 2000. Shifts over time are also consistent.

The percentage distribution of data on Fig. 13 includes additional Health Department data at Warwick. The distribution indicates that sulfate samples at Warwick never exceeded 300 mg/L before 2,000 and did so only about 25% of the time after 2000. Harvey samples, however, exceeded 300 mg/L about 40% of the time during the 1990s, and were below 300 mg/L only three times following the year 2000. This would indicate that concentrations at the Warwick gage are fairly robust with respect to the 300 mg/L standard. In fact, during the wet period they were below 250 mg/L 80% of the time and below 220 mg/L half of the time.

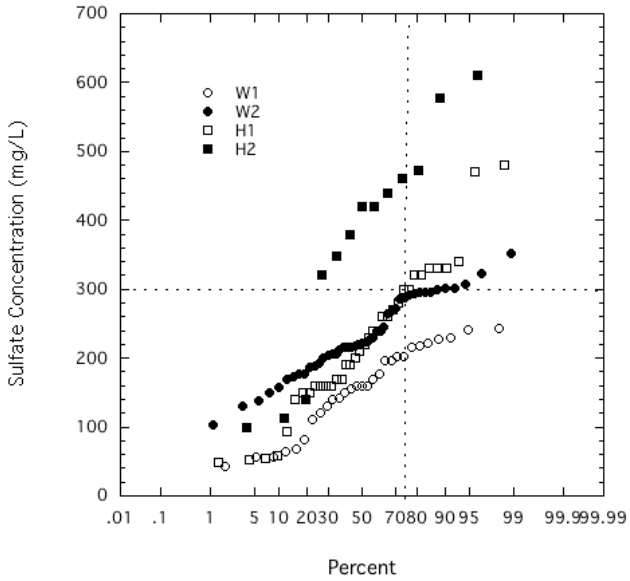


Figure 13. Percent (%) distribution of sulfate concentrations at:
(H1) Harvey before 2000, (H2) Harvey after 2000,
(W1) Warwick before 2000, and (W2) Warwick after 2000. Warwick data includes both Health Department and USGS data.

Effect of Gage Variability on Outlet Operational Constraints

These data indicate that the water quality assumption of the HEC5Q model for the upper Sheyenne River is disjunct from the actual concentrations and salt dynamics of the upper river, and that applying the 300 mg/L standard derived at Warwick upstream is over aggressive. That standard could evidently be confidently maintained at Warwick with double the concentration at Harvey. A similar transfer function for the Outlet, measured at Flora, would be useful to assess actual Outlet impact. Unfortunately, there is no historical data at Flora, and measurements first commenced in 2005.

We have only one set of comparative water quality for multiple sites on the Upper Sheyenne River, and that was provided by Skip Vecchia of the U.S. Geological Survey, Bismarck, ND, for the river on September 12, 2005 (Fig. 14). West and east of Harvey, sulfate concentrations are 589 and 582 mg/L respectively. The low measurement at the Harvey gage is suspect, since there do not appear to be reasonable hydrologic explanations for such extreme freshening in such a short span of river.

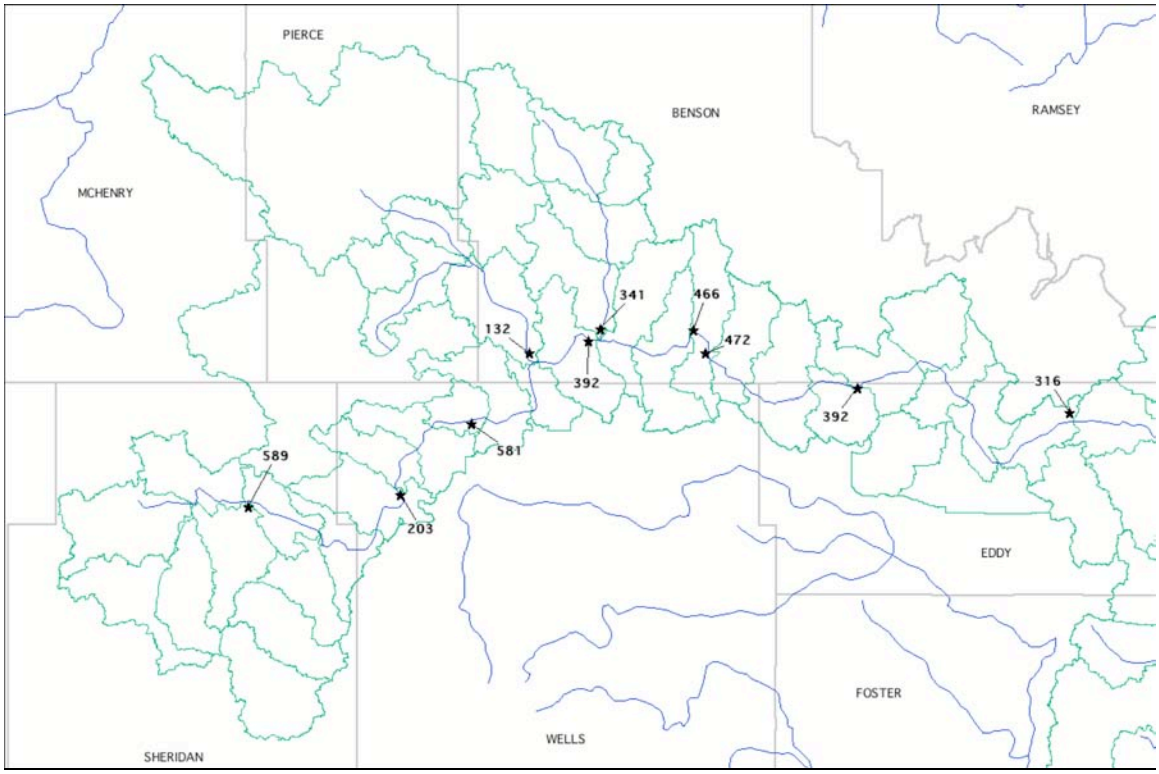


Figure 14. Map distribution of sulfate in water samples collected by the U.S. Geological Survey on September 12, 2005.

If we take the mean (appr. 585 mg/L) bracketing the Harvey gage and compare it with the Warwick gage (316 mg/L), the Warwick concentration is 54% of that at Harvey. This is almost identical to the long-term comparisons (53% and 57%). A relative comparison with the Flora gage (466 mg/L) and the Bremen gage (472 mg/L) with the Warwick Gauge indicates sulfate at Warwick is 68% of that at Flora and 67% of that at Bremen. Sulfate concentrations at Flora and Bremen are almost an exact approximation of the mean of the Harvey and Warwick gages (451 mg/L), which is also a close approximation of the Flora and Bremen gage measurements (-21 mg/L). The Harvey to Flora gage differences constitutes 42% of the difference between Warwick and Harvey measurements, while the Flora to Warwick gage differences constitute 48%. There is a slightly larger difference between Flora and Warwick than between Harvey and Flora. These compare with approximately similar (60 mile) river miles between Flora and the other two measurement points. Based on the September 12 measurements, 300 mg/L at Warwick would be equivalent to about 448 mg/L at Flora and Bremen calculated pro

rata. If equivalency with the Warwick gage were allowed using 448 mg/L as an operational standard, this would permit operation of the Outlet at some level of release about 70% of the time in the 2005 scenario (probability plot below). At a conservative 400 mg/L pro rata standard, some level of operation would be allowable about 50% of the time.

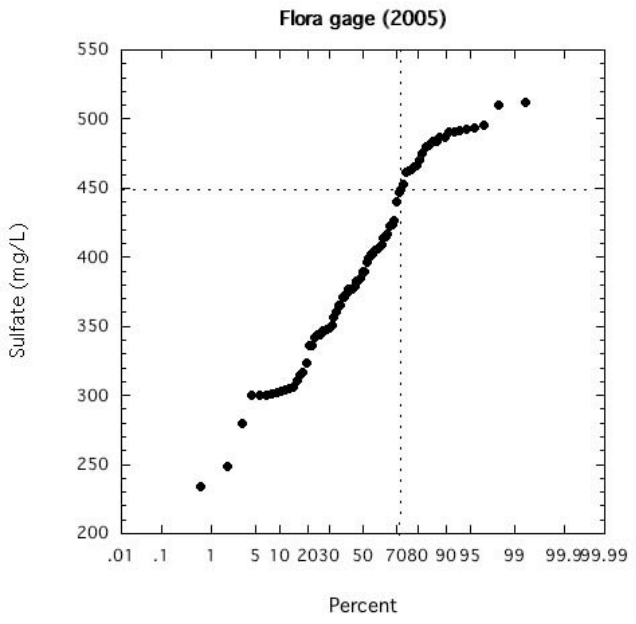


Figure 15. Percent (%) distribution of sulfate in water samples collected at the Flora gage in 2005.

Sulfate Sources in the Upper Sheyenne River

The USGS 9/12/06 water samples decrease in sulfate from 589 mg/L in the upper reaches of the South Branch of the Sheyenne River west of Harvey to 316 mg/L at Warwick. Values between are intermediate. Water entering from the North Branch are very fresh, with sulfate of 132 mg/L. Water samples downstream are lower (392, 341 mg/L), likely reflecting mixing with North Branch waters. Flow rates in the North Branch are not measured, but a 50/50 mixture of waters from the two branches would give a sulfate concentration of 357 mg/L, within the range of the two immediate downstream samples (341 mg/L to 392 mg/L).

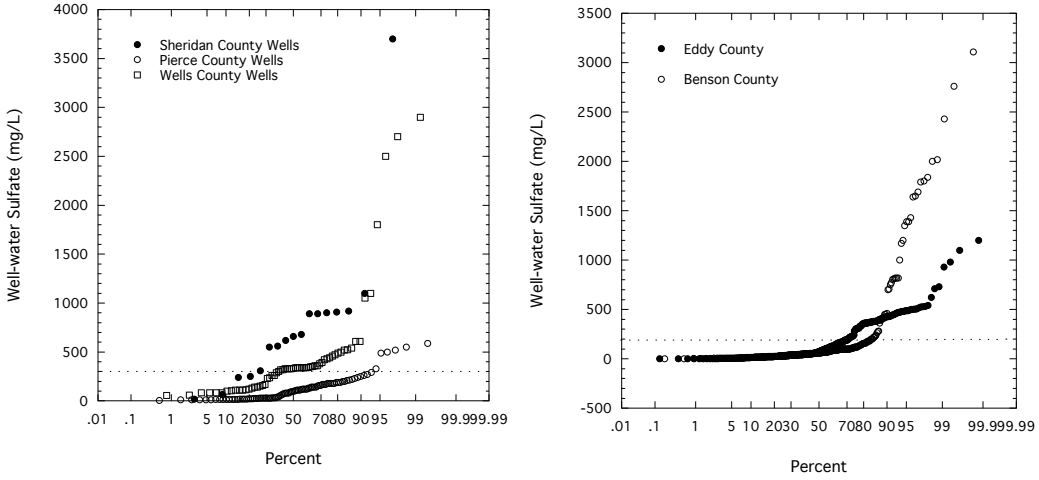


Figure 16. Probability distribution for sulfate concentrations collected from the Sheyenne River basin by county, including Benson, Eddy, Pierce, Sheridan and Wells counties.

