CHEMICAL WEATHERING AND LAND DENUDATION OF PALEOZOIC CARBONATE ROCKS IN THE BLACK HILLS, SOUTH DAKOTA AND WYOMING

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ABSTRACT

The chemical solution of limestone and dolomite is a major factor in the erosion of carbonate terrain. Solutes, consisting primarily of calcium, magnesium, and bicarbonate, are removed by thirteen large springs in the Black Hills whose average discharge totals 6.66 m^3/s. The product of discharge and total dissolved load (TDS) concentration of each of the thirteen springs discharging from the Madison Limestone and Minnelusa Formation totals 188 million kg annually. Cascade Spring and Crow Creek remove almost half of this mass. Recharge to the carbonate belt occurs not only from precipitation but also from disappearing streams; the product of discharge and TDS concentration for eighteen major disappearing streams adds 18 million kg/year of solutes to ground water in the carbonate belt. The difference between the spring discharge and stream recharge is 170 million kg/year. Dissolved load carried downdip through the aquifer is estimated at 26 million kg/year. The total resulting load removed from the carbonate belt is 196 million kg/year. This value provides an estimate of the chemical weathering over the 2,948 km^2 outcrop area of the Paleozoic carbonate belt. Using a simple model wherein calcium, magnesium, and bicarbonate solutes originate from the solution of 280 m thick dolomite, the rate of lowering of the land surface by chemical solution is 1.55 cm per 1,000 years.

Keywords

Weathering, land denudation, geochemistry, dolomite, carbonate

AREA OF INVESTIGATION

During the past decade the U. S. Geological Survey (USGS) has made a concerted effort to collect hydrologic data for the Black Hills area. This paper primarily uses discharge and water quality data published by the USGS to determine the dissolved load from the Paleozoic carbonate rocks. From these data, the chemical weathering and rate of denudation of the landscape can be evaluated.

The Black Hills is a Laramide domal uplift whereby erosion of the overlying Paleozoic and Mesozoic sedimentary rocks exposed the Precambrian core of metamorphic and igneous rocks. The sedimentary strata now dip gently away from the Precambrian core. The focus of this study is the belt of Paleozoic carbonate rocks consisting of two units: the Mississippian Madison Limestone and the Pennsylvanian Minnelusa Formation (Figure 1). The Madison Limestone consists largely of massive dolomite and dolomitic limestone. This unit contains many caves including Jewel Cave and Wind Cave, the second and third longest

