

Salt Accumulation in the Groundwaters of North Dakota

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Summary

This preliminary study based on the chemical determinations of 6,500 water samples collected and analyzed by the United States Geologic Survey between 1962 and 1983 from 71 aquifers. These determinations were used to establish salt accumulation patterns in North Dakota groundwaters. Major ion concentration and sodium adsorption ratio (SAR) values were related to the total salt concentration as measured by electrical conductivity of each aquifer. Of the 71 investigated aquifers, 28 had sufficient data for a regression analysis.

Studying these regressions, some patterns of salt brine ion concentration, termed here salt accumulation in groundwaters, were established using the following criteria: the dominant anion (or anions) which accumulates continuously with increases in total salinity; the accumulation rate of the dominant anion; the change of ratio between anions at different limits of total salinity; and the salts which accumulate in larger quantities.

Using these criteria, a genetic classification of aquifers was developed based on three categories: classes, groups, and stages. A class includes all aquifers in which the percentage of the dominant anion (or anions) increases continuously as total salinity increases. Three classes were obtained: chloride, sulfate-chloride, and sulfate accumulation. Eight groups of aquifers were established based on the similarities in the accumulation rate of the dominant anion, and the salts which accumulate in larger quantities. In each group, between two and five stages of salt accumulation were distinguished based on the change of ratio between anions at different intervals of total salinity. The classes, groups and stages express the characteristic geochemistry of the groundwaters in the aquifers of various geologic periods.

The complexity of aquifers in different regions makes the geochemical characterization and comparison of the groundwaters difficult, especially in predicting potential salinization of soil from these waters. Some attempts to develop this relationship have been made, but only for the shallow groundwaters that determine the genesis of salt-affected soils in the Soviet Union by Kovda (1946, 1954, 1961) and Bazilevich (1970) and in Romania by Florea (1956, 1976) and Maianu (1964a, 1964b). In North Dakota, detailed geochemical data have been published by Groenewold et al (1979) on the aquifers in the Knife River basin and adjacent areas of west-central North Dakota, and

by Groenewold et al. (1983) on the subsurface waters in undisturbed and surface mined landscapes, but no attempt has been made to establish the patterns of salt accumulation in the groundwater as a function of the geochemical characteristics of the North Dakota principal aquifers and to develop these characteristics into a usable classification system for predicting soil salinization potential. The object of this article is to develop a genetic classification of North Dakota aquifers based on the relationships between their total salinity and chemical composition.

In this article we use electrical conductivity (EC) as the basic measure of total salinity. Soil and water with a high salt content can transmit electricity easily. The correlation between the amount of salts and ease of electrical transmission is very high. Measurements of EC are cheap and accurate. We simply wet a soil until it is barely saturated and extract water under vacuum. We pass an electrical current through the extract and measure electrical conductivity. The EC is expressed in decisiemens per meter (dSm^{-1}). Saline soils have an EC of 4.0 dSm^{-1} and greater. Sea water has about 6 percent salt and an EC of 14 dSm^{-1} .

Results

Total salinity of the groundwaters

North Dakota aquifers present large variation in total salt content and chemical composition. The mean electrical conductance of all groundwaters based on 6,500 samples is 2.03 dSm^{-1} with a range from 0.1 dSm^{-1} to 87.5 dSm^{-1} . In the eight groups of aquifers (Fig. 1) the mean total salinity of groundwaters increases from the first group of aquifers to the eighth, with the exception of group 6 (Table 2).

Aquifers of groups 1 to 4 include Pleistocene sediments (Table 1). The groundwaters in group 1 have the lowest mean total salinity of 0.9 dSm^{-1} , with a maximum of only 2.5 dSm^{-1} (Table 2). Quaternary aquifers of groups 2 and 3 have slightly higher mean total salinity, but the maximum values are much higher (14.4 , respectively 19.6 dSm^{-1}). The group 4 includes buried glaciofluvial deposits and undifferentiated glacial drift. Groundwaters in group 4 have different total salt contents. The mean total salinity is moderate (2.20 dSm^{-1}), but the maximum values in this group are the highest (87.5 dSm^{-1}) observed in this study (Table 2).