Well water may provide a general indicator of sulfate availability as: (1) direct seepage to surface-water bodies through discharge; (2) a source of sulfate to the overlying soils which then provide a source to streams through seepage; and (3) a source of sulfate in stream flow which then deposits as evaporite along streams which can be remobilized when water tables are high. A general survey of well chemistry for Sheridan, Wells, Pierce, Benson and Eddy counties within the Sheyenne River basin sheds some light on the sulfate contributions of different reaches of the river. Only 20% of the wells in Sheridan County in the upper reaches of the South Branch have sulfate less than 300 mg/L (Fig. 16). High sulfate in Sheridan County wells corresponds with historically high sulfate in the Sheyenne River at the Harvey gage, and with the high concentrations measured in the 9/12/05 USGS samples west of Harvey. It also corresponds with a long disposition of highly saline Natraquoll soils within the river channel west of Harvey (see appended soil maps). While Natraquoll soils need not be high in sulfate, they frequently are in North Dakota, and indicate an strong evaporative environment adjacent to the upper Sheyenne River west of Harvey. With complementary high sulfate in the river wells of Sheridan County, it is likely that the Natraquolls include sulfate evaporites deposited over many years. It is suspected that these soils provide the

source for the increase in sulfate following 2000 through mechanisms described above for higher ground water in a wet environment.

Only 30% of Wells County ground-water samples have sulfate concentrations less than 300 mg/L, slightly more than Sheridan County, but 90% are less than 700 mg/L, compared with only 50% for Sheridan County. This is consistent with sustained high sulfate in the USGS 9/12/05 samples between Harvey and the confluence of the North Branch.

Table 3. Flow measurements in Trappers Coulee in 2005.

DATE	15307208DDA	15307121CCCD	15207106CDDC
	cfs	cfs	cfs
7/12/05	5.89	3.65	11.00
8/16/05	0.40	0.11	2.13
9/13/05	0	0.25	2.84
10/11/05	0.20	1.45	3.22
11/21/05	0.74	3.62	4.32

Pierce County wells have the lowest sulfate content, with all below 700 mg/L, 95% below 300 mg/L, and almost 50% below 100 mg/L. This concurs with sulfate contributions for North Branch (only 132 mg/L) in the USGS sample. Royce Cline of the SWC sampled Trappers Coulee and measured flows on five dates in 2005 (See Table 3). Historical water samples and samples collected in 2005 (Table 4) indicate that the water has very high sodium bicarbonate and carbonate, and relatively little sulfate. Ground-water distribution and discharge from Trappers Coulee to the North Branch are consistent with the low sulfate measurement at the confluence of the North Branch and the South Branch on 9/12/05, and indicate that low sulfate contributions from the North Branch may be common. It is suggested that the usual sulfate contribution from the North Branch should generally be small, but pending further data, we must reserve the possibility that in some specific rainfall scenarios there may be exceptions. Notably in the far upper reaches between Selz and Clifton there are Natriboroll (now Natrudoll) and Natraquoll soils that may (or may not) have high sulfate, and may yield that sulfate during local storms (see appended soil maps).

Table 4. Water chemistry for Trappers Coulee

Location	Sample Date	Field EC	Field pH	CA	Mg	Na	HCO_3	CO_3	SO_4	Cl	NO3	Fe	TDS	SAR
15307118CB	8/11/1998	1791		15.000	7	450	790	96	220	18	6.3	0.62	1220	24
15207106CDDC	8/12/1998	987		60.000	25	140	597	0	85	4.5	1	0.1	616	3.9
15307118CCB	9/22/2005	2220	9.2000	12.100	6	569	905	60	364	19.5	0.09	1.03	1490	33.4
15307121CCCD	9/22/2005	880	10.180	87.800	43.6	53.8	516	1	86.7	6.12	3.9	0.042	543	1.17
15207106CDDC	9/22/2005	830	8.7800	58.000	23.7	106	491	1	76.3	7.1	1.06	0.068	521	2.96

The USGS water sample collected at the Hwy 30 crossing reflects the mixture of North and South Branch waters. But sulfate is added between there and the Flora gage. Sulfate in a water sample collected from a large coulee discharging to the river (at the road crossing between Sections 2 and 11 of T 151 N, R 70 W) is similar to the river but somewhat lower in sulfate, and is an unlikely source for increased sulfate. There are natric soils associated with the channel in this reach of the river, more than between Harvey and the North Branch confluence, and it seems likely that increased sulfate measured at Flora were derived gradually from bank porewater between the North and South Branch confluence and the Flora gage.

Wells in Eddy and Benson Counties have relatively low sulfate. More than 70% and 85% of the wells, respectively, have less than 300 mg/L sulfate, and 90% for both have less than 500 mg/L. From Peterson Coulee to Sheyenne natric soils in the channel decrease and more of the river is associated with soils mapped to the deeper and less sulfatic Hapludoll Great Group. From Sheyenne to the north loop 7 miles east of Sheyenne there are some natric soils in the channel. But from the north loop to Warwick soils indicative of an evaporative regime near the river are sparse, with a predominance of deep non-evaporitic soils. Ground water north of the Sheyenne River between Warwick and Tolna is of the Warwick aquifer, and is some of the freshest ground water in the state. From Warwick to Cooperstown there is little evidence of evaporative soils within the Sheyenne River valley or its tributaries. Most soils adjoining the river and its tributaries are deep and predominant recharge soils of the Hapludoll great group, with likely deep placement of salts. Evaporative soils are recessed from the river valley.

Expectations for Change in Sulfate Loading

The change in post-2000 sulfate loading in the upper Sheyenne River is a result of long-term processes of sulfate deposition being reversed by high water tables and large rainfall events; and a higher proportion of base-flow to surface runoff in stream hydrographs resulting from high ground-water elevations and enhanced discharge. Because sulfate concentrations vary over the upper basin source area, there is a possibility of short-term increases over present high concentrations due to concentrated storms in sulfate "hot spots." But persistent increases over current levels are unlikely. In general, we believe that conditions must improve. The problem is that the time period for doing so is indeterminate.

Considering the two possibilities of drier conditions or continuance of the current climate scenario, either must lead to decreased sulfate concentrations. If drier conditions become prevalent, lower water tables will occur. This will result in less aquifer discharge, lower bank discharge, and deposition rather than flushing of salts from banks and tributaries. The time for such a response would depend on the intensity of dry conditions. It could occur within two or three years, or it could take several years.

The possibility of continued dissolution under current conditions must, based on conservation of mass, cause depletion of the sulfate reservoir and eventual diminution of sulfate in the River. The only way that this could be prevented, is if further sulfate sources through ongoing oxidation of organic matter and pyrite would be activated. However, high water tables tend to abate rather than accelerate oxidation, so enhancement of sources is unlikely. Unfortunately, the time to noticeable depletion is dependent on a sulfate pool of unknown size and cannot be determined. We would suspect several years for eventual depletion.

SULFATE VS. SPECIFIC CONDUCTANCE (EC) RELATIONSHIPS

Hem[8] observed that predictive relationships between EC and specific ions could be established in certain limited systems. An example is the sulfate vs. EC relationship for several eastern North Dakota surface-waters and well sources was illustrated on Fig. 5. Such a relationship, if sufficiently tight and robust, could be used to decrease full laboratory sample frequency. Where variability impairs predictability the relationships can still yield good information on the sources of variability.

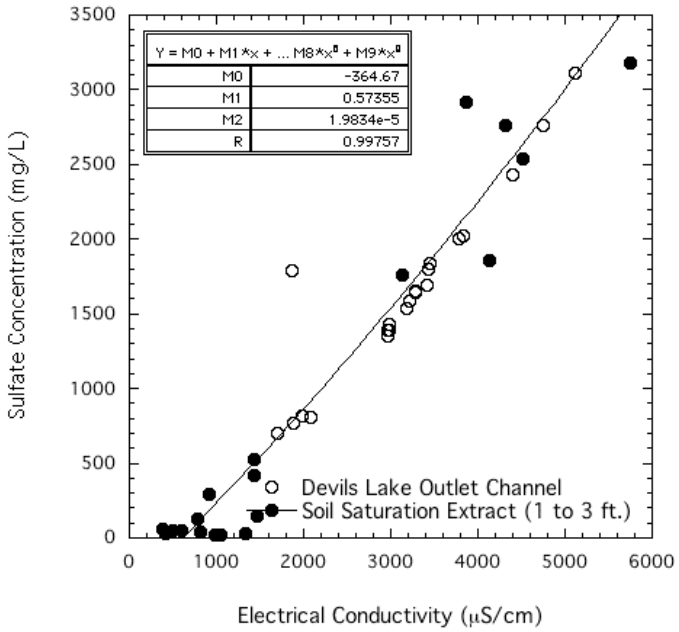


Figure 17. Sulfate vs. EC for the Devils Lake Outlet channel in 2005.

Devils Lake Outlet Channel

Sulfate and EC data collected in 2005 from the Devils Lake Outlet channel is very consistent, and highly predictive (Fig. 17). Barring one anomaly, a quadratic regression drived from local soil saturation extracts can account for 99% of all variability in the data. A linear relationship fitted to the channel data:

$$Sulfate = 0.70294\,EC - 640.49$$

can also be used to form a predictive model at r^2>0.99. There are two sources of sulfate in the channel water. These are: (1) Devils Lake water, and (2) groundwater adjacent to the channel. Because water in the channel was static for much of the summer of 2005, the regression curve likely is dominated by ground water. Because of the integrating capacity of Devils Lake, however, a highly predictive model may also be possible during periods of operational flow. If it can be sustained at a high predictive level, it may be sufficient to take less water samples and rely on real-time measurements in the channel applied to a transfer function to predict sulfate, and sample every couple of weeks to confirm the relationship. More data is needed to confirm the robustness of this relationship.