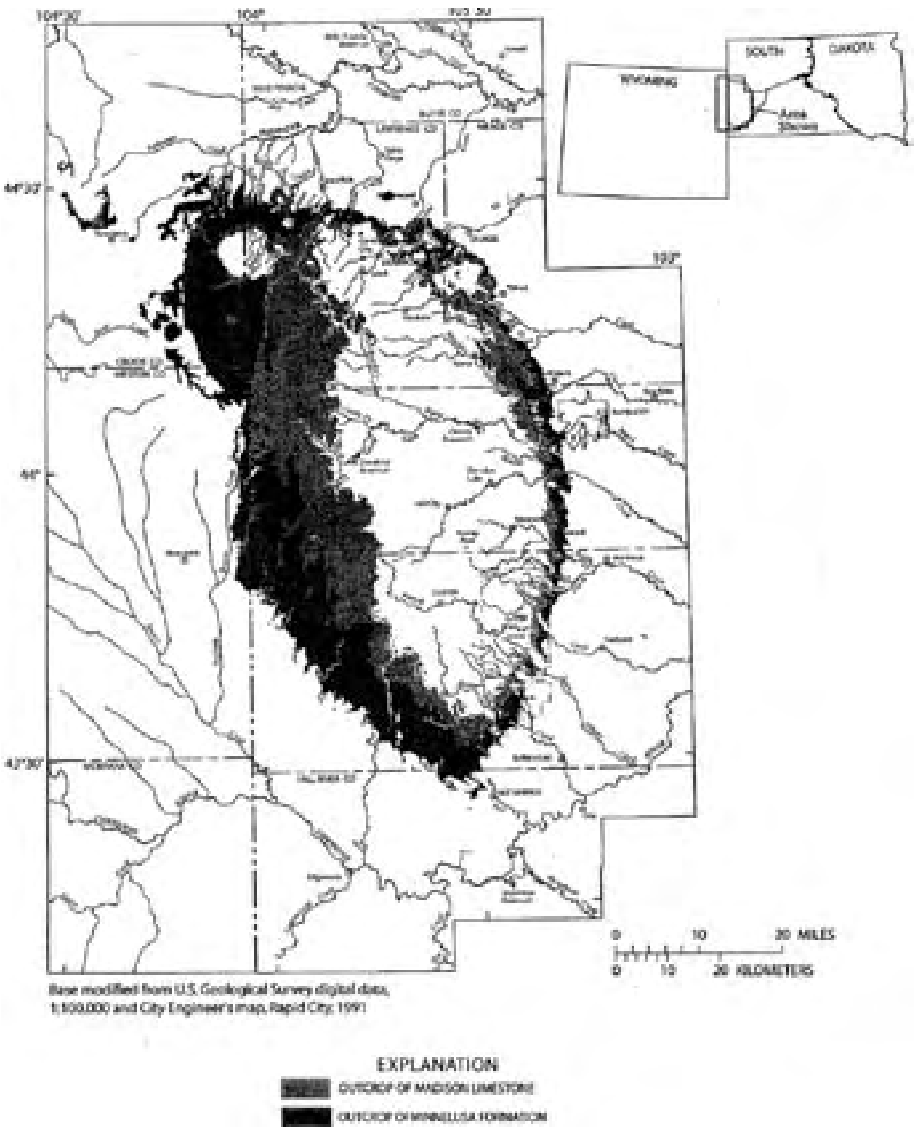

Figure 1. Geological map of the Black Hills (from USGS). The Paleozoic carbonate aquifer is highlighted.

caves in the nation. The Minnelusa Formation consists of interbedded calcareous sandstone, limestone, dolomite, and shale. These two units have been referred to as the "Paleozoic Carbonate Aquifer" (Rahn and Gries, 1973). The total thickness of these two units is approximately 280 m.

Geologic maps of the Black Hills of South Dakota and Wyoming show the Madison Limestone is exposed over an area of 1,219 km^2 and the Minnelusa Formation 1,729 km^2 (Carter, in prep.). Thus the total exposure area of these two formations in the Black Hills is 2,948 km^2.

MAJOR SPRINGS

Numerous large springs occur in the Black Hills area at the outer contact of the Minnelusa Formation where it abuts against the Permian Opeche Formation. In some places the springs appear at the contact of the Permian Minnekahta Limestone where it abuts against the Triassic Spearfish Formation. A few artesian springs discharge through the lower section of the Spearfish Formation red beds along Crow Creek and the lower reaches of Spearfish Creek; these springs presumably follow "breccia pipes" originating from collapse of gypsum in the Minnelusa Formation (Epstein, 2000).

Figure 2 shows the approximate location of the fifteen largest springs in the Black Hills. Some of the springs are actually streams draining spring complexes. The discharge of each of these springs is shown in Table 1. The discharge totals 7.126 m^3/s.

The dissolved ions in the spring water principally include calcium, magnesium, and bicarbonate. Because of the high concentration, small deposits of calcareous tufa (travertine) are found within a few kilometers of some springs. These deposits form waterfalls at Roughlock Falls, Cascade Falls, and along the Fall River below Hot Springs (Ray and Rahn, 1997). In the past decade, the USGS has published substantial data for the total dissolved solids (TDS) concentration of the spring water (Table 1). The TDS concentration for each spring is remarkably consistent even though the spring was sampled at different times. Generally the springs draining the southern Black Hills have greater TDS concentration than those in the northern Black Hills. This is probably because the ground water has traveled greater distance in the southern Black Hills and had more opportunity to dissolve the carbonate rocks.

The product of the discharge and the TDS concentration is the load delivered by the spring. Table 1 shows the annual load removed from the big springs surrounding the carbonate belt totals approximately 193 million kg. Nearly all this water flows into the Cheyenne River and exits the Black Hills area.

Two springs shown on Table 1 are unusual in that the water does not flow directly to the Cheyenne River. Rhoads Fork and Castle Creek discharge into the headwaters of Rapid Creek. This water then crosses Precambrian terrain; farther downstream the water re-enters the Paleozoic carbonate belt. From Table 1, the total load of these two springs is 4.60 million kg/year. The discharge of the remaining 13 springs not re-entering the Paleozoic belt is 6.66 m^3/s; their total load is 188.3 million kg/year, or roughly 188 million kg/year.

