Interrelationships of Selected Physical Properties and Chemical Constituents of Ground Water in Northwestern Nebraska

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INTERRELATIONSHIPS OF SELECTED PHYSICAL PROPERTIES

AND CHEMICAL CONSTITUENTS OF GROUND WATER IN NORTHWESTERN NEBRASKA

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This study provides baseline data for many of the chemical constituents occurring in ground water in northwestern Nebraska and contiguous parts of Wyoming and South Dakota; it also projects the chemical behavior of water from similar geologic environments. Samples were collected from springs issuing mainly from the Pine Ridge escarpment and wells tapping aquifers in Upper Cretaceous and Tertiary rocks. The 139 water samples were analyzed for fifteen chemical constituents, including lithium and heavy metals (i.e., uranium, manganese, silver, lead, cadmium, and copper). The chemical composition of spring water is similar to that of well water from mid-Tertiary sandstones. Water from the older formations tend to have increasing concentrations of many chemical constituents. Uranium concentrations in excess of 100 ppb occurred in water from eight wells. Although a few metal pairs exhibit narrow correlation values, most pairs show a wide correlation-coefficient pattern from well water of the various formations.

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INTRODUCTION

As the demand for water increases, the need to know more about the chemical composition of available water supplies becomes more important. This need is vital to water-deficient areas such as northwestern Nebraska. This study reports on the chemical constituents of spring and well water samples that were collected from several different geologic formations in northwestern Nebraska and adjacent areas. Concentrations of uranium, lithium, and thirteen other chemical constituents were determined. Also, coefficients were calculated between the chemical constituents to evaluate their relationship.

This collection area consisted primarily of the region north of the Pine Ridge escarpment in Dawes and Sioux counties in Nebraska and in parts of the adjacent Fall River and Shannon counties in South Dakota and Niobrara County in Wyoming. The exposed formations in the area are of late Cretaceous and middle Tertiary age. The formations, from oldest to youngest, are the Carlile Shale, Niobrara Chalk, and Pierre Shale of the Upper Cretaceous Series and the Chadron,

Brule, Gering, Monroe Creek, Harrison, and Marsland formations of the Tertiary System (Witzel, 1974). The Carlile Shale and Niobrara Chalk are exposed northeast of Chadron near the Nebraska-South Dakota border. Most of the Pierre Shale outcrops are north of the White River. The Brule and Chadron formations crop out at the base of the Pine Ridge escarpment and in local outliers; whereas, the Gering Formation and younger formations crop out higher in the escarpment.

Because water is not readily obtainable in the collection area, the wells are erratically spaced, and this fact prevented sampling on a grid basis. Water from those wells sampled was collected from flowing wells, or in a few cases, was collected from nonflowing wells only after the storage water was replaced with a fresh supply. Most samples came from wells less than 100 feet deep, but a few came from wells ranging in depth from 100 to 400 feet. Collections were made during the fall, winter, and spring of 1975-76. (In Figure 1, well sources are identified on a map of the collection area.)

METHOD

Only new, acid-washed polyethylene containers were used for collection and storing the samples. The time-dependent tests, pH and bicarbonate, were made at the collection site. Less time-dependent tests were made at the end of each collection day and included specific conductance (SC), sulfate, chloride, calcium, and magnesium. The remaining analyses were made in the Chadron State College laboratories from either non-acidified water or water acidified with nitric acid to pH 1.8. These samples were kept frozen until analyzed to minimize possible adsorption of ions on the container surfaces.