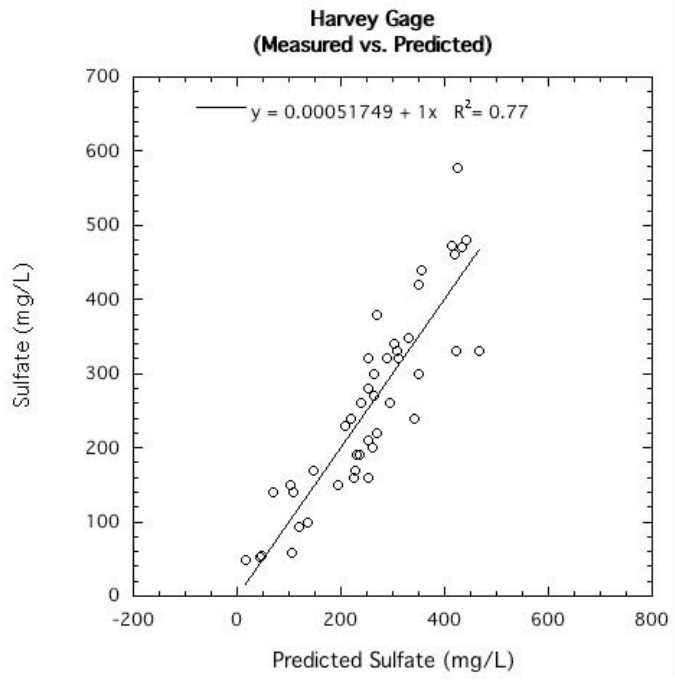


Figure 18. Sulfate vs. EC and flow x EC interaction for historical sulfate concentrations measured at the Harvey Gage.

Harvey Gage

EC can account for about 68% of EC variability for the Harvey gage from 1992 through 1994 as shown on Table 5. Predictive value increases to about 77% for an equation employing EC (µS/cm), and Flow x EC interaction (µS/cm x cfs), are shown on Table 5 and Fig. 18. The multiple regression equation is semi-predictive, and would

provide sulfate predictions that would approximate a good long-term mean, with some slight short-term random variance. The period of record includes both the lower (pre-2000) and higher (post-2000) sulfate values and a variety of flow scenarios, so it should be reasonably robust.

Table 5. Statistical summary for regression model of Sulfate vs. EC for historical data at the Warwick Gage.

Dependent variable is: **SULFATE**
No Selector
115 total cases of which 70 are missing
R squared = 68.7% R squared (adjusted) = 68.0%
s = 73.22 with 45 - 2 = 43 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	506450	1	506450	94.5
Residual	230528	43	5361.12	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-39.4357	32.33	-1.22	0.2292
COND	0.236647	0.0243	9.72	≤ 0.0001

Table 6. Statistical summary for regression model of Sulfate vs. EC and Flow x EC interaction (µS/cm x cfs) as shown on Figure 15.

Dependent variable is: **SULFATE**
No Selector
115 total cases of which 70 are missing
R squared = 78.1% R squared (adjusted) = 77.0%
s = 62.01 with 45 - 3 = 42 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	575486	2	287743	74.8
Residual	161493	42	3845.06	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-148.014	37.50	-3.95	0.0003
COND	0.291815	0.0244	12.0	≤ 0.0001
INT	1.24819e-3	0.0003	4.24	0.0001

The added predictive value from flow data is informative because they are positively correlated with higher flows and higher flow interaction terms. This means that sulfate concentrations tend to be higher at higher flows. These are consistent mechanisms governed by enhanced soil and stream-bank discharge rather than overland flow.

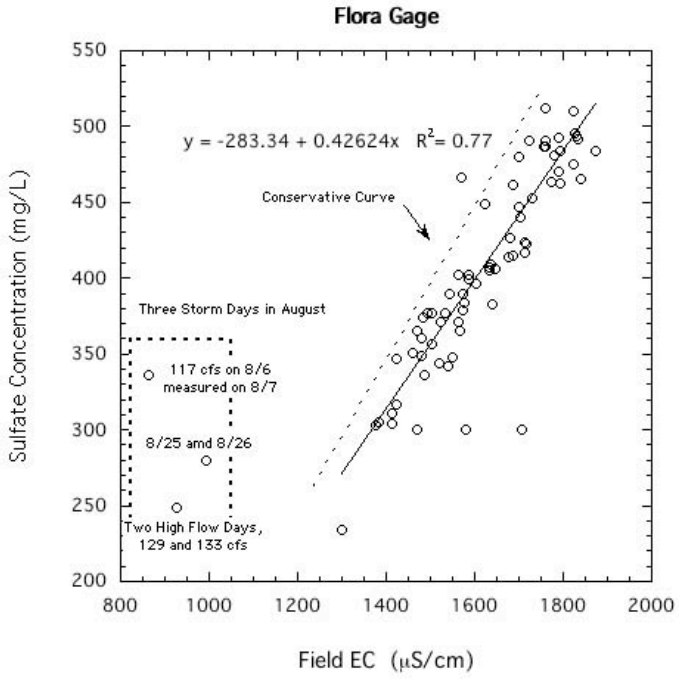


Figure 19. Sulfate vs. EC for water samples collected at the Flora gage.

Flora Gage

The Flora gage represents the upstream regulatory reference point for the Outlet. Measurements were only initiated in mid-July of 2005 and were measured into mid-November, so the period of record is limited compared with Warwick and Harvey data. The sulfate vs. EC relationship for the Flora gage accounts for about 77% of all variability, if three outliers are excluded in the lower EC (< 1200 µS/cm) range (Fig. 19). In the lower EC range sulfate concentrations are higher than would be predicted by the regression equation. The lower EC data all represent periods of high flow in August 2005. These indicate that waters from summer storms in 2005 had less dissolved salts than normal base flows, but that sulfate comprised a larger proportion than at base flow.

This is consistent with high water-table mechanisms described above, wherein Calciaquoll soils and natric soils adjoining the river channel and tributaries fill quickly following storms and yield sulfatic water. The regression equation is semi-predictive and capable of predicting long-term mean sulfate concentrations with reasonable precision at high EC values, but less precise for individual days and events, with a rough predictive error of about 50 mg/L at any given point above EC=1200 μS/cm. The higher low EC Sulfate vs. EC relationship in the low EC range suggests a relationship similar to Harvey which may permit a better predictive model with inclusion of the flow term. However, there is insufficient high-flow data at this time to warrant its inclusion. Relationships may also be affected by differences between runoff on frozen ground in spring, and by water-table conditions at various times in summer. In addition, variability will likely be affected by storm location, likely being less sulfatic from storms located in the North Branch than in the South Branch. Much more data is needed to establish a satisfactory relationship between sulfate and EC at Flora.

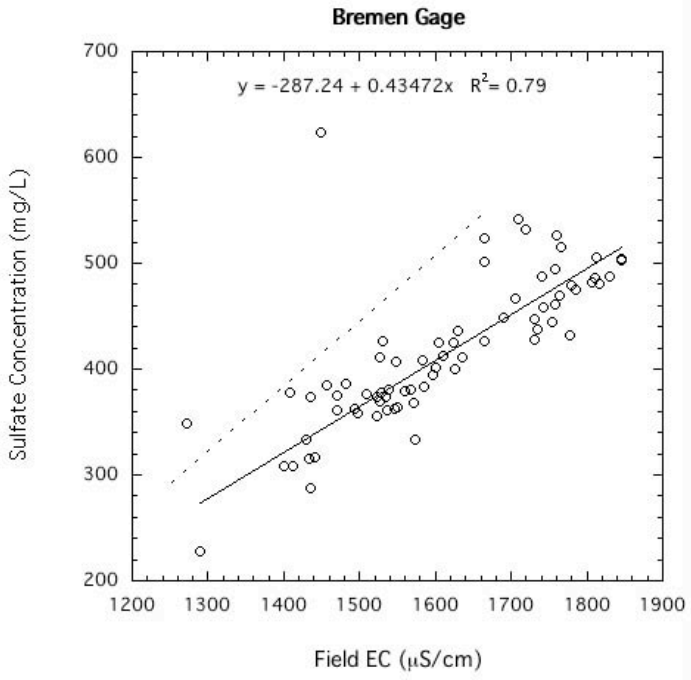


Figure 20. Sulfate vs. EC for water samples collected at the Bremen gage.

Bremen Gage

The Bremen gage represents the downstream regulatory reference point for the Outlet. Measurements were only initiated in mid-July of 2005 and were measured into mid-November, so the period of record is limited compared with Warwick and Harvey data. The sulfate vs. EC relationship for the Bremen gage accounts for about 79% of all variability (Fig. 20). The predictive equation and predictive efficiency is almost identical to that of the Flora gage. Since all EC are greater than 1,200 mg/L, the anomalous high-flow values in the lower range for Flora are absent at Bremen. All relationships discussed for the Flora gage apply to the Bremen gage as well.

Warwick Gage

The Warwick gage has water quality data dating from 1976, usually two measurements per year, one during high flows and one during low flows. A model using EC alone predicts about 75% of sulfate variation, which is similar to other (Harvey, Flora and Bremen) models (Fig. 21).

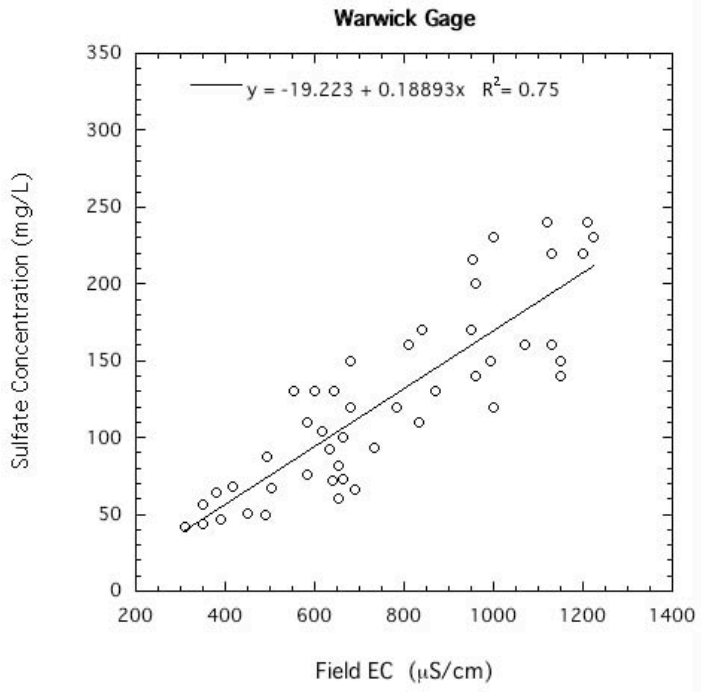


Figure 21. Sulfate vs. EC for water samples collected at the Warwick gage.