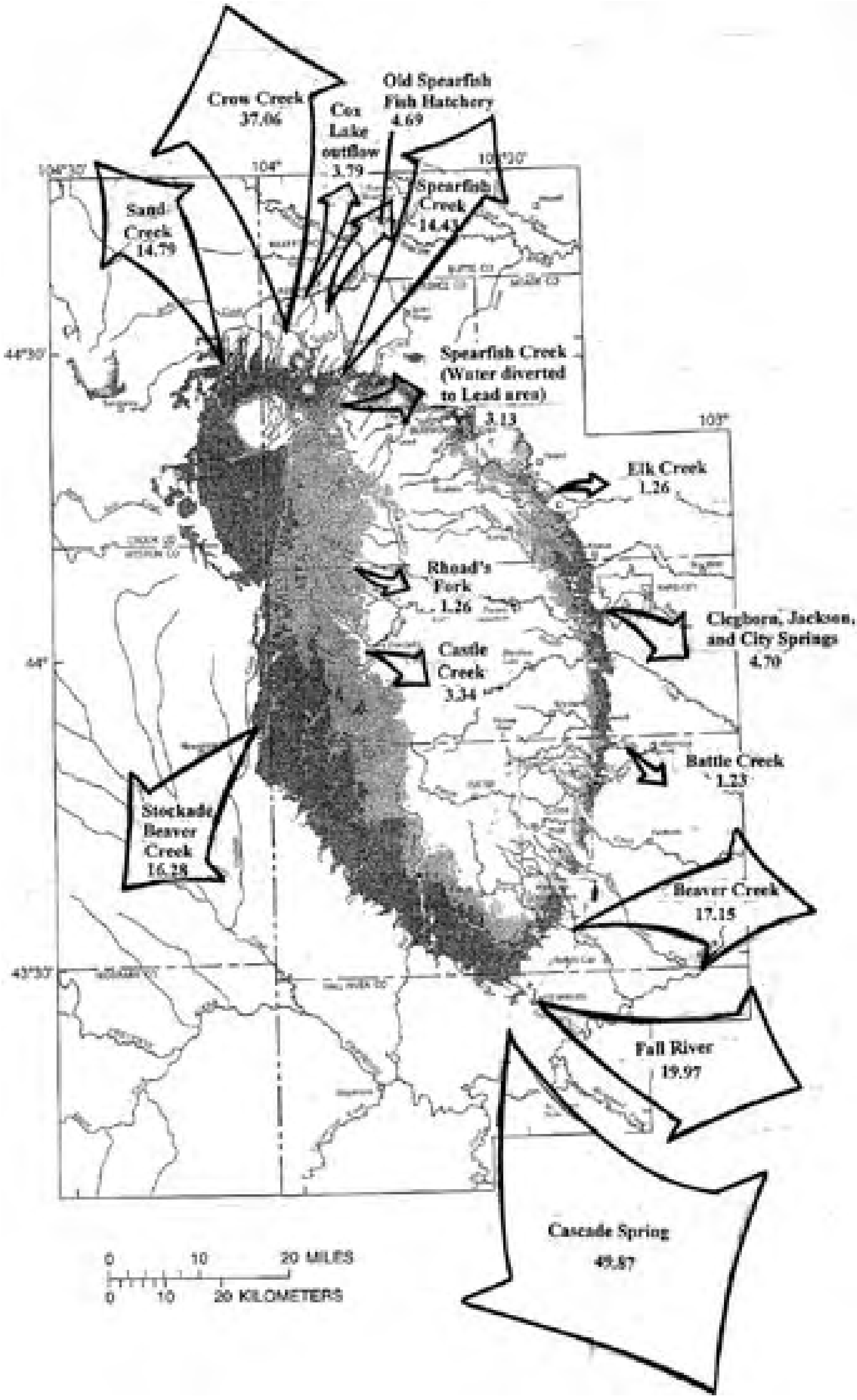

Figure 2. Map showing the approximate location of the major springs in the Black Hills. The size of the arrow is roughly proportional to the dissolved load (million kg/year).

Table 1. Dissolved load of major springs in the Black Hills[1].

Name	Discharge		TDS concentration[2]		Dissolved Load[3]
	cfs	m^3/s	mg/L	kg/m^3	10^6 kg/yr
Cascade Spring	22.7	0.643	2460	2.46	49.87
Fall River	21.5[4]	0.609	1040	1.04	19.97
Beaver Creek	9.6	0.272	2000[5]	2.00	17.15
Battle Creek	7.0	0.198	197	0.197	1.23
Cleghorn, Jackson, and City Springs	25.9[6]	0.733	203[7]	0.203	4.70
Elk Creek	1.73[8]	0.049	816[9]	0.816	1.26
Spearfish Creek	53.87[10]	1.526	300[11]	0.300	14.43
Spearfish Creek (Water diverted to Lead area)	10[12]	0.283	350[13]	0.350	3.13
Old Spearfish Fish Hatchery	7.6	0.215	691	0.691	4.69
Cox Lake outflow	4.2	0.119	1010	1.01	3.79
Crow Creek	40.68[14]	1.152	1020	1.02	37.06
Sand Creek	18.4[15]	0.521	900[16]	0.900	14.79
Rhoad's Fork	5.6	0.159	251	0.251	1.26
Castle Creek	10.7[17]	0.303	350[18]	0.350	3.34
Stockade Beaver Creek	12.15[19]	0.344	1500[20]	1.50	16.28
Total		**7.126 m^3/s**			**192.95 x 106 kg/yr**