The chemical constituents were analyzed by the following methods: acidimetric titration for bicarbonate, mercuric titration for chloride, potentiometry for pH, complexometric titration for calcium and magnesium, conductivity for specific conductance, spectrophotometry for sulfate and fluoride,
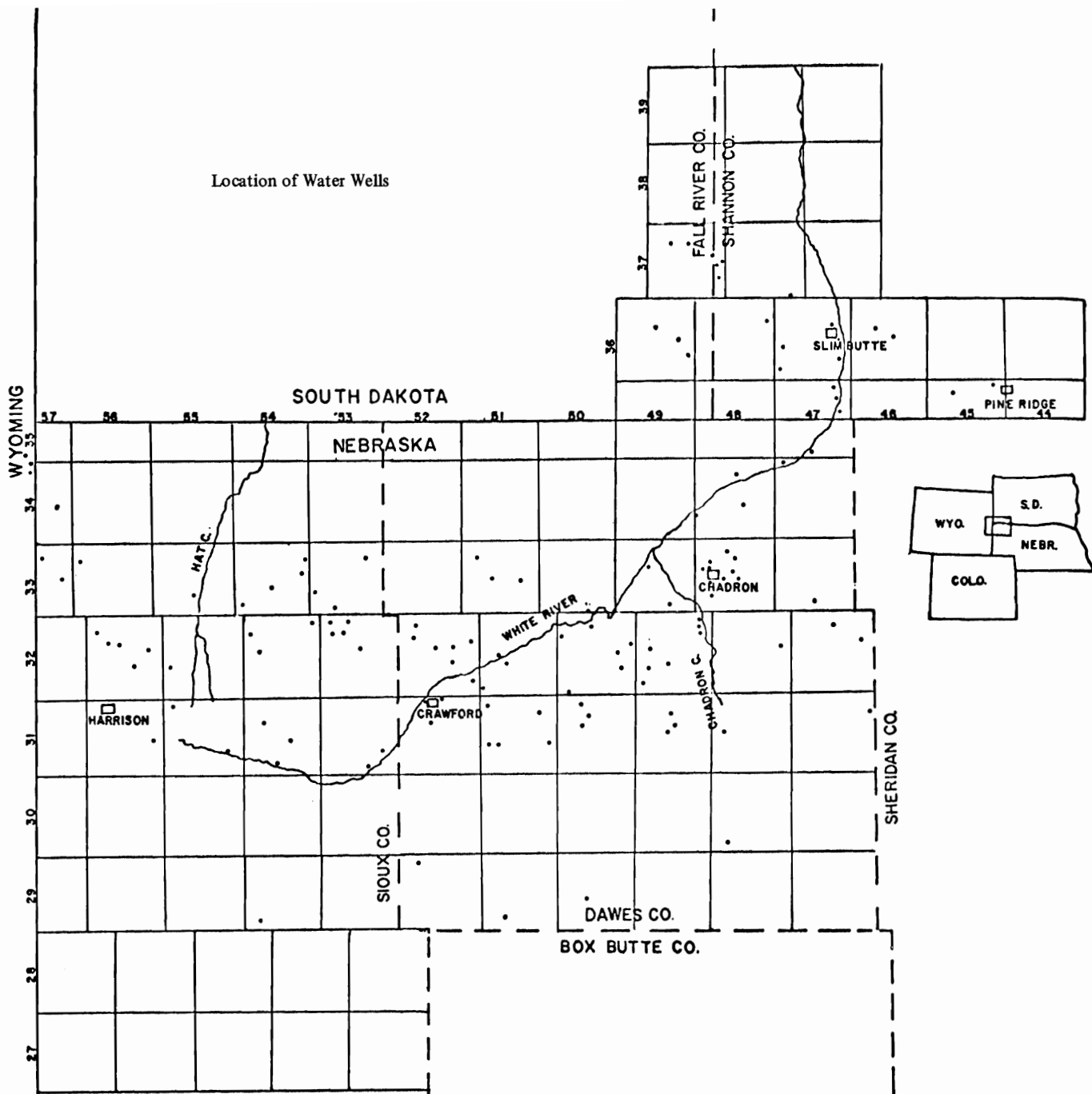
Figure 1. Location of water wells sampled.

flame photometry for sodium and potassium, complexometric-spectrophotometry for uranium, and flameless atomic absorption spectrophotometry for lithium, manganese, copper, lead, cadmium, and silver.

RESULTS AND DISCUSSION

Table I summarizes the analytical results for samples grouped according to their geological source. Shown for each group of samples is the mean chemical composition (upper line) and the standard deviation (lower line). Elemental and anionic concentrations are expressed as parts per million (ppm) or parts per billion (ppb), and specific conductance is expressed as micromhos per centimeter at 25° C.