Models formed using both river flow (cfs) and flow x sulfate concentration interaction improve model efficiency by about 5% (Table 7, Fig. 22).

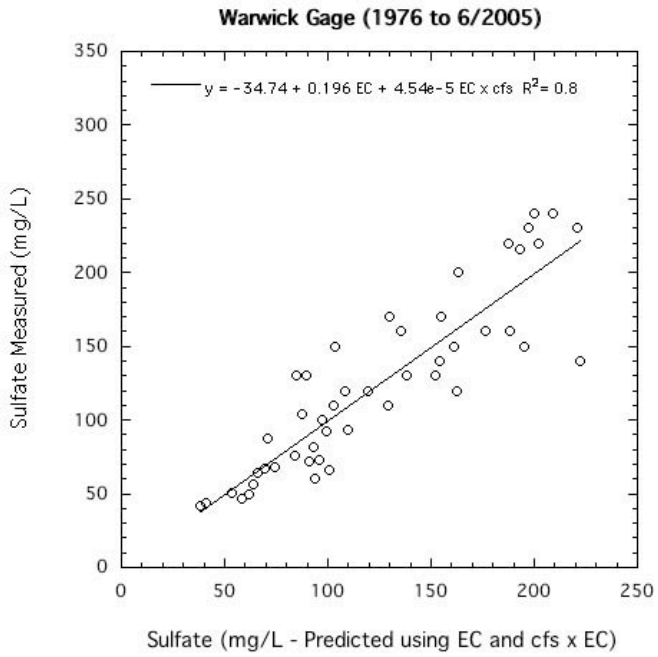


Figure 22. Sulfate vs. EC and flow x EC interaction for historical sulfate concentrations measured at the Warwick Gage.

Table 7. Statistical summary for regression model of Sulfate vs. EC and Flow x EC interaction (µS/cm x cfs) as shown on Figure 22 above.

Dependent variable is: **sulf**
No Selector
52 total cases of which 4 are missing
R squared = 79.8% R squared (adjusted) = 78.9%
s = 27.12 with 48 - 3 = 45 degrees of freedom

Source	Sum of Squares	df	Mean Square	F-ratio
Regression	130330	2	65164.8	88.6
Residual	33088.3	45	735.295	

Variable	Coefficient	s.e. of Coeff	t-ratio	prob
Constant	-34.7398	12.59	-2.76	0.0084
ec	0.196232	0.0148	13.2	≤ 0.0001
int	4.54357e-5	0.0000	3.33	0.0018

It is of particular interest that at Warwick all of the EC values are less than 1,250 µS/cm, and all of the sulfate concentrations are less than 250 mg/L, when one recalls that almost all of the Flora EC values in 2005 are above 1,200 mg/L. There is clearly a large separation that has occurred between the Warwick and Flora sulfate data. Sources other than the upper Sheyenne River source waters strongly influence water quality near the Warwick gage. As previously noted, the soils of the Sheyenne River valley east of Sheyenne are mostly deep alluvial soils of the Hapludoll Great Group. They are not strongly evaporative soils, and bank seepage in this area is likely much fresher than west of the Bremen gage. In addition, aquifers bordering and discharging to the river and its tributaries have low sulfate. These include the Warwick aquifer abutting the Sheyenne River on the north, and an alluvial extension of the Tokio aquifer in the Sheyenne River channel northeast of the town of Sheyenne on Hwy 281. These are some of the freshest aquifers in the state. In addition, the Cherry Lake aquifer in Eddy County discharges to the Sheyenne River through Colvin Creek. Shallow aquifers in this reach of the Sheyenne River are shown on the map below.

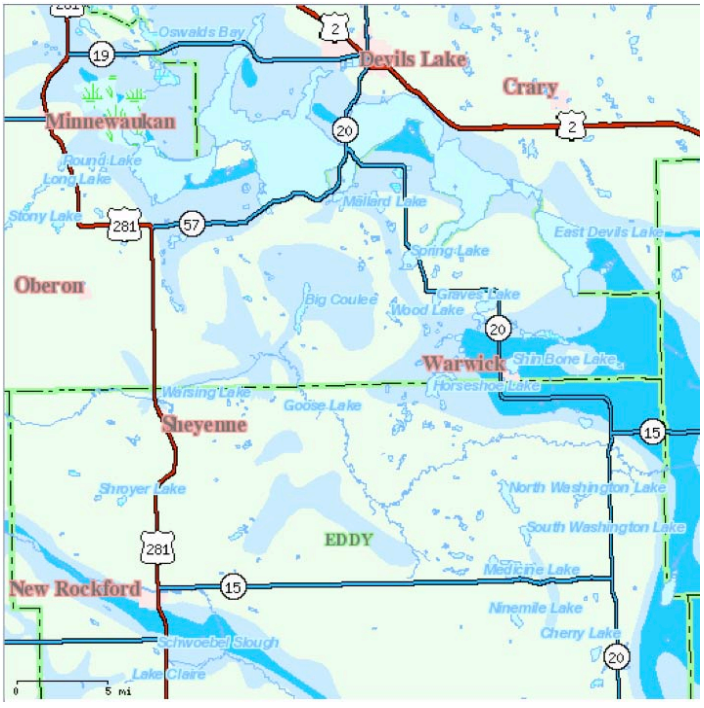


Figure 23. Map illustrating location of shallow glacial aquifers adjacent to the Sheyenne River between Sheyenne and Harvey.

Probability plots comparing the sulfate concentrations of the Sheyenne River at Flora and Warwick with ground water adjacent to the river and its tributaries are shown below (Fig. 24). More than 70% of Cherry Lake aquifer water (via Colvin Creek) and more than 90% of Warwick aquifer water are less than 100 mg/L of sulfate, and most samples have lower concentrations. Five wells in the Tokio aquifer (just northwest of the town of Sheyenne) all have TDS between 414 and 690 mg/L and sulfate between 11 and 33 mg/L. We must consider that the data of the Flora gage is limited to the wet and high sulfate (post-2000) sample set and is therefore biased high. Earlier analysis (above) indicated that this would likely compare to about half that concentration in the pre-2000 climate scenario. Since the Warwick gage includes both climate periods, the half estimate would be a conservative comparison. The effect of low TDS and low sulfate ground water on Sheyenne River water quality between Flora and Warwick is clearly indicated by these distributions.

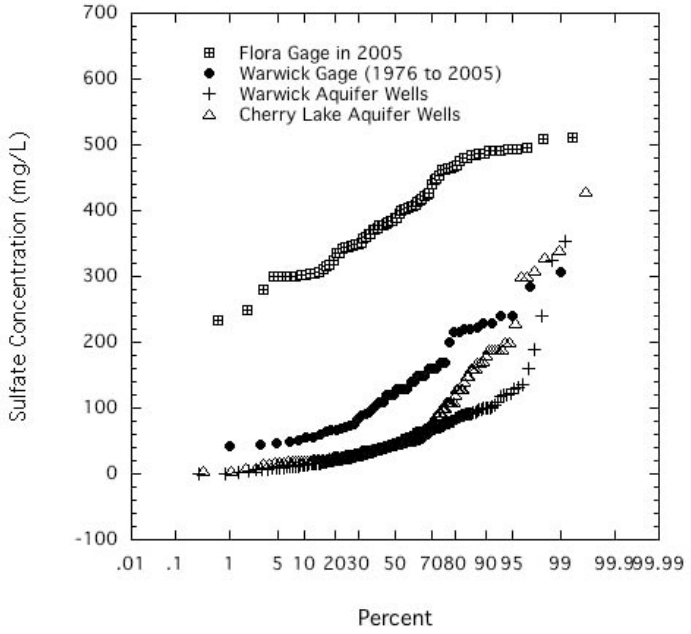


Figure 24. Comparison of percent (%) distribution of aquifer sulfate concentrations and concentrations measured in the Sheyenne River at Flora in 2005 and at Warwick from 1976 through 2005.

SUMMARY AND CONCLUSIONS

1. The Sheyenne River at Flora exceeded the 450 mg/L prescribed for a Class 1A stream 30% of the time under natural flow conditions in 2005. At what point does the stream classification change to reflect natural conditions?

2. The point of protection for application of the 250 mg/L secondary MCL for sulfate is the Valley City water supply. The 300 mg/L maximum sulfate standard at the Outlet is based on application of a HEC5-Q model which assumes that the water chemistry of the upper Sheyenne River can be represented by historical measurements at the Warwick Gage, and freshening of the river between Warwick and Valley City. Application of the standard at Flora is also based on the uniform upper Sheyenne River base chemistry, which allows transference of the historical Warwick data to Flora. This assumption is untrue.

3. Sulfate in the upper Sheyenne River, as measured at Harvey, has historically differed from Warwick measurements by an average factor of about 2 to 1.

4. Sulfate measurements at both Harvey and Warwick vary with climate, and approximately doubled from the 1990s to the post-2000 period.

5. Measurements for Flora and Bremen are limited to the 2005 operational year. In a single river transect measured by the USGS in September of 2005 the Flora gage sulfate was close to the mean of the Harvey and Warwick gages. The Flora gage is located about halfway from Harvey to Warwick.

6. The source of the highest sulfate concentrations is in the South Branch of the Sheyenne River which generally has more sulfatic ground water than the area of the North Branch, and where soils adjacent to the river are more saline. North Branch waters, in a single measurement, contribute fresher waters at the confluence. North Branch sub-basin ground water is generally less sulfatic and more bicarbonatic than in the South Branch, as

exemplified by water in Trappers Coulee and by the ground-water sample record in Pierce County. Between the confluence of the North and South Branches and the Flora gage there appears to be an influx of sulfate from drainageways or from soils within the river channel. This comparison is based on a single river transect. Conditions can change with varying conditions and storm locations, so further sampling is needed to confirm or expand understanding of this relationship.