(1) Data from Driscoll et al. (2000), Driscoll and Carter (2001), Carter et al. (2001a), Carter et al. (2001b) and Williamson and Carter (2001) unless otherwise stated.
(2) Unless otherwise stated, the total dissolved solids concentration reported here is "sum of solids", which is nearly the same as "residue".
(3) The dissolved load is the product of the discharge and the concentration. For example, Table 5 (Carter et al., 2001b) showed the discharge of Cascade Spring plus "other small springs" near Cascade Spring totals 22.7 cfs = 0.643 m^3/sec. The TDS is 2.46 kg/m^3. Therefore the dissolved load is 2.46 kg/m^3 (0.643 m^3/s) =1.58 kg/sec = 49.87 x 10^6 kg/year.
(4) From Table 5 showing "springflow" (Carter et al., 2001b).
(5) From Burr et al. (1990), the conductivity of Beaver Creek = 2500 µS/cm. Therefore from Fig. 35 (Williamson and Carter, 2001) the TDS = 2000 mg/L.
(6) This 25.6 cfs discharge also includes some small springs near the cement plant (Table 5, Carter et al., 2001b).
(7) From Back et al. (1980).
(8) Rahn and Gries (1973) showed a 1.73 cfs spring in Elk Creek near I-90 (Sec 11, T3N, R6E).
(9) The total dissolved solids of Elk Creek is from the USGS gage located approximately 8 miles east of the actual spring near I-90.
(10) The discharge of Spearfish Creek at Spearfish is 53.87 cfs (Table 24, Driscoll and Carter, 2001). Note: the discharge of Spearfish Creek is difficult to quantify because of man-made diversions. Additionally, there is a losing reach below the tunnel diversion for Hydro #1, reported at 6.5 cfs; however this 6.5 cfs most likely reappears near the DC Booth Fish Hatchery and hence 53.87 cfs is used for the purpose of this paper. Miller and Driscoll (1998) show a discharge of 51.04 cfs near Maurice. Since the diversions for Homestake Mine have nearly ceased, the discharge of Spearfish Creek has increased and is reportedly 62 cfs (Janet Carter, pers. comm., 10/26/04). Rahn and Gries (1973) estimated the base flow of Spearfish Creek at Spearfish to be 39.83 cfs.
(11) Burr et al. (1990) showed the conductivity = 400 µS/cm. Therefore, from Figure 35 (Williamson and Carter, 2001) the TDS = 300 mg/L.
(12) The discharge of water diverted to the Homestake Mine and Lead-Deadwood Sanitary District is estimated at 10 cfs (Burr et al., 1990).
(13) Burr et al. (1990) showed conductivity = 450 µS/cm. Therefore, from Figure 35 (Williamson and Carter, 2001), the TDS = 350 mgL.
(14) The discharge of Crow Creek is given in Table 22 (Driscoll and Carter, 2001).
(15) Rahn and Gries (1973) reported that the springs at Ranch A have a discharge of 23.81 cfs. According to Carter et al. (2001b) Sand Creek has a "springflow" discharge of 18.4 cfs. Table 22 (Driscoll and Carter, 2001) shows 22.58 cfs.
(16) From Burr et al. (1990), the Redwater River at the SD/WY border shows conductivity = 1500 µS/cm. Therefore, from Fig. 35 (Williamson and Carter, 2001), the TDS = 900 mg/L.
(17) From Miller and Driscoll (1998).
(18) From Burr et al. (1990) the specific conductivity = 450 uS/cm. Therefore, from Fig. 35 (Williamson and Carter, 2001), the TDS =350 mg/L.
(19) The U. S. Geological Survey (1980) found the average discharge of Stockade Beaver Creek is 12 cfs. Carter et al. (2001b, Table 5) reported the "spring flow" to be 9.6 cfs. The springs, located above LAK reservoir, were measured at 14.6 cfs (Rahn and Gries, 1973). Driscoll and Carter (2001, Table 22) show 12.15 cfs.
(20) The U. S. Geological Survey (1980) found conductivity = 2200 µS/cm. Therefore, from Fig. 35 (Williamson and Carter, 2001), the TDS = 1500 mg/L.

RECHARGE

Water discharging from the major springs in the Black Hills is not completely derived from precipitation falling on the outcrops of the Madison Limestone and Minnelusa Formation. Rahn and Gries (1973) showed that some streams draining the Precambrian core lose much of their water where they cross the carbonate belt. Dye tests (Rahn and Gries, 1973; Greene, 1999) show that much of the water lost by a disappearing stream emerges as a "resurgent" spring at the outer contact of the Paleozoic carbonate belt. The amount of water recharging the carbonates by the disappearing streams varies seasonally depending on climatic conditions. Hortness and Driscoll (1998) measured recharge rates to the carbonate belt by the disappearing streams. The eighteen disappearing streams listed in Table 2 show the total average recharge to be 2.89 m^3/s.

The chemistry of the water sinking into the carbonate belt varies seasonally and hence is difficult to quantify. Conductivity is related to TDS. For example, Battle Creek near Keystone has a low conductivity (150 µS/cm) during high discharge (0.57 m^3/s) conditions in June, but has high conductivity (300 µS/cm) during the low discharge (0.028 m^3/s) conditions in January (Williamson and Carter, 2001; Carter et al., 2002). For this study, Table 2 shows an assumed TDS concentration of 191 mg/L for all eighteen of the disappearing streams. This value is the mean TDS concentration of waters in the Precambrian "crystalline core sites" (Table 10, Williamson and Carter, 2001). This assumption is a simplification of a complex phenomenon, but for the purpose of this investigation provides a general indication of the dissolved load recharging ground water in the carbonate belt by the disappearing streams. Table 2 shows that the load delivered annually totals approximately 18 million kg.

The difference between the load removed by the springs (188 million kg/year) and the load delivered by the disappearing streams (18 million kg/year) is 170 million kg/year. The annual removal of this mass is indicative of the rate of chemical weathering within the belt of carbonate rocks. An additional consideration is that some water leaves the Black Hills area as ground water flowing downdip through the carbonate aquifer.