The data show that water from spring and well samples are slightly basic, but that water from wells tapping the older formations tends to be more neutral. Average concentrations of sulfate, sodium, calcium, lithium, and copper in water from older formations (Carlile, Niobrara, and Pierre) were about

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TABLE I

Average Chemical Composition, Specific Conductance, pH, and Standard Deviations
of Water from Northwestern Nebraska and Adjoining Parts of South Dakota and Wyoming

Source and Formation	No. of Samples		SC	pH	ppm								ppb						
					HCO$_3$	SO$_4$	Cl	F	Na	K	Ca	Mg	Li	Mn	Cu	Pb	Cd	U	Ag
Spring: Pine Ridge Escarpment	32	$\bar{x}$	727	7.9	257	20	24	0.6	74	12	19	9	30	19	15	4.8	1.0	14	1.1
		$\bar{o}$	932	0.4	63	29	61	0.3	103	12	13	6	20	22	19	8.8	0.2	9	0.2
Well: Gering, Monroe, Harrison, Marsland	21	$\bar{x}$	356	7.7	221	6	22	0.6	31	8	18	8	18	8	9	4.4	1.0	11	1.0
		$\bar{o}$	96	0.2	57	6	38	0.2	27	6	10	4	16	14	13	5.6	0.0	10	0.0
Well: Brule	17	$\bar{x}$	556	7.5	311	18	16	0.8	28	15	24	7	41	8	30	6.8	1.2	18	1.0
		$\bar{o}$	124	0.4	66	21	13	1.2	53	14	21	4	20	16	58	16.0	0.7	16	0.0
Well: Chadron	30	$\bar{x}$	1109	7.4	492	122	55	0.9	256	21	28	8	87	16	24	2.3	1.8	47	1.7
		$\bar{o}$	444	0.3	154	92	59	0.5	191	20	28	8	43	21	65	2.1	2.0	36	1.7
Well: Pierre	30	$\bar{x}$	2159	7.3	554	745	30	1.4	275	13	108	39	195	41	91	2.6	2.2	57	2.8
		$\bar{o}$	1246	0.3	140	710	18	1.3	190	13	90	40	138	21	245	2.2	2.5	41	2.8
Well: Carlile-Niobrara	9	$\bar{x}$	2327	7.2	493	847	27	1.5	343	9	182	53	125	51	93	17.0	1.0	46	1.9
		$\bar{o}$	822	0.3	216	434	17	0.5	294	5	80	19	92	19	198	24.0	0.0	27	2.3

$\bar{x}$ − arithmetic mean
$\bar{o}$ − standard deviation

ten times greater than the average concentrations of the same constituents in water from the younger formations (Gering and younger rock units). The average concentration of magnesium and manganese is about five times greater, of fluoride and silver, two times greater, of water from the older formations than in water from the younger.

Not included in the table are data on concentrations of hydrogen sulfide, or selenium. Although analyzed in all samples, hydrogen sulfide was detected in only three samples— 5ppm in a sample from the Pierre Shale and 2 ppm and 5 ppm in two samples from the Chadron Formation. Selenium concentrations were less than 50 ppb (the minimum of detection) even in water from sources that had been thought to be most favorable to detectable concentrations.

Of the 137 samples analyzed, eight contained more than 100 ppb uranium: one of these was from the Carlile Shale and Niobrara Chalk undifferentiated, five were from the Pierre Shale, and two were from the Chadron Formation. The mean uranium concentration in the water from the Chadron Formation is in line with that obtained from rocks of the same age in Wyoming (Butler, 1969) and northwestern South Dakota (Denson, et al., 1955).

To determine the relationship of pH and selected chemical constituents and of one chemical constituent to another, correlation coefficients between them have been calculated. Table II shows these relationships (correlation coefficients x 100) for eleven variables in water from wells tapping the Carlile Shale, Niobrara Chalk, Pierre Shale, and the Chadron and Brule formations. The table reveals wide variations for many variable pairs with respect to geologic sources. On the other hand, several narrow and consistent patterns emerge upon closer examination. For example, pH correlates negatively with sulfate and calcium; fluoride correlates negatively with potassium; calcium correlates positively with magnesium. Sodium and potassium do not correlate consistently either positively or negatively. Uranium concentrations do not correlate strongly with concentrations of any other constituent. Lithium does not show a consistent positive correlation pattern with magnesium, sulfate, or chloride as documented in a study by Mertz, et al. (1974). More complete analytical data grouped by geologic sources of water and by location of sampled wells or springs are available from the author. Also available are correlation data for eleven chemical variables in water from wells tapping into, and springs issuing from, the Gering and Monroe Creek formations.