7. Sources of increased sulfatic water after 2000 are likely higher water tables and flushing of evaporative salts from the riverbanks and soils bordering drainageways, coulees and tributaries. Under prolonged dry conditions and with lower water tables they should decrease somewhat. The time required for change is unknown, but we believe it could occur within two or three years with very dry conditions followed by moderate rainfall. Under prolonged wet conditions mass balance indicates that TDS and sulfate may decrease through depletion in their sources. This would depend on the amount of salt stored in mobile situations and the rates of depletion. These are unknown and cannot be easily determined. Our best guess would be several years, based on a large subsoil pool of salts that may yet be moved upward under high water-table conditions.

8. Substantial freshening of river water from Bremen to Warwick is most likely caused by a major change in soil and ground-water sources. Valley soils downstream of Flora are increasingly characterized as deep and predominantly recharge soils, compared with the evaporative soils upstream. Moreover, saline soils mapped near the riverbed decrease in strength of saline expression moving eastward, as exemplified by weaker ("glossic") natric horizons. Aquifers neighboring and discharging to the Sheyenne River and its tributaries, particularly east of the town of Sheyenne, are very fresh and have very low sulfate concentration distributions. These include the Warwick aquifer, the Tokio aquifer, and the Cherry Lake aquifer.

There are four conclusions from this analysis:

(1) There is substantial evidence that natural and historical conditions at the Flora gage are sufficiently different from those at Warwick, that the 300 mg/L standard established using the uniform upstream water quality assumption cannot be reasonably applied.

(2) Natural freshening of the river between Flora and Warwick is substantial enough that larger sulfate concentrations at Bremen could most likely be sustained without causing concentrations above 300 mg/L at Warwick and above 250 mg/L at Cooperstown.

(3) While general historical data support these conclusions, there is an insufficient period of record at Flora and Bremen to fully understand the quantitative relationship between Warwick and Flora concentrations of TDS and sulfate. Intensive comparative measurements are needed to discern the relationship. Temporally coordinated data are particularly needed to examine cause and effect, rather than limiting the analysis to general statistical relationships.

(4) Sulfate vs. EC within the Outlet channel may be sufficiently predictive to allow for an eventual decrease in sulfate measurement frequency and use of an EC transfer function alone to estimate sulfate during operation. More data is needed to test the robustness of this possible application.

(5) A rational adjustment to the operational permit for the Devils Lake Outlet which would allow for reasonable adaptation to variability of natural flow conditions with respect to Valley City protective criterion and without substantially altering the TDS effect at Halstad should be possible. The basis for this adjustment should be maintenance of the 300 mg/L maximum sulfate concentration at the Warwick gage, which provided the basis for the flow model, and the 250 mg/L maximum sulfate concentration at Valley City (measured at the Cooperstown gage). However, operational requirements need to ascertain downstream effects of loading between Flora and Bremen to meet that standard at Warwick. The key to management of sulfate loading at the Outlet without violating

downstream standards seems to be a thorough understanding of, and likely a correlation between, the sulfate concentrations at Flora and Warwick.

RECOMMENDATIONS

#1. A thoroughly representative data base documenting concurrent water chemistry at Warwick and at the Flora and Bremen gages should be collected. Ongoing samples on a weekly basis should be collected at these two sites beginning at first free flow in the river. They will be used to examine and hopefully establish a working correlation between the Sheyenne River at the Outlet and at Warwick. Water Chemistry samples should minimally include field EC and laboratory sulfate and TDS.

#2. The full sample scheme represented by the USGS river survey in September of 2005 should be replicated at least monthly in 2006 and 2007, beginning at first free flow. The Harvey and Warwick gages are particularly important in this sampling. These samples should include minimally (1) Field EC, and (2) full general chemistry, including sulfate and TDS. This will require both a filtered sample and an unfiltered sample. This data will be used to examine the robustness and reliability of preliminary conclusions from the single transect, discussed above.

#3. Exploratory operational tests should be conducted in 2006 and 2007 to ascertain the actual effects of operation on water chemistry at Warwick and Cooperstown and their conformance to Health Department standards and goals. This approach is justified not only from the standpoint of potential enhanced operation based on river dynamics, but from the standpoint of verification of adequacy of environmental protection. All models are preliminary, and the actual, as opposed to virtual impact should be assessed in real operational scenarios and fine tuned. There is no substitute for actual data.

It is recommended that the proposed tests be (1) conservative with respect to points of protection; (2) constrained by existing preliminary knowledge of the system; (3) progressive with respect to impact on points of protection, beginning at lower loading rates and proceeding upward systematically to test the boundaries of impact; (4) fully documented in ambient monitoring, with consideration of river flow rates and "windows" of likely impact; (5) sufficiently long to reliably ascertain effect; and (6) short enough to minimize impact from possible operational errors. With respect to (6) it should be

stressed that the sulfate MCL is a "secondary" MCL, and that toxicological risk to human beings and livestock is negligible in the prescribed range. Thus, small error that may result from cautious and progressive application of the tests should not be a health risk.

Preliminary evidence indicates that 300 mg/L at Warwick would not be exceeded with 450 mg/L in ambient flow at Bremen. Further confirmation of the relative concentrations at Flora and Warwick should be obtained (Recommendation #1 above). In addition, exploratory tests should be conducted to establish a clear and factual understanding of the relationship between outlet discharge and sulfate concentrations at the Warwick gage.

We would suggest the following test criteria and design:

(1) During 2006 exploratory tests should be conducted during ***operation under current permit constraints.*** *For each exploratory test water samples and ambient EC should be collected at Flora, Bremen and Warwick. Following release of water, samples and EC measurements should be collected at all three sites daily until effects of the release are detected and stabilized at the Warwick gage. The same procedure should be repeated before cessation of outlet discharge and repeated daily until changes at Warwick caused by return to natural conditions are detected and stabilized.*

(2) ***If data acquisition from monthly synoptic samples for multiple river locations from Harvey to Warwick (#1 and #2 above), and data acquired from monitoring Outlet releases in 2006 (described in #3(1) above) confirm preliminary indications of substantial freshening of the river between the Outlet and Warwick,*** *it is suggested that further tests be conducted in 2007 to explore the limits of Outlet effects on the 300 mg/L limit at Warwick. A progressive and conservative adaptive management scheme is suggested as follows.*

Test incremental format:

It is suggested that the first test be conducted with combined ambient sulfate concentrations at Bremen not exceeding 400 mg/L, ***or a smaller amount if 2006 data indicate that it would be prudent to do so.*** *Thus, applying the formula:*

$$Q_o = \frac{Q_i(400 - C_i)}{(C_o - 400)} \qquad (3)$$

at the Outlet.

(a) The first test should be conducted for three days.

(b) If 300 mg/L is not exceeded at Warwick after an appropriate period allowing for mass transfer, then it should be replicated at 5 days.

(c) If the replicated first test does not exceed 300 mg/L at Warwick, the progressive formula should be elevated to:

$$Q_o = \frac{Q_i(425 - C_i)}{(C_o - 425)} \qquad (4)$$

and should be operated for three days.

(d) If 300 mg/L is not exceeded at Warwick after an appropriate period allowing for mass transfer, then it should be replicated at 5 days.

(e) If the replicated second test does not exceed 300 mg/L at Warwick, the progressive formula should be elevated to:

$$Q_o = \frac{Q_i(445 - C_i)}{(C_o - 445)} \qquad (5)$$

Or alternately, if more caution is warranted, a smaller increment. Maximum test sulfate at Bremen should be less than 450 mg/L because of the sulfate goal for a Class 1A stream.

(3) For each test operation,EC, sulfate and TDS at the Outlet should be monitored before, during and following test operation for a suitable period.

(a) Samples should be collected at Warwick and at Cooperstown to assure at least three days of pre-effect baseline data, sampling during the period of likely impact, and at least three days following. Flow velocity of the river should be considered in planning the sample schedule.

(b) If sulfate tests resulting from test operation exceed 300 mg/L at Warwick or 250 mg/L at Cooperstown at any time, they should be discontinued at the problematic concentration level and confined to lower concentrations.

(c) Results should be considered to evaluate the re-issuance of the operational standards of the operational permit.

(d) If routine operation is allowed under the current standard at Bremen, downstream monitoring at Warwick and Cooperstown as per (3) above should be implemented.

4. Supplemental Data:

(a) LANDSAT data are very useful for evaluating changes in hydrologic conditions and their effects on water quality. A review and recommendation is appended.

(b) One water sample from each of the major coulees and tributaries, particularly those west of the Sheyenne would be helpful in fully characterizing salt sources.

CITATIONS

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2. U.S. Army Corps of Engineers (St. Paul District). April 2003. Final DEVILS LAKE, NORTH DAKOTA, Integrated Planning Report and Environmental Impact Statement. Two volumes.

3. Beven, Keith and Peter Germann. 1982. Macropores and water flow in soils. Water Resources Research. 18:5:1311-1325.

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APPENDIX A: EFFECTS OF PRECIPITATION PATTERNS

Figure A-1 illustrates the long-term distribution of precipitation at Harvey. Following 1988 there is a general pattern of a larger proportion of precipitation occurring from May through September. Precipitation in 1999 and 2000 are the largest in the period of record.