DEEP GROUND-WATER LOSS

The Madison Limestone and Minnelusa Formation dip gently outward from the Black Hills and constitute a vast artesian aquifer beneath the Mesozoic strata. Thus there is some ground water in the carbonate belt that does not discharge from the springs, but slowly percolates through the permeable carbonate strata. This unknown deep ground- water loss rate has been described as "x" by Rahn and Gries (1973).

Using Darcy's Law, an estimate of the discharge lost by deep ground water flow can be made:

$$Q = KA\ (H/L)$$

Q = discharge (m^3/d).

Table 2. Dissolved load of recharged water in the Black Hills

Name	Discharge		TDS Concentration		Dissolved Load
	cfs	m^3/s	mg/L	kg/m^3	10^6 kg/yr
Beaver Creek	2.86(1)	0.081	191(2)	0.191	0.488
Reaves Gulch	0.18(3)	0.005	”	”	0.031
Highland Creek	1.52(3)	0.043	”	”	0.259
S. Fork Lame Johnny + Flynn Creeks	0.98(3)	0.028	”	”	0.167
N. Fork Lame Johnny Creek	0.41(3)	0.012	”	”	0.70
French Creek	8.97(4)	0.254	”	”	1.53
Grace Coolidge Creek	6.27(5)	0.178	”	”	1.070
Battle Creek	4.54(6)	0.129	”	”	0.774
Spokane Creek	0.92(3)	0.026	”	”	0.157
Bear Gulch	1.48(7)	0.042	”	”	0.252
Spring Creek	15.02(8)	0.425	”	”	2.562
Victoria Creek	1.15(3)	0.033	”	”	0.196
Rapid Creek	9.81(9)	0.278	”	”	1.673
Boxelder Creek	14.24(10)	0.403	”	”	2.429
Little Elk Creek	2.28(3)	0.065	”	”	0.389
Elk Creek	9.99(11)	0.283	”	”	1.704
Bear Butte Creek	16.08(12)	0.455	”	”	2.743
False Bottom Creek	5.35(3)	0.152	”	”	0.913
Total		**2.892 m^3/s**			**18.037 x 10^6 kg/yr**

(1) The discharge for Beaver Creek near Pringle is from Table 20 (Driscoll and Carter, 2001).
(2) The total dissolved solids concentration used for all the recharging streams is assumed to be 191 mg/L, the mean of 134 samples of “crystalline core sites” given in Table 10 (Williamson and Carter, 2001). TDS fluctuates with discharge (see Table 42, Williamson and Carter, 2001); however, TDS values for every day are not available. Hence the average value 191 mg/L is used.
(3) Discharge data for several small streams recharging the Paleozoic carbonate belt are from Table 8 (Carter et al., 2001a).
(4) The recharge rate of French Creek above Fairburn was given in Table 17 (Carter et al., 2001a).
(5) The recharge rate for Grace Coolidge Creek near the Game Lodge is from Table 17 (Carter et al., 2001a).
(6) The recharge rate for Battle Creek below Keystone is from Table 17 (Carter et al., 2001a).
(7) The discharge for Bear Gulch near Hayward is from Table 20 (Driscoll and Carter, 2001).
(8) The recharge rate for Spring Creek near Hermosa was given in Table 17 (Carter et al., 2001a).
(9) The average annual recharge rate for Rapid Creek was given in Table 12 (Carter et al., 2001a).
(10) The discharge for Boxelder Creek below Nemo is from Table 17 (Carter et al, 2001a).
(11) The discharge of Elk Creek below Roubaix is from Table 17 (Carter et al., 2001a).
(12) The discharge of Bear Butte Creek near Deadwood also includes smaller drainages above Sturgis as shown in Table 17 (Carter et al., 2001a).

K = hydraulic conductivity (m/d). Values of K for the Madison Limestone in the Black Hills area were summarized by Rahn (1992, and references contained therein). Four general sources of K estimates are:

(1) Isotope dating by Back et al. (1983) shows the ^{14}C age of four artesian wells surrounding the Black Hills. From these data the average value of K for the Madison aquifer = 1.34 m/d.

(2) Transmissivity estimates using specific capacity data from Madison wells in the Black Hills area average 38 m^2/d. Using the saturated thickness of the Madison Limestone (b = 130 m) indicates an average value of K = 0.29 m/d.

(3) USGS and other reports of the northern Black Hills area found T for the Madison Limestone is approximately 100 m^2/d. Using b = 130 m leads to average value of K = 0.77 m/d.

(4) The US BLM Environmental Impact Statement for the Energy Transportation Systems, Inc., proposed well field in Niobrara County, WY, found T for the Madison Limestone averages approximately 50 m^2/d. Therefore K = 0.38 m/d using b = 130 m. The permeability of the Minnelusa Formation was found to be less than the Madison Limestone.