SUMMARY

Pronounced differences in the chemical composition and correlation patterns of paired constituents in ground water from different geologic sources in northwestern Nebraska demonstrate the need to identify all analytical data from ground water according to geologic source. Greater minerali-
zation, due to larger concentrations of bicarbonate, sulfate, sodium, calcium, magnesium, fluoride, lithium, manganese, and copper, correlates positively with increasing age of the geologic source. No consistent correlation pattern could be detected for potassium, lead, cadmium, and silver concentrations with respect to the age of geologic source. Average concentrations of uranium in water from the Chadron and Brule formations are nearly the same as those in water in the same or equivalent formations in adjacent states. Correlation coefficients between pH and selected chemical constituents and between selected chemical constituent pairs generally manifest a wide range of values. Exceptional to this generalization are the narrow ranges of correlation coefficients between pH and calcium (-0.38 to -0.57) and between calcium and magnesium (0.51 to 0.60). Prior to this study, virtually no data on concentrations of heavy metals, and other selected elements, were available for northwestern Nebraska.

ACKNOWLEDGEMENTS

REFERENCES

Butler, A. P. 1969. Ground water as related to the origin and search for uranium deposits in sandstone. *Contribution to Geology, University of Wyoming* (Uranium issue) 8(2), pt. 1:81-86.

Denson, N. M., H. D. Zeller, and J. G. Stephens. 1955. Water samplings as a guide in the search for uranium deposits and its use in evaluating widespread volcanic units as potential source beds for uranium. (Contributions to Geology of Uranium and Thorium) *Professional Papers of the United States Geological Survey,* 300:673-680.

Mertz, W., E. E. Angion, H. L. Cannon, K. M. Hambidge, and A. W. Voors. 1974. Lithium, geochemistry and the environment. *In* Volume I, *The relation of selected trace elements to health and disease.* Washington, D.C., National Academy of Sciences: 36-42.

Witzel, F. L. 1974. Guidebook and road logs for the geology of Dawes and northern Sioux counties, Nebraska. M.S. Thesis, Chadron State College, Chadron, Nebraska.

TABLE II

Correlation Coefficients (x 100)
Betweeen Chemical Constituents in Well Water Samples

		pH	HCO₃	SO₄	Cl	F	Na	K	Ca	Mg	Li	U
pH	a		- 5	-33	67	79	15	0	-38	-23	-25	39
	b		-21	-22	40	40	-11	-23	-57	-57	28	-19
	c		3	-12	- 1	3	- 3	15	-42	6	-30	2
	d		49	-72	4	5	-27	9	-49	-27	50	24
HCO₃	a			16	19	15	14	- 6	-13	0	16	6
	b			10	-18	-17	5	-27	- 3	28	34	23
	c			6	16	0	2	-10	-12	-16	- 4	38
	d			-42	-29	30	-22	-36	-32	- 9	80	6
SO₄	a				- 6	-23	5	-18	4	-19	28	-17
	b				12	18	-21	-22	32	55	14	5
	c				17	-20	7	-17	84	51	73	36
	d				27	-30	12	49	80	15	-23	-20
Cl	a					85	12	-14	-12	-35	- 7	8
	b					63	-12	-26	-12	-13	33	-15
	c					- 2	-14	- 4	25	-11	9	10
	d					- 8	-20	0	2	-17	-67	35
F	a						3	-25	-18	-20	5	4
	b						-17	-25	16	-10	14	- 7
	c						- 7	-20	-24	-19	-20	-46
	d						- 2	-34	-29	46	- 1	22
Na	a							76	-34	-32	-16	26
	b							81	-10	-12	- 9	16
	c							- 5	- 1	-15	11	10
	d							-45	13	4	-14	-12
K	a								-10	- 8	-20	40
	b								- 6	- 1	-24	2
	c								-11	-17	- 6	-10
	d								57	7	-12	- 7
Ca	a									51	26	-23
	b									54	29	25
	c									60	82	24
	d									49	1	- 2
Mg	a										43	20
	b										-20	13
	c										49	29
	d										0	33

a=Brule Formation; b=Chadron Formation; c=Pierre Formation; d=Niobrara and Carlile Formations.