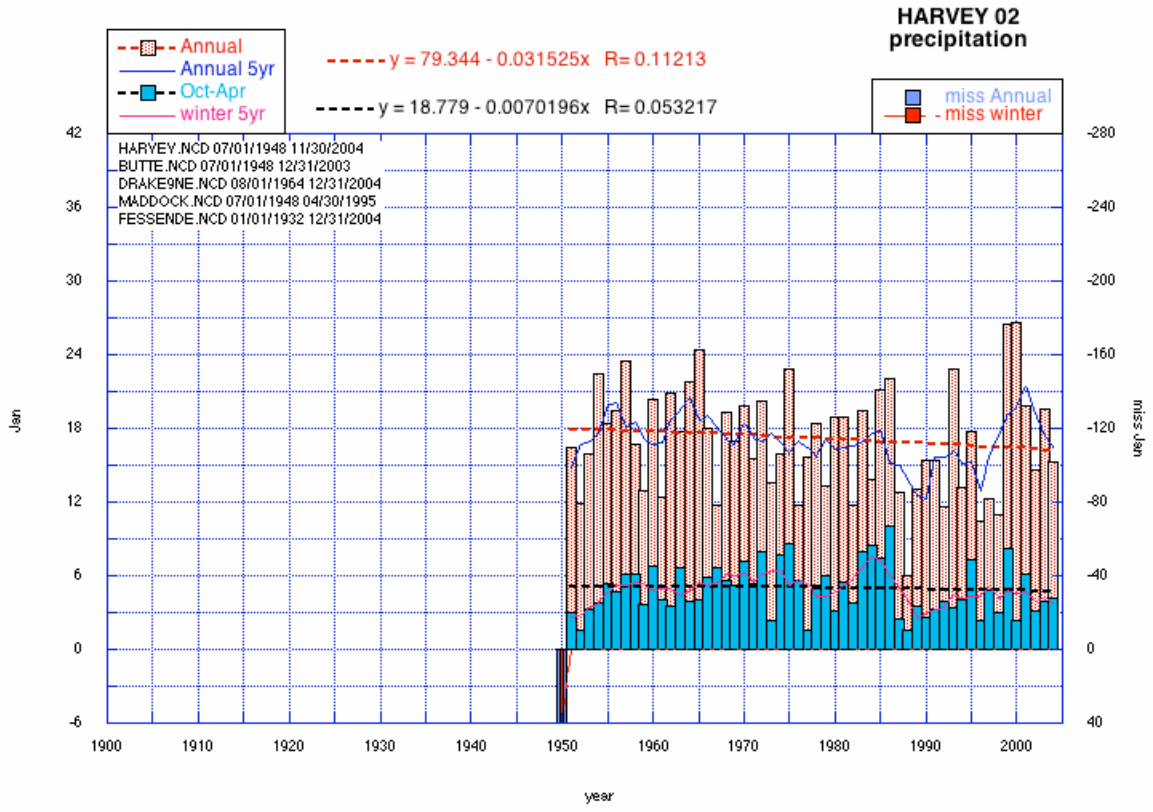


Figure A-1. Summary of annual precipitation and 5-year moving average for total and winter precipitation for the period of record at Harvey. Captions "miss Annual" and "miss winter" indicate missing data. Data was compiled and presented by Royce Cline.

Figure A-2 illustrates the distribution of annual May through September precipitation for four clusters of North Dakota State Water Commission Atmospheric Resources Board precipitation measurement sites, centered at Trappers Coulee. The central group consists of six sites near Trappers Coulee, the west group consists of seven sites about six to 12 miles northwest of Trappers Coulee; the northeast group consists of seven sites about 10 to 20 miles northeast of Trappers Coulee, and the south group consists of nine wells about 10 to 20 miles south of Trappers Coulee. The south group is located predominantly in Wells County near Harvey. These illustrate the spatial and temporal variability and five-year moving averages of climate variability in the Upper Sheyenne River Basin.

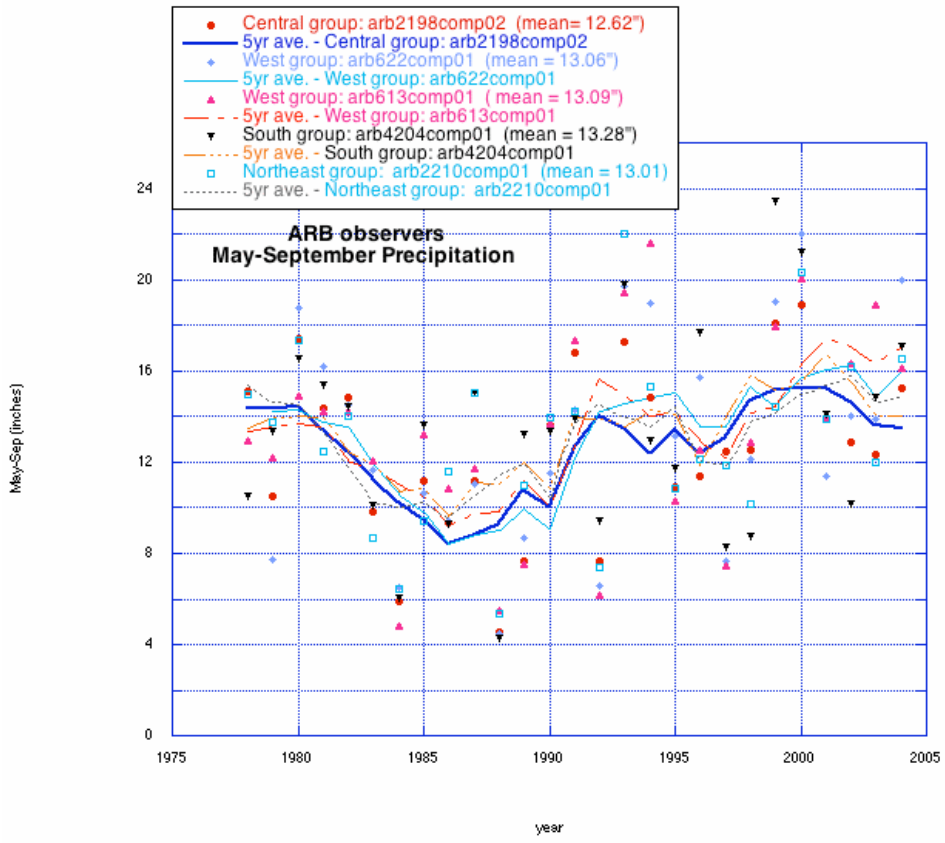


Figure A-2. Precipitation distribution and trends for the Upper Sheyenne River Basin near Trappers Coulee, based on NDSWC ARB data. Data was compiled and presented by Royce Cline.

Figures A-3 and A-3a show interpolated maps (inverse-square distance weighted) of total May through September precipitation from 1993 through 2004. Figure A-4 shows the precipitation distribution in 2005. The maps are clipped from state maps provided by the North Dakota State Water Commission Atmospheric Resources Board (ARB) precipitation-measurement network which includes over 800 measurement sites.

Maps for 1993 through 2004 include an overlaid graph of the specific conductance (Field Conductance) vs. flow (CFS) in the Sheyenne River measured at the Harvey gage. Field Conductance is used as a surrogate indicator of salinity in the Sheyenne River. Field Conductance and CFS values include measurements from May through November.

The response pattern indicates that: when a large rain follows an extended dry period (for example 1993), discharge to the Sheyenne River is fresher (lower specific conductance) with larger discharge rates. This most likely occurs because during the preceding dry period water tables are lower and not conducive to salt deposition on the surface, and because during storms water infiltrates into the dry soil, carrying salts deeper with the wetting front. There is also less seepage. Thus, surface runoff is a larger proportion of discharge to the river and it is likely to carry less salts. The larger the storm, the larger the runoff proportion and the fresher the water. Following a wet year sufficient to raise the water table, the Field Conductance vs. CFS relationship reverses and larger storms tend to carry more salts. The result is a larger load of dissolved salt in the river following larger storms. This is observed for 1994. For a succession of drier years the Field Conductance vs. CFS relationship tends to gradually level (1995 through 1998) and trend again toward fresher water with larger flows.

The pattern is repeated with greater intensity from 1999 through 2004. Following somewhat drier years (1995 through 1998) two years of large general summer precipitation exhibited fresher water with larger flows similar to 1993. In the following somewhat drier years Field Conductance vs. CFS trended toward a level curve (2001) and then consistently exhibited increasing salinity with increasing flows (2002 through 2004). These patterns indicate that fresher water with larger flows may occur after only one or two dry years. Two previous wet years in 2004 and 2005 also indicate that more salts at higher flows are a strong possibility for 2006.

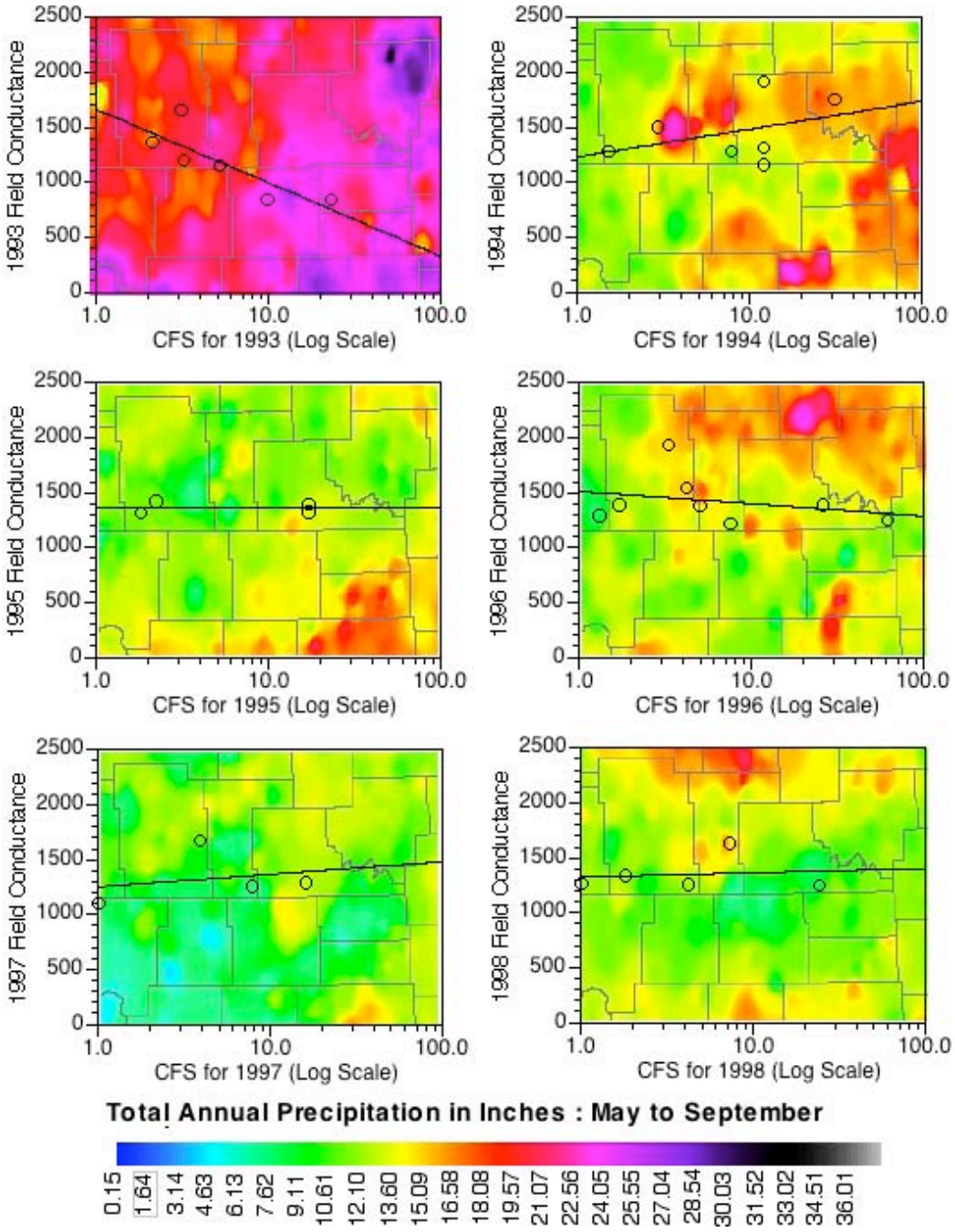


Figure A-3. Map of total May through September precipitation in the upper Sheyenne River Basin, with a superimposed graph of specific conductance (Field Conductance) vs. flow (CFS), for measurements taken in May through November, in the Sheyenne River at Harvey (1993 through 1998).