Groups 5 and 6 include aquifers from Tertiary and Upper Cretaceous formations (Table 1). Their mean total salinity is intermediate between the first three groups of aquifers from Quaternary formations and the last two groups (7 and 8) from Cretaceous and Jurassic formations (Table 2). Group 5 is a complex of Paleocene-Tertiary formations (Tongue

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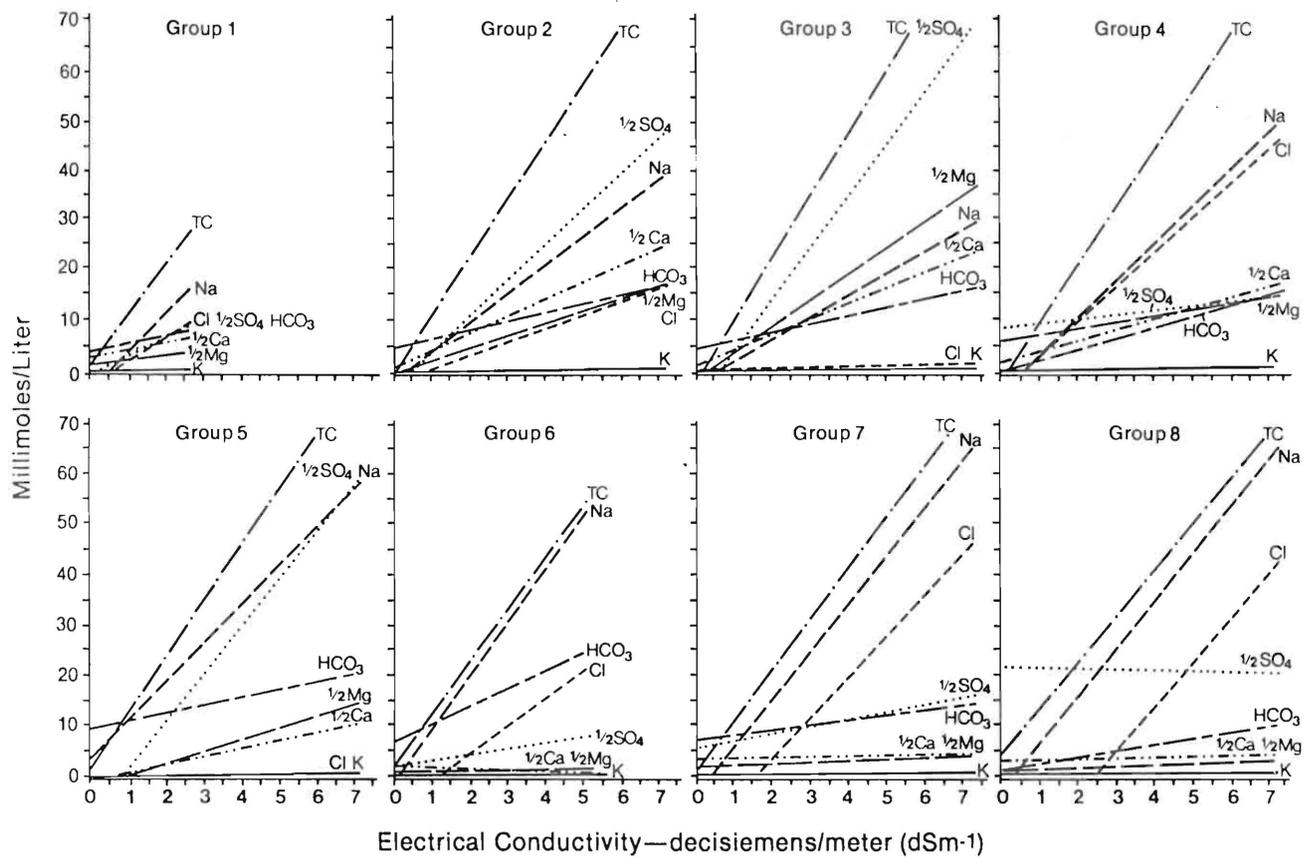


Figure 1. Relationships between specific conductivity and ion concentration by groups of groundwaters.

Table 1. The groups of aquifers in North Dakota based on similarities in salt accumulation.