The average value of hydraulic conductivity from these four field studies yields: K = 0.70 m/d. This value is largely determined for the Madison Limestone but for this investigation it is assumed to be representative of the entire 280 m thickness of the carbonate rocks. This is admittedly great simplification of a complex hydrogeologic situation. Local areas may have greater permeability; for example Long and Putnam (2002) found large transmissivities in the western Rapid City area due to extensive fracturing and converging flowpaths into the valley of Rapid Creek. Anisotropic transmissivity undoubtedly exists within the carbonate aquifer. Anisotropic transmissivity correlates to cave passageway orientation in the Madison Limestone (Greene and Rahn, 1995), but for this paper isotropic hydraulic conductivity was assumed for the entire 280 m thickness.

A = cross sectional area (m^2). The total thickness of the Madison Limestone and Minnelusa Formations is approximately 280 m. The perimeter of the Paleozoic carbonate belt encircling the Black Hills is approximately 240 km.

H/L = potentiometric gradient. Back et al. (1983), Rahn (1992), and Carter and Redden (1999) showed the potentiometric surface slopes from the Black Hills area into the adjoining prairies. These maps reveal a somewhat steeper gradient to the west of the Black Hills and a somewhat gentler gradient to the east. A general value of 0.0017 was used for this study.

From Darcy's Law:

$Q = (0.70 \text{ m/d}) (280 \text{ m} \times 240{,}000 \text{ m}) (0.0017) = 80.0 \times 10^3 \text{ m}^3\text{/d} = 0.93 \text{ m}^3\text{/s}$.

This deep ground-water loss is equivalent to 14% of the discharge (6.66 m^3/s) of the 13 springs around the periphery of the carbonate belt. Assuming the TDS of the deep ground-water loss is the same as the spring water, the load carried by deep ground water loss = 14% (188×10^6 kg/yr) = 26×10^6 kg/yr. Therefore the resultant load removed from the carbonate belt by the thirteen springs plus the deep ground water loss = 170×10^6 kg/yr + 26×10^6 kg/yr = 196×10^6 kg/yr. Figure 3 is a cross-sectional sketch that summarizes the model used in this investigation.

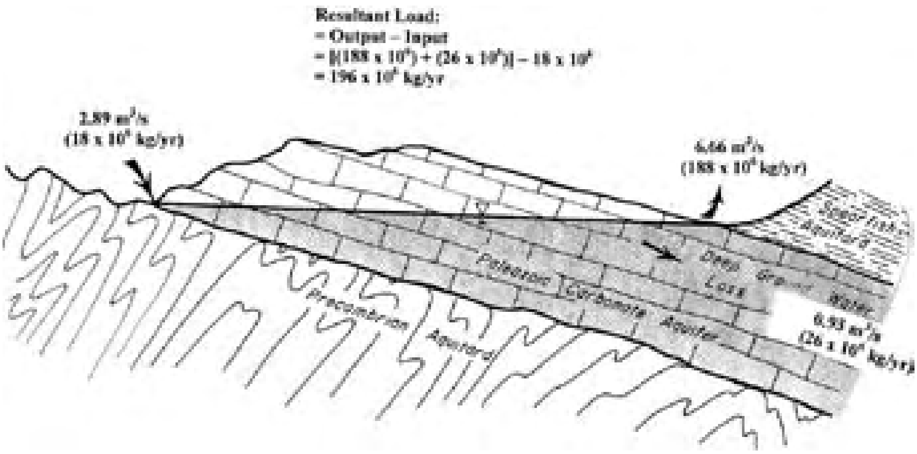

Figure 3. Cross-sectional sketch showing discharge and resultant dissolved load derived from the Paleozoic carbonate belt.

CHEMICAL WEATHERING

A traditional approach to determine land denudation by chemical weathering is simply to equate the load determined from TDS data as a direct measure of the mass removed from the watershed (Fleischer, 1963). This paper uses the chemical weathering reaction and resulting principal solutes to adjust the TDS values and more closely reflects the mass of carbonate removed. The primary dissolved ions of the water from the major springs are calcium, magnesium, and bicarbonate. Laboratory analyses for common ions show the median concentrations (mg/L) for the Madison aquifer (Table 4, Williamson and Carter, 2001) are: TDS 260, calcium 54, magnesium 25, sodium 5, bicarbonate 222, sulfate 23, and chloride 4. For this paper, a model was developed to use the conventional carbonate weathering reactions and resolved the abundant TDS data into chemical reactions illustrating the solution of limestone and dolomite.