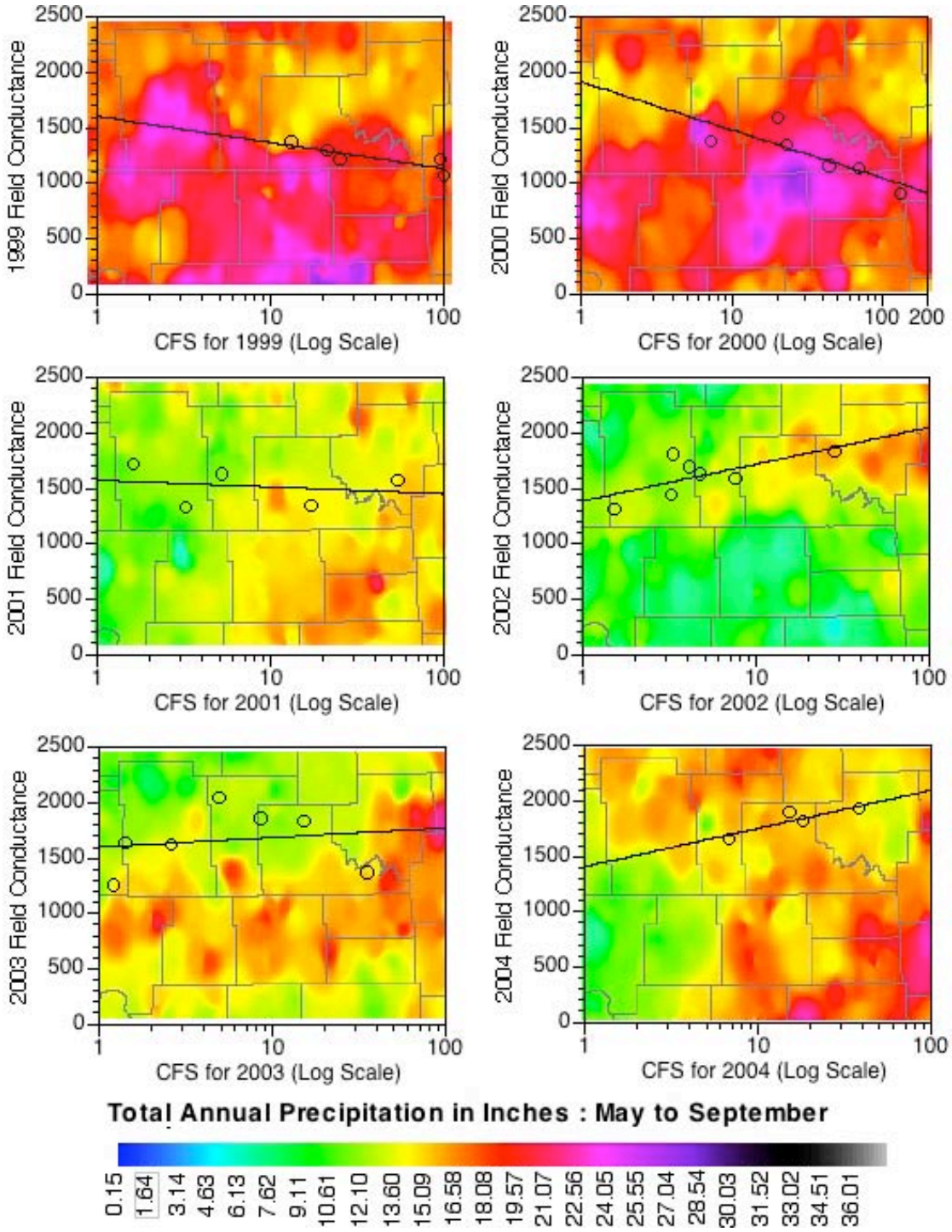


Figure A-3a. Map of total May through September precipitation in the upper Sheyenne River Basin, with a superimposed graph of specific conductance (Field Conductance) vs. flow (CFS), for measurements taken in May through November, in the Sheyenne River at Harvey (1999 through 2004).

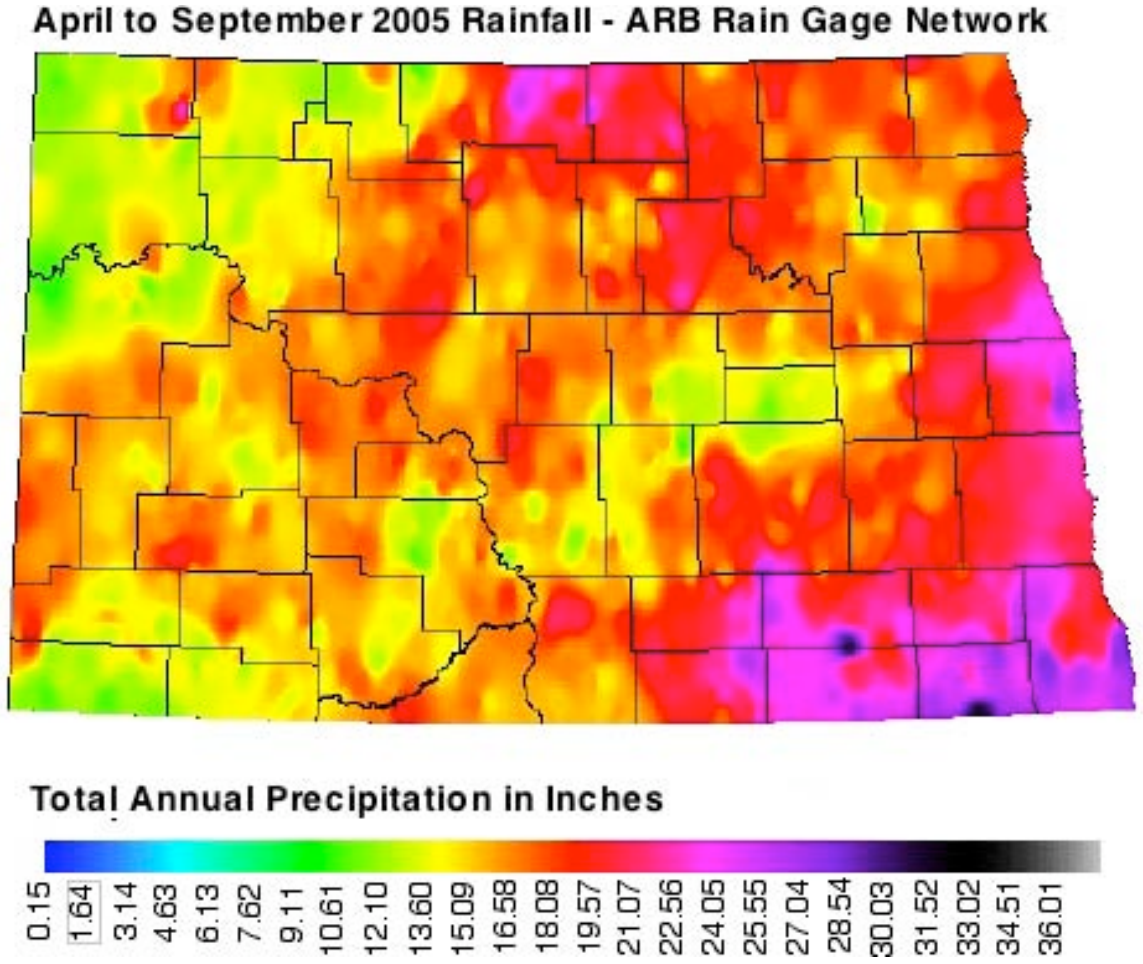


Figure A-4. Map of total April through September precipitation for the state of North Dakota in 2005.

APPENDIX B: LandSAT Data Review & Recommendations:

Data Review:
LandSAT data allowed for both a quantitative and qualitative analysis of water boundary areas in the Upper Sheyenne River Basin. While this analysis provided useful insights to the surface water areas being examined, there are limitations to the functionality of the State Water Commission's current LandSAT data.

The State Water Commission has collected a number of LandSAT data sets over the years. Nearly all LandSAT data has been purchased for the analysis of the Devils Lake Basin flooding issues. The collection dates range from 1989 to 2005. The scenes also cover a range of seasons, from April to August. Also, the scenes were purchased at different times. Rarely has more than one scene been purchased at a time.

There are four key issues that should be addressed for any further LandSAT analysis.

1. LandSAT scenes should represent the same season of the year, for comparing yearly differences. Comparing July 1999 water areas, to April 2005 water areas is problematic. An annual comparison between July to Sept. is more appropriate.

2. Most of the LandSAT scenes only cover the eastern half of the Upper Sheyenne Basin area. The acquisition of the Path32/Row27 scene would allow for the analysis of over 90% of the Upper Sheyenne Basin area.

3. Since each scene was purchased at a different time, the scenes are not radiometrically calibrated to each other. This causes each scene to have a unique visual appearance that is not easily corrected. This results in a substantial amount of time spent on color compensation.

4. Since each scene was purchased at a different time, the data are in many different geographic projections. Data reprojection was done in-house. Data reprojection should be done by the USGS EROS data center. This ensures a high level of data integrity, which helps to support the conclusions from the analysis.

Data Recommendations:
The only way to effectively deal with the data issues outlined above, is to purchase consecutive, yearly LandSAT scenes, which are radiometrically calibrated to each other at the time of purchase from the USGS EROS Data Center. At the time of this purchase each scene can be specified to be in one single UTM Zone 14 - NAD83 projection. The purchased scenes should also be for the July to Sept. time-frame, representing a single season for each year. Ideally, the SWC should purchase a July to Sept. scene for each year, from 1992 to 2006. Each scene covers 12,000 square miles, has 7 bands, and costs $625.00 per scene. This results in 15 scenes at $625.00 each, for a total cost of $9,375.00.