Groups of Aquifers	Geology			Aquifers		
	Era	Period	Epoch			
1	Cenozoic	Quaternary	Pleistocene	—Englevale	—West Fargo	—LaMoure
2				—Beach	—Denbigh	—Ellendale
				—Buried outwash	—Edgeley	—Elk Valley
3				—Brampton	—Ice contact deposits	—Napoleon
	—Killdeer	—Ray	—Voltaire			
	—Lake Nettie (Upper)	—Till deposits	—Warwick			
4			—Buried glaciofluvial deposits			
			—Glacial drift, undifferentiated			
5	Cenozoic Mesozoic	Tertiary—Paleocene		—Tongue River (undifferentiated)*	—Sentinel Butte	—Hell Creek (Upper)
					—Ludlow	
6	Mesozoic	Upper Cretaceous		—Hell Creek	—Fox Hills	
7		Cretaceous		—Pierre		
8		Lower Cretaceous Upper Jurassic		—Dakota —Upper Jurassic		

*Tongue River aquifer includes Sentinel Butte Formation

River undifferentiated and Ludlow) Sentinel Butte, and Upper Cretaceous formations (Hell Creek). Its mean total salinity is 2.3 dSm⁻¹, but some of the aquifer formations included in this group have groundwater with high maximum total salt contents. The shale and sandstone deposits of the Cannonball and Ludlow Formations were deposited at the beginning of the Tertiary during the most westerly invasion of Tertiary sea into North Dakota. Unfortunately, the available groundwater samples from the Cannonball Formation are scarce and therefore were not considered in this group of aquifers. The highest values of total salt content in this group are of the Ludlow Formation. The groundwaters in group 6 of Fox Hills and Hell Creek Formations have about the same mean total salinity (2.0 dSm⁻¹) as group 5, but the maximum value is much lower. (Table 2).

High mean and maximum total salinity values are characteristic for group 7 and 8 aquifers. Group 7 includes only the Pierre Formation of the Middle Cretaceous period. It has a high mean salinity (4.7 dSm⁻¹) and a maximum salinity of 34.4 dSm⁻¹. The last group of aquifers, including the Dakota Formation of Lower Cretaceous and some Upper Jurassic Formations. Group 8 has the highest mean total salinity (5.2 dSm⁻¹) and a maximum salinity value of 58.0 dSm⁻¹ (Table 2). The salinity of groundwater in these last two groups illustrates their marine origin.

Relationship between total salt content and chemical composition

We found that ion content trend with increasing salinity was different from geologic ages (Fig. 1 and Table 1). We analyzed these trends with a series of statistical tests.

The rates of salt accumulation in group 1 are very high for Na⁺, high for SO₄²⁻ and Cl⁻, moderate for HCO₃⁻ and Ca⁺⁺, low for Mg⁺⁺, and very low K⁺ (Fig. 1). The

main salts in these waters are Na₂SO₄ and NaCl in approximately equal proportions. In group 2, SO₄²⁻ accumulates at a very high rate, followed by Na⁺. The other ions accumulate at moderate rates, except K⁺. The main salt in the waters of this group is NaSO₄. In group 3, SO₄²⁻ accumulates at a very high rate and Mg⁺⁺ accumulates at a higher rate than Na⁺. The dominant salts in this group of groundwater are MgSO₄ and Na₂SO₄.

The rate of Cl⁻ accumulation in group 4 is the highest observed of the aquifers in North Dakota. The Cl⁻ rate approached the rate of Na⁺ accumulation. Sulfate, HCO₃⁻, Ca⁺⁺, and Mg⁺⁺ accumulate at a moderate rate. A large range of total salinity was also observed in this group. The large range of total salinity and high rate of Cl⁻ accumulation with an increase in total salinity are characteristic of groundwaters which have been exposed for long durations to intensive, near surface evaporation. Their high chloride content may also be related to the diffusion of chloride salts from adjacent marine deposits such as the Cannonball or Pierre Formations (Groenewold et al., 1979).

Group 5 represents aquifers characterized by a predominant accumulation of SO₄²⁻ and a moderate accumulation of HCO₃⁻; Na⁺ accumulates at a very high rate; Mg⁺⁺ and Ca⁺⁺ accumulate at a low rate (Fig. 1). The groundwater chemistry of the Tertiary and Upper Cretaceous deposits which constitute this group of aquifers has been studied by Groenewold et al. (1979, 1983). In shallow setting (<100 meters), they consider that the chemical composition of these groups of aquifers is due to five processes which take place in the shallow Tertiary deposits: 1. the CO₂ production in the organic horizon of the soil; 2. oxidation and hydrolysis of pyrite which abounds in these formations; 3. dissolution of calcite and dolomite; 4. precipitation and dissolution of gypsum; and 5. exchange of Ca⁺⁺ with

Table 2. The mean and maximum salt content of North Dakota aquifers by groups of similar salt accumulation.