The simplest method of analysis would be to assume that calcium and bicarbonate make up all the dissolved constituents and that the Madison Limestone and Minnelusa Formations are pure limestone. Carbonic acid from precipitation dissolves calcite, as follows (from Freeze and Cherry, 1979):

$$CaCO_3 + H_2CO_3 \longleftrightarrow Ca^{+2} + 2HCO_3^{-1}$$

Because the solutes in the Black Hills carbonate belt contain magnesium as well as calcium, a more accurate analysis would be to consider the dissolution of dolomite:

$$CaMg(CO_3)_2 + 2H_2CO_3 \longleftrightarrow Ca^{+2} + Mg^{+2} + 4HCO_3^{-1}$$

Using atomic weights for this reaction:

$$40 + 24 + 2[12 + 3(16)] + 2[2(1) + 12 + 3(16)] \longleftrightarrow 40 + 24 + 4[1 + 12 + 3(16)]$$
$$184 + 124 \longleftrightarrow 40 + 24 + 244$$
$$308 \longleftrightarrow 308$$

The molecular weight of dolomite is 184. The TDS is the sum of the reactants = 308 gm/mole. In this equation the ratio of dolomite/TDS is 184/308 = 59.74%. Therefore, for every 100 kg of TDS, only 59.74 kg of dolomite is actually dissolved. The resultant load removed from the carbonate belt from the TDS data as determined above is 196 x 10^6 kg/year. Using the dolomite model for supply of these TDS constituents, the rate of solution of dolomite is 59.74% (196 x 10^6 kg/year) = 117 x 10^6 kg/year.

If only dolomite were being dissolved, calcium and magnesium solute ions would be present in equal numbers. Because the atomic weights of these two elements are 40 and 24, respectively, a laboratory analysis of dolomite solution would show the same ratio of concentration of these two substances, such as Ca^{+2} = 40 mg/L and Mg^{+2} = 24 mg/L. These values are, in fact, very close to the median values cited above, and are consistent with the assumed model that the solution within the carbonate belt is essentially the solution of dolomite. In fact, the name "Madison Limestone" is really a misnomer because detailed petrologic studies show that this unit is primarily a dolomite (Barnum, 1973; Schneider, 1973).

A more precise method of determining the weathered mass would be to quantify all the common ions in the water of each spring, and to evaluate the lithologies and weathering reactions present along each ground-water flow path. The precipitation of calcite near some springs indicates that complex, interdependent reactions take place. In order to mass balance calcite, dolomite, anhydrite dissolution, calcite precipitation, dedolomitization, and other chemical reactions, the program NETPATH could be employed along a hypothetical groundwater travel path to its exit point. Hayes (1999), for example, showed that the NETPATH model simulates the geochemical evolution of Cascade Spring water and the mixing of water from the Madison and Minnelusa aquifers.

Despite the presence of gypsum, halite, and other soluble lithologies within the carbonate belt this paper admittedly uses a simple model whereby: (1) the entire carbonate belt is assumed to be dolomite, and (2) the solutes consist only of calcium, magnesium, and bicarbonate. Sulfate and other dissolved constituents are found in spring waters. In fact, dissolved sulfate at Cascade Spring and Evans Plunge at Hot Springs is slightly greater than dissolved bicarbonate. Sulfate is a complicating factor; indeed, the very presence of gypsum influences the solubility of calcite and dolomite (Back et al., 1983).

LANDSCAPE DENUDATION

To determine denudation rates, it is necessary to convert dolomite mass into volume. The density of pure dolomite = 2.85 gm/cm^3. Based on a primary (interstitial) porosity = 10% (Rahn, 1992), the in-situ density of the carbonate rocks is 2.57 gm/cm^3 = 2.57 x 103 kg/m^3.

The annual volume of dolomite removed = annual mass removed/density = (117 x 10^6 kg/year)/(2.57 x 10^3 kg/m^3) = 45,600 m^3/year. [This is equivalent to a solid cube 35.7 meters on a side.] It is assumed that the solution is derived from the exposed 2,948 km^2 of carbonate rocks. Therefore the denudation rate = (45,600 m^3/year)/(2.948 x 10^9 m^2) = 15.46 x 10^{-5} m/year, or roughly 1.55 cm per 1,000 years.

ASSUMPTIONS

There are many assumptions in the model presented and calculations used in this paper. They include:

(1) Tables 1 and 2 show discharge and TDS concentration data generally obtained during the past decade. This interval of time might not be reflective of geologic time and long-term denudation. In the Black Hills stream discharge and ground- water recharge rates are related to tree density; stream discharge has decreased in the last century because of forest fire suppression (Rahn and Davis, 1993).

(2) The discharge and TDS concentration of the disappearing streams (Table 2) could reflect anthropogenic activities such as urbanization and mining. However, the total load recharging the carbonates (18 million kg/year) is relatively small compared to the load permanently discharged by the 13 springs (188 million kg/year).

(3) It is assumed that the Paleozoic carbonates are pure dolomite with 10% porosity. The fact that other soluble lithologic units including gypsum constitute part of the sedimentary rocks affects these calculations to some degree. Shale, sandstone, and chert constitute part of the Minnelusa Formation; however these chemically inert lithologies do not affect the chemical land denudation rate calculations.

(4) It is assumed that the TDS of spring water is derived from calcium, magnesium, and bicarbonate ions. Laboratory analyses of spring water show that sulfate and other ions also constitute part of the solutes. However the land denudation analysis using more precise model including dissolved gypsum would be little different from the results of this investigation. In fact, the calculation of a land denudation rate involving both calcium and magnesium bicarbonate solutes derived from a dolomitic terrain is nearly the same as the calculation of a land denudation rate based only on calcium bicarbonate solutes derived from a limestone terrain. A complete analysis of chemical solution from all lithologies and all solutes is beyond the scope of this investigation.