APPENDIX C: Sheyenne River Valley Soil Maps

Map Sheet S1

Map Sheet S2

Map Sheet S3

Map Sheet S4

Sheyenne River Valley Soils

Index to Map Series Sheets

Map Sheet

US Highway

County Lines

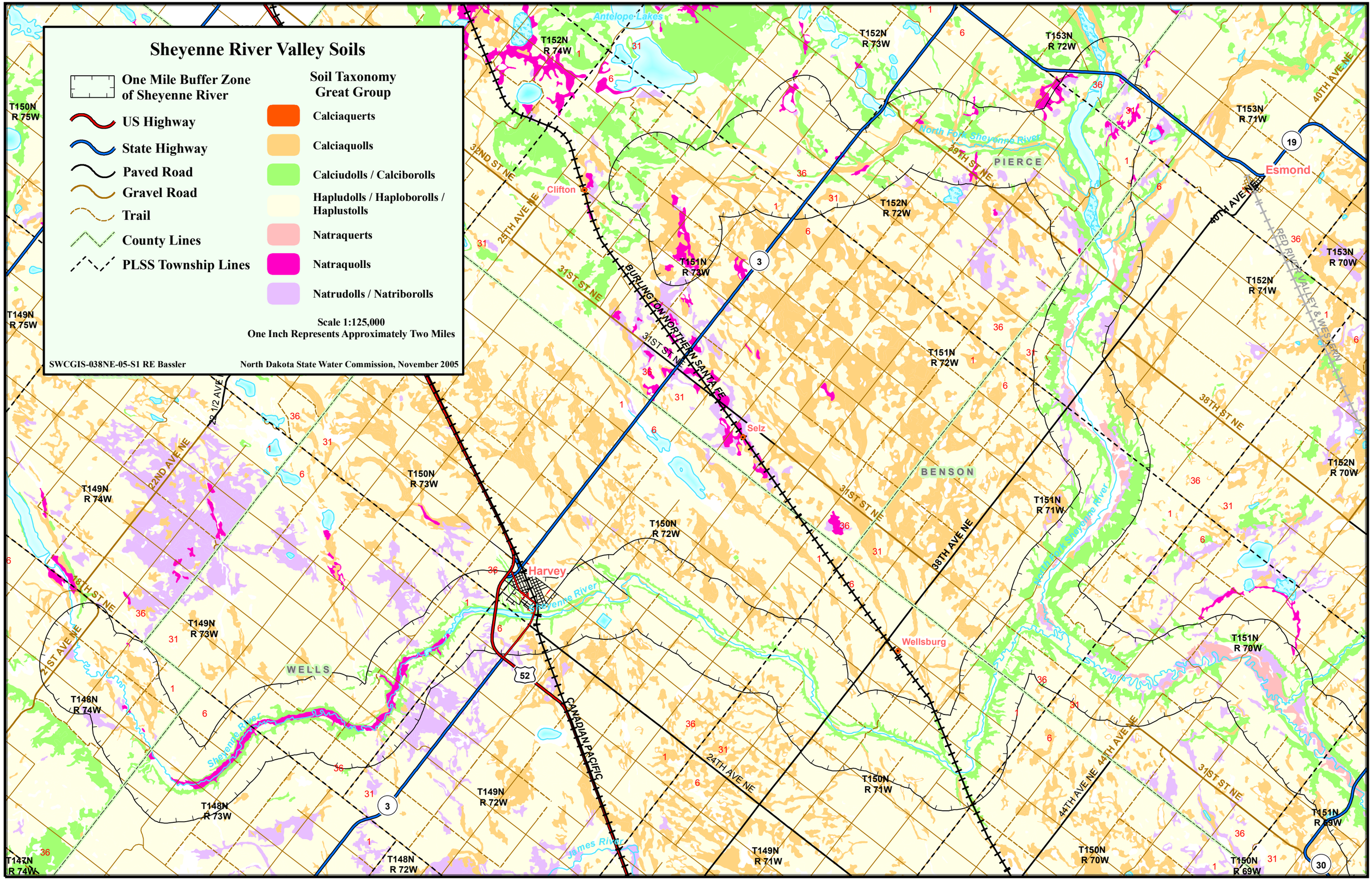
State Highway

Scale 1:400,000
One Inch Represents
Approximately 6.3 Miles

SWCGIS-038NE-05-Index RE Bassler

ND State Water Commission, November 2005

Balta
Silva
Fillmore
Baker
Harlow
Brinsmade
Tilden
Comstock
Ramsey
Darby
Dry Lake
Sweetwater Lake
Southam
Rohrville
Pelto
Whitman
Dahlen
Cranberry Lake
RAMSEY
Devils Lake
Essex
Keith
Crary
Oswalds Bay
Minnewaukan
Girard Lake
Isabel
Camp Grafton
Devils Lake
Bartlett
Lakota
Mapes
Michigan
PIERCE
Esmond
Petersburg
Hesper
BENSON
Maddock
Lallie
Saint Michael
East Devils Lake
NELSON
Antelope Lakes
Flora
Josephine
Oberon
Tokio
Wamduska (historical)
Stump Lake
Harrisburg (historical)
Clifton
Warwick
Hamar
Martin
Tolna
Pekin
McVille
Heimdal
Harvey
Hamberg
Divide
EDDY
Bremen
Munster
Kloten
Aneta
New Rockford
Manfred
Fessenden
Dundas
Brantford
Barlow
Guptill
Grace City
McHenry
Mose
Binford
Jessie
SHERIDAN
Goodrich
Hurdsfield
Juanita
GRIGGS
STEELE
Mardell (historical)
Cooperstown
FOSTER
Carrington
Glenfield
Sutton
Shepard
Bordulac
Revere
Melville
Kensal
Hannaford
Karnak
Lake Ashtabula
Arrowwood Lake
BURLEIGH
KIDDER
STUTSMAN


Sheyenne River Valley Soils
One Mile Buffer Zone of Sheyenne River
US Highway
State Highway
Paved Road
Gravel Road
Trail
County Lines
PLSS Township Lines
Soil Taxonomy Great Group
Calciaquerts
Calciaquolls
Calciudolls / Calciborolls
Hapludolls / Haploborolls / Haplustolls
Natraquerts
Natraquolls
Natrudolls / Natriborolls
Scale 1:125,000
One Inch Represents Approximately Two Miles
SWCGIS-038NE-05-S1 RE Bassler
North Dakota State Water Commission, November 2005
Antelope Lakes
Clifton
Selz
Harvey
Wellsburg
Esmond
PIERCE
BENSON
WELLS
North Fork Sheyenne River
Sheyenne River
James River
BURLINGTON NORTHERN SANTA FE
CANADIAN PACIFIC
RED RIVER VALLEY & WESTERN
T150N R 75W
T149N R 75W
T149N R 74W
T148N R 74W
T147N R 74W
T150N R 73W
T149N R 73W
T148N R 73W
T149N R 72W
T148N R 72W
T150N R 72W
T149N R 71W
T150N R 71W
T151N R 72W
T151N R 71W
T150N R 70W
T151N R 70W
T150N R 69W
T151N R 69W
T152N R 74W
T152N R 73W
T152N R 72W
T151N R 73W
T153N R 72W
T153N R 71W
T153N R 70W
T152N R 71W
T152N R 70W
32ND ST NE
25TH AVE NE
31ST ST NE
22ND AVE NE
18TH ST NE
21ST AVE NE
22 1/2 AVE
39TH ST NE
40TH AVE NE
38TH ST NE
38TH AVE NE
24TH AVE NE
44TH AVE NE
19
3
52
30

Sheyenne River Valley Soils

One Mile Buffer Zone of Sheyenne River

US Highway

State Highway

Paved Road

Gravel Road

Trail

County Lines

PLSS Township Lines

Soil Taxonomy Great Group

- Calciaquerts
- Calciaquolls
- Calciudolls / Calciborolls
- Hapludolls / Haploborolls / Haplustolls
- Natraquerts
- Natraquolls
- Natrudolls / Natriborolls

Scale 1:125,000
One Inch Represents Approximately Two Miles

SWCGIS-038NE-05-S2 RE Bassler

North Dakota State Water Commission, November 2005

Sheyenne River Valley Soils

One Mile Buffer Zone of Sheyenne River

US Highway

State Highway

Paved Road

Gravel Road

Trail

County Lines

PLSS Township Lines

Soil Taxonomy Great Group

- Calciaquerts
- Calciaquolls
- Calciudolls / Calciborolls
- Hapludolls / Haploborolls / Haplustolls
- Natraquerts
- Natraquolls
- Natrudolls / Natriborolls

Scale 1:125,000
One Inch Represents Approximately Two Miles

SWCGIS-038NE-05-S3 RE Bassler

North Dakota State Water Commission, November 2005

Sheyenne River Valley Soils

One Mile Buffer Zone of Sheyenne River

US Highway

State Highway

Paved Road

Gravel Road

Trail

County Lines

PLSS Township Lines

Soil Taxonomy Great Group

- Calciaquerts
- Calciaquolls
- Calciudolls / Calciborolls
- Hapludolls / Haploborolls / Haplustolls
- Natraquerts
- Natraquolls
- Natrudolls / Natriborolls

Scale 1:125,000
One Inch Represents Approximately Two Miles

SWCGIS-038NE-05-S4 RE Bassler

North Dakota State Water Commission, November 2005

McVille

Kloten

Aneta

NELSON

GRIGGS

STEELE

Binford

Jessie

Finley

Pickert

Blabon

Mardell (historical)

BURLINGTON NORTHERN SANTA FE

BN

24TH ST NE

22 1/2 ST NE

21ST ST NE

19TH ST NE

16TH ST NE

10TH ST NE

8 1/2 ST NE

7TH ST NE

2ND ST NE

1ST ST SE

117TH AVE NE

116TH AVE NE

113TH AVE NE

111TH AVE NE

120TH AVE NE

122ND AVE NE

132ND AVE NE

T150N R 60W

T150N R 59W

T150N R 58W

T149N R 60W

T149N R 59W

T149N R 58W

T149N R 57W

T148N R 61W

T148N R 60W

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T147N R 61W

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T147N R 57W

T146N R 60W

T146N R 59W

T146N R 58W

T146N R 57W

T146N R 56W

T146N R 55W

T145N R 57W

T145N R 56W

T147N R 56W

T149N R 55W

T148N R 55W

T147N R 55W

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200