Group of aquifers	EC dSm ⁻¹	Anions (meq/l)			Cations (meq/l)				SAR	
		HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺		
1	mean	0.9	5.4	1.4	2.6	4.2	2.3	2.7	0.1	3
	max	2.6	12.9	13.3	12.3	9.0	6.7	20.4	0.9	13
2	mean	1.3	7.3	1.5	6.4	5.4	3.3	6.1	0.2	3
	max	14.4	32.6	18.9	184.5	28.4	87.2	111.7	2.6	37
3	mean	1.5	7.0	0.3	13.5	5.8	9.8	4.9	0.2	2
	max	19.6	21.5	6.3	329.0	25.9	189.1	164.4	2.5	24
4	mean	1.5	8.4	6.1	10.4	6.7	4.4	13.2	0.3	6
	max	87.5	31.9	998.3	106.2	75.0	54.3	947.8	13.9	161
5	mean	2.3	13.1	0.4	13.0	2.6	2.8	21.0	0.1	33
	max	13.0	41.2	18.2	183.2	51.8	95.4	14.7	2.3	145
6	mean	2.0	13.7	3.7	4.3	1.4	1.0	19.3	0.1	44
	max	5.7	33.1	45.1	52.1	28.4	20.6	52.2	0.7	200
7	mean	4.7	10.4	26.0	13.6	4.8	4.1	40.0	0.4	28
	max	34.3	16.7	361.0	167.8	69.4	62.5	268.7	1.4	122
8	mean	5.2	7.0	28.3	21.7	4.8	3.0	47.6	0.6	37
	max	58.0	34.8	451.2	50.0	59.9	36.3	400.0	6.6	184

Na⁺. These processes are responsible for the predominant ions in these groundwaters, especially Na⁺, SO₄²⁻, and HCO₃⁻. In deeper units (>100 meters), sulfate-reducing bacteria account for loss of SO₄²⁻ relative to HCO₃⁻.

Group 6 represents the only aquifers (Hell Creek and Fox Hills) where HCO₃⁻ equals Cl⁻ (Fig. 1). However, chloride exceeds the content of sulfate, which, according to Groenewold et al (1979), is unlikely to result from dissolution of chloride-bearing minerals in the aquifers. A more reasonable explanation of the high Cl⁻ concentration may be the molecular diffusion from underlying marine shale of the Pierre Formation into Hell Creek and Fox Hills Sandstones. Swenson (1968) and Thorstenson et al. (1979) believe that chloride can diffuse from the underlying Dakota and Pierre Formations. The very high content of Na⁺ and very low content of Ca⁺⁺ and Mg⁺⁺ result in the high SAR values of these aquifers. The fact that Hell Creek and Fox Hills Aquifers are in the same salt composition group may be explained by Moran et al. (1976), who observed continuous leakage from the Fox Hills through the Hell Creek Formation on one county. Some stratigraphic interpretation problems exist in the column at this interval and these two aquifers maybe cannot be separated in the data.¹

Group 7, which includes only the Pierre Formation, has a very high accumulation of Na⁺ and Cl⁻, a low accumulation of SO₄²⁻ and HCO₃⁻ and a very low accumulation of Ca⁺⁺, Mg⁺⁺ and K⁺ (Fig. 1).

Group 8 includes the Cretaceous Dakota Sandstone and Upper Jurassic aquifers with a very high total salinity and

¹G.H. Groenewold, personal communication.

high content of NaCl (Fig. 1; Table 2). The groundwaters from the Dakota Formation are under artesian pressure which contributes to the salinization of the shallow groundwaters and many soils in the Red River Valley of North Dakota (Benz et al., 1961).

Classes and stages of salt accumulation in groundwaters

The change in salt composition with an increase in total salinity may be explained by general trends of salt solubility (Maianu, 1964b). The differentiation of these changes from one group of aquifers to another results from the variation in minerals and ions present and the geologic history including post-depositional history of the rock units of the aquifers. Both the general trends of salt solubility and the salt species differentiation in geologic periods create distinct classes and stages of salt accumulation in the aquifers.