(5) The amount of deep ground water loss from the carbonate belt is estimated at 0.93 m^3/s/. Numerous assumptions were used in this calculation, e.g., the estimated value of K = 0.70 m/d. This hydraulic conductivity, largely based on field tests for the Madison Limestone, is assumed to represent the permeability of the entire carbonate section. Limited data for the Minnelusa Formation

indicate that its permeability is only approximately 50% that of the Madison Limestone (Long and Putnam, 2002). Hence the 0.70 m/d value may be somewhat high. This would result in a slight decrease in the land denudation rate. A parameter sensitivity analysis would show that hydraulic conductivity is the most sensitive parameter in this model. If, for example, hydraulic conductivity were doubled, the load carried by deep ground-water loss would double, leading to an increase in the calculated land denudation rate from 1.55 cm/1,000 years to 1.89 cm/1,000 years.

(6) The 2,948 km^2 outcrop area of Madison Limestone and Minnelusa Formation is assumed to be the only area undergoing solution. However some artesian springs discharge through the Spearfish Formation in places such as the lower Spearfish Valley area, including Cox's Lake (Epstein, 2000). Some solution occurs in these places, including dissolution of gypsum/anhydrite beds in the Minnelusa Formation downdip from the actual carbonate belt outcrops (Redden, 2000). If, for example, the area under the outcrops of the Permian Opeche Formation and Minnekahta Limestone (272 km^2) were added to the 2,948 km^2 outcrop area, the resulting denudation rate would decrease slightly from 1.55 to 1.42 cm/1,000 years.

DISCUSSION

Land denudation is caused by physical erosion as well as chemical erosion. This paper addresses only chemical weathering and erosion. This is presumably the more important process within the carbonate belt, a conclusion supported by an examination of the geomorphology of the Paleozoic carbonate belt, which exhibits solution features such swales and ephemeral valleys as well as numerous caves beneath the land surface. The carbonate belt generally lacks surface erosion features such as fine-grained stream patterns and fluvial features such as found in the Precambrian rocks. Nevertheless, dramatic precipitation events, such as the floods of June 9, 1972, can produce runoff and physical erosion from the Paleozoic carbonate belt. The land denudation rate for chemical solution as determined in this paper, 1.55 cm/1,000 years, is augmented to some degree by physical erosion.

Estimates of physical land denudation rates are generally derived from clastic load measurements of suspended load in rivers or sedimentation into reservoirs behind dams. The 1.55 cm/1,000 year chemical denudation rate of the carbonate belt in the Black Hills is less than typical landscape denudation rates based on the suspended load of streams (Ritter et al., 1995). Judson and Ritter (1964) found the average rate of denudation for the United States is 6.1 cm per 1,000 years. They found that suspended load constitutes the dominant factor of stream load, although solution is the most important erosional process in the southeastern U.S. The Mississippi River was found to have roughly three times the clastic load as dissolved load. Hadley and Schumm (1961) found the average annual suspended-sediment discharge of the Cheyenne River near Hot Springs, SD, was 64 metric tons per square kilometer over the 207,000 square kilometer watershed; using a rock density of 2.6 gm/cm^3, this is equivalent to a denudation rate of approximately 2.45 cm/1,000 years.

The 1.55 cm/1,000 years chemical denudation rate of the carbonate belt determined in this paper can be compared to the Cenozoic downcutting rate of Rapid Creek based on Cenozoic erosion levels determined by geomorphologic, stratigraphic, and paleontological evidence. Rahn (1996) found that late Pliocene to early Pleistocene (approximately 2 million year old) high-level alluvial deposits on the eastern slope of the Black Hills are approximately 200 m above the present day flood plain of Rapid Creek, yielding an average down-cutting rate of 100 cm/1,000 years. Presumably this rate of erosion is greater because it reflects recent local canyon cutting and not regional denudation.

Another comparison of the rate of land denudation for the Black Hills is to evaluate the long-term erosion rate of the Black Hills uplift. According to Gries (1996) and Carter et al. (2002), the Black Hills uplift began approximately 62 million years ago and by approximately 37 million years ago the uplift was eroded to near its present topography. Thus the time interval for the erosion of this uplift was approximately 25 million years. The uplifted mass consisted of the Paleozoic and Mesozoic sedimentary rocks that were domed up and eroded through, exposing the underlying Precambrian metamorphic and igneous rocks. The thickness of the sedimentary rock is estimated at approximately 2,060 m (Gries, 1996). The thickness of Precambrian rock eroded below the Cambrian Deadwood Formation can be estimated by examination of geologic cross sections (DeWitt et al., 1999); in the central Black Hills area the thickness of eroded Precambrian rock is estimated to average 280 m. Therefore the total thickness of eroded rock is 2,340 m. Thus the rate of denudation in the Central Black Hills region during this time interval = 2,340 m/25 million years = 93.6 m/million years = 9.36 cm/1,000 years. This rapid rate probably reflects vigorous physical erosion during the Laramide Orogeny as the easily-eroded Pierre Shale and other Mesozoic sediments were being domed up.

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