A class includes all the groups of aquifers with the same dominant anion (or anions). For each class, the dominant anion increases simultaneously with the increase of total salinity. The interpretation of the chemical data used for establishing classes was obtained by graphically comparing the regression curves between the relative concentration values of the anions (as a percentage of total anions) and their corresponding values of total salinity. Figure 2 presents these regressions for the main anions: Cl⁻, SO₄²⁻, and HCO₃⁻.

A stage represents a special salt composition at a specific interval of groundwater total salinity. The stages were established using computerized scheme for classification of the groundwaters based on the change of the ratio between anions with the increase of total salinity (Held and Maianu, 1984). These ratios change at a different interval of total

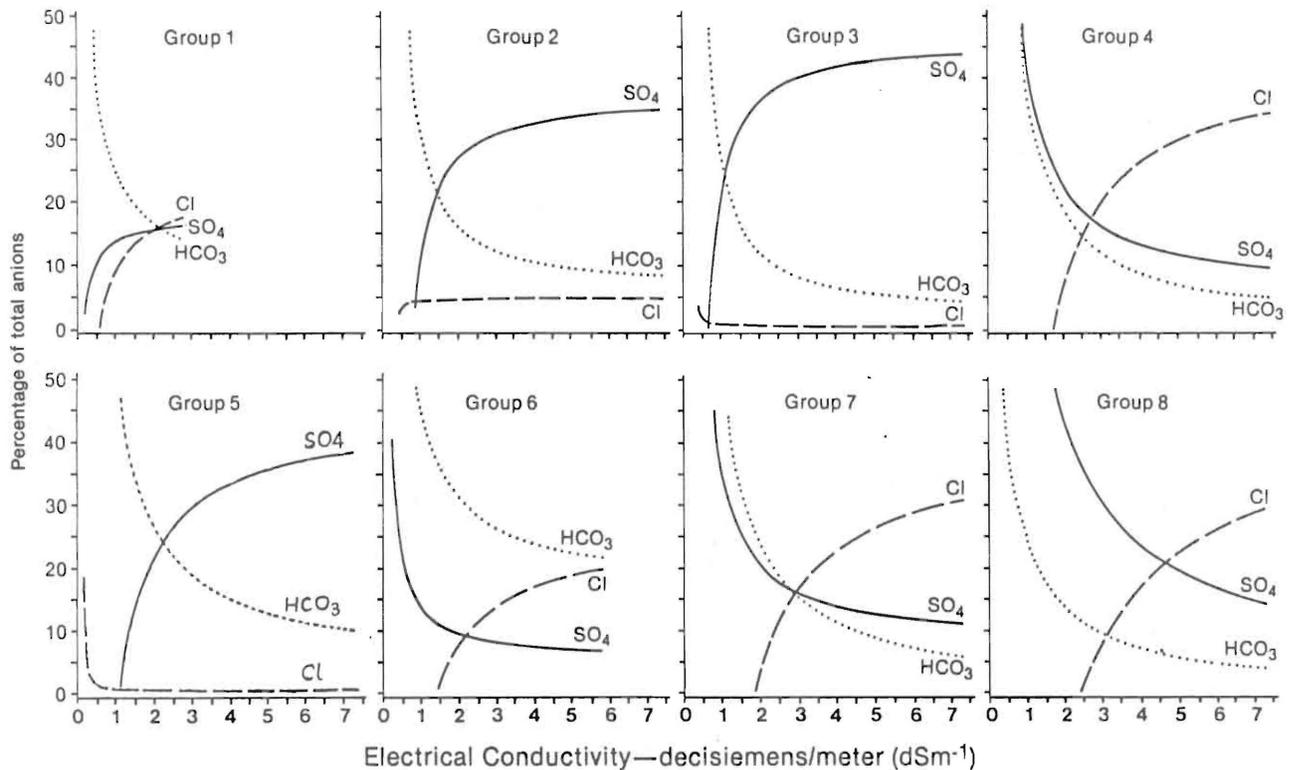


Figure 2. Relationships between specific conductivity and relative concentration of anions (as percentage of total anions) by groups of groundwaters.

salinity for each group of aquifers. Table 3 shows the stages for aquifers of group 6.

The specific shape of the curves, the particular rate of anion accumulation and the change of ratios between the anions express the characteristic geochemistry of the groundwaters in different aquifers of various geologic periods.

In group 1, the percentage of both Cl^- and SO_4^{--} increases with increases of total salinity, and HCO_3^- decreases as in all other groups. In groups 4, 6, 7 and 8, Cl^- increases and SO_4^{--} and HCO_3^- decrease as the total salinity increases, but at different rates from one group to another. However, in groups 2, 3 and 5, the percentages of SO_4^{--} increase and those of Cl^- and HCO_3^- decrease, excepting Cl^- in group 2.

In group 7 and 8, chloride is the key anion which accumulates continuously with increased total salinity due to groundwaters confined in marine geologic formations (Pierre and Dakota). Chloride is also accumulating in aquifers which are confined in the Hell Creek and Fox Hills Formations (Group 6). The origin of Cl^- accumulation in group 4 is not clear.

The sulfate is predominant and accumulates continuously with increased total salinity in the aquifers confined in glacial deposits; Cl^- is practically absent. According to Groenewold et al. (1983), two major sources of sulfate in the groundwater exist. One may be the existing soluble salts and gypsum in the soil. The second may be a sporadic flushing of sulfate salts from the upper (oxidized) portion of the landscape which may result in gypsum accumulation in soils lower in the landscape. The second source of sulfate is considered to be recently oxidized sulfides which had been accumulated under reducing conditions in flood basin environments.

The CO_3^{--} and HCO_3^- ions have the same general pattern of distribution in groundwaters with increased total salinity (Fig. 2). In relative values they decrease continuously from low to high total salinity values, but the rate of such a decrease is different from one group of aquifers to another. This depends on the influence of the groundwater soluble salts on the dissolution of low soluble carbonates accumulated in the deposits of the aquifers. In Figures 1 and 2, the lines labeled HCO_3^- actually represent both CO_3^{--} and HCO_3^- .

Table 3. Stages of salt accumulation in the group of aquifers No.6.

		Electrical Conductivity— dSm^{-1}				
		1	2	3	4	5
Stages of salt accumulation		C—S*	C—S—Cl	C—Cl—S	Cl—S—C	
Principal anions		HCO_3^-				
Secondary anion		SO_4^{--}		Cl^-		
Principal cation		Na^+				
Secondary cations		$\text{Ca}^{++}, \text{Mg}^{++}$				
HCO_3^-	% of total anions	rapid decrease**		moderate decrease		
Cl^-		rapid increase			moderate increase	
SO_4^{--}		rapid decrease	moderate decrease	slow decrease		
Ca^{++}	% of total cations	rapid decrease	moderate decrease	slow decrease	very slow decrease	
Mg^{++}		rapid decrease	moderate decrease	slow decrease	very slow decrease	
Na^+		very rapid increase	rapid increase	moderate increase	slow increase	
K^+		moderate decrease	very slow decrease			

*C—bicarbonate; S—sulfate; Cl—chloride

**See the curves in figure 2.

Genetic classification of aquifers

A genetic classification of aquifers was developed based on four criteria or factors: 1. the predominant anion(s) which accumulate continuously; 2. the accumulative rate of the predominant anion(s); 3. the salt accumulation stages determined by the change of the ratio between different anions at specific intervals of total salinity for each group of aquifers; and 4. the SAR intervals which are characteristic for each stage of salt accumulation.

The hierarchies established are classes, groups, and stages (Table 4). A class includes all groups of groundwaters in which the percentages of the dominant anion or anions increase continuously as total salinity increases. Three classes of groundwaters were established in North Dakota: chloride, chloride-sulfate, and sulfate accumulation. The chloride class includes the groups 4, 6, 7 and 8; the chloride-sulfate class includes group 1; and the sulfate class includes groups 2, 3 and 5 (Table 4).

Table 4. Genetical classification of aquifers in North Dakota according to the stages of salt accumulation.

Classes ¹	Groups of aquifers ²		Stages of salt accumulation ³		
	No. of the groups	Characteristics	Salt composition	Total salinity (dSm ⁻¹)	SAR
Chloride accumulation	7	= Cl—high accumulation	CS ⁴	0.47- 2.25	10
			CS Cl	2.25- 2.95	10-13
			Cl S C	2.95- 5.75	13-25
			Cl S	5.75-34.30	25-122
	8	= NaCl—main salt = SAR—high	SC	1.59- 3.05	11
SC Cl			3.05- 3.15	11-12	
S Cl C			3.15- 3.75	12-15	
S Cl			3.75- 4.75	15-19	
Cl S			4.75-15.50	19-62	
4		Cl	15.50-58.00	62-184	
		CS	0.33- 0.55	1	
		SC	0.55- 1.95	1-4	
		SC Cl	1.95- 2.35	4-5	
		S Cl C	2.75- 2.65	5-6	
		Cl SC	2.65- 4.35	6-9	
		Cl S	4.35-12.00	9-24	
Cl	12.00-87.50	24-161			
Chloride-sulfate accumulation	6	= Cl—moderate accumulation = SAR—high	CS	0.30- 1.95	6-41
			CS Cl	1.95- 2.05	41-43
			C Cl S	2.05- 2.95	43-62
			C Cl	2.95- 5.68	62-120
Chloride-sulfate accumulation	1	= Cl, SO ₄ —moderate accumulation = Na Cl, Na ₂ SO ₄ —main salts = SAR—low	C	0.10- 0.35	1
			CS	0.35- 0.95	1-2
			CS Cl	0.95- 2.15	2-4
			C Cl S	2.15- 2.25	4-5
			Cl SC	2.25- 2.62	5-13
Sulfate accumulation	3	= SO ₄ —high accumulation = MgSO ₄ , Na ₂ SO ₄ —main salts = SAR—low	C	0.26- 0.75	0.5
			CS	0.75- 1.15	0.5-1
			SC	1.15- 3.25	1-6
	2	= SO ₄ —high accumulation = Na ₂ SO ₄ —main salts = SAR—moderate	S	3.25-19.60	6-14
			C	0.10- 0.85	2
			CS	0.85- 1.35	2-3
			SC	1.35- 8.95	3-20
	5	= SO ₄ —high accumulation = Na ₂ SO ₄ , Mg SO ₄ —main salts = SAR—high	S	8.95-14.40	20-37
			C	0.94- 1.35	15
CS			1.35- 2.35	15-26	
5		SC	2.35-11.00	26-125	
		S	11.00-13.00	125-145	

¹Classes - according to the anion(s) that accumulate as a continuum with increased total salinity.

²Groups of aquifers - according to: (i) the accumulative rates of the main anion(s), (ii) the main accumulated salts, and (iii) the SAR levels.

³Stages of salt accumulation - according to the change of salt composition between specific intervals of total salinity; SAR limits are provided for each stage.

⁴C—bicarbonate; S—sulfate; Cl—chloride

A group is characterized by the accumulation rate of the dominant anion(s), the principal salt(s) present in the water, a characteristic succession of the stages of salt accumulation, and the interval of SAR values. The eight groups of aquifers which have been distinguished in North Dakota include between one and nine aquifers (Table 1).

A stage of salt accumulation represents the interval of total salinity in which the anionic composition of the groundwater is the same and the SAR varies between specific limits (Table 4).

This system may be used for classifying the largest aquifers of North Dakota by knowing only the stratigraphic placement of the aquifer (Table 1) and its total salt content expressed as electrical conductivity. The anionic composition and the SAR interval of that groundwater may be approximated before intensive laboratory determinations are made (Table 4).

Conclusions

Salt accumulation in North Dakota groundwaters occurs according to specific patterns determined by the characteristics of the geological formation in which they are confined. These patterns were established based on the relationship existing between the total salinity and the concentrations of various ions present in 28 aquifers.

For these groundwaters, the accumulation of salt takes place in stages between particular limits of total salinity. The succession of stages differs for eight groups of aquifers. These aquifer groups have similar patterns of total salinity and accumulation rates of each anion and cation.

A genetic classification of groundwater was proposed here which include three categories: classes, groups, and stages of salt accumulation. The class takes into consideration the anion(s) which accumulate continuously with the increase of total salinity. In each class, the concentration of the anions not mentioned in the class-name decreases as the total salinity increases. Three groundwater classes were established: chloride, sulfate-chloride, and sulfate accumulation.

The group includes the groundwaters with similar patterns of salt accumulation due to the geochemical similarities of their aquifers. Each group is differentiated by four chemical characteristics of the groundwaters: 1. the accumulation rate of the dominant anion; 2. the specific succession of salt accumulation stages between particular limits of total salinity; 3. the characteristic intervals of the SAR; and 4. the salts which accumulate in larger quantities.

The salt accumulation stages represent changes in groundwater salt composition with increases in total salinity. They are different due to specific ratios between the main anions (HCO_3^- , Cl^- , and SO_4^{--}) and cations (SAR values) at different intervals of total salinity.

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