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Interpretation of Region Wide Groundwater Flow in Glacial Deposits by Means of Hydrogeochemistry

by CHARLES HAEFELI¹⁾

ZUSAMMENFASSUNG

Mit Hilfe chemischer Analysen von Grundwasser aus Bohrungen > 50 m werden die regionalen Grundwasserströmungen zwischen dem Ontario- und dem Simcoe-See, Ontario, Kanada, ermittelt, wobei eine etwas modifizierte Methode nach SCHOELLER Anwendung findet. Zum Vergleich werden Daten aus dem Gebiet von Winnipeg, Manitoba, herangezogen. Die folgenden Kriterien erscheinen besonders wertvoll, um die Grundwasserverhältnisse in glazialen Ablagerungen zu interpretieren: Gesamtmineralisation, elektrische Leitfähigkeit, Cl-Gehalt, Cl/HCO₃, SO₄/HCO₃, Basenaustausch-Indizes und zu einem geringeren Grad CaSO₄ und CaCO₃. Die Untersuchungen erlauben das Hauptanreicherungsgebiet mit den Strömungsrichtungen zu ermitteln. Die Resultate stehen im Einklang mit gleichzeitig ausgeführten piezometrischen und numerischen Studien und erlauben den Nachweis eines Nord und eines Süd gerichteten Grundwasserflusses.

1. Introduction

The changes in the chemical composition of water during its underground passage can be used as a means to analyze groundwater flow systems. Due to the interactions with the rock – mainly dissolutions, base exchanges and reductions – the total concentration as well as the ratios between the different ions change continuously. The initial chemical composition of the groundwater entering the zone of saturation varies very much depending on climate, soil and the rock of the unsaturated zone. But whatever the original chemical content may be, the mineralization of the groundwater on its trajectory always changes according to certain consistent patterns. By knowing the main hydrogeochemical criteria, it is therefore possible to determine origin, recharge and discharge areas or the flow direction of the groundwater.

Well over a dozen diagrams have been proposed to present chemical water analyses, to show the relative ratios of the elements in one type of water and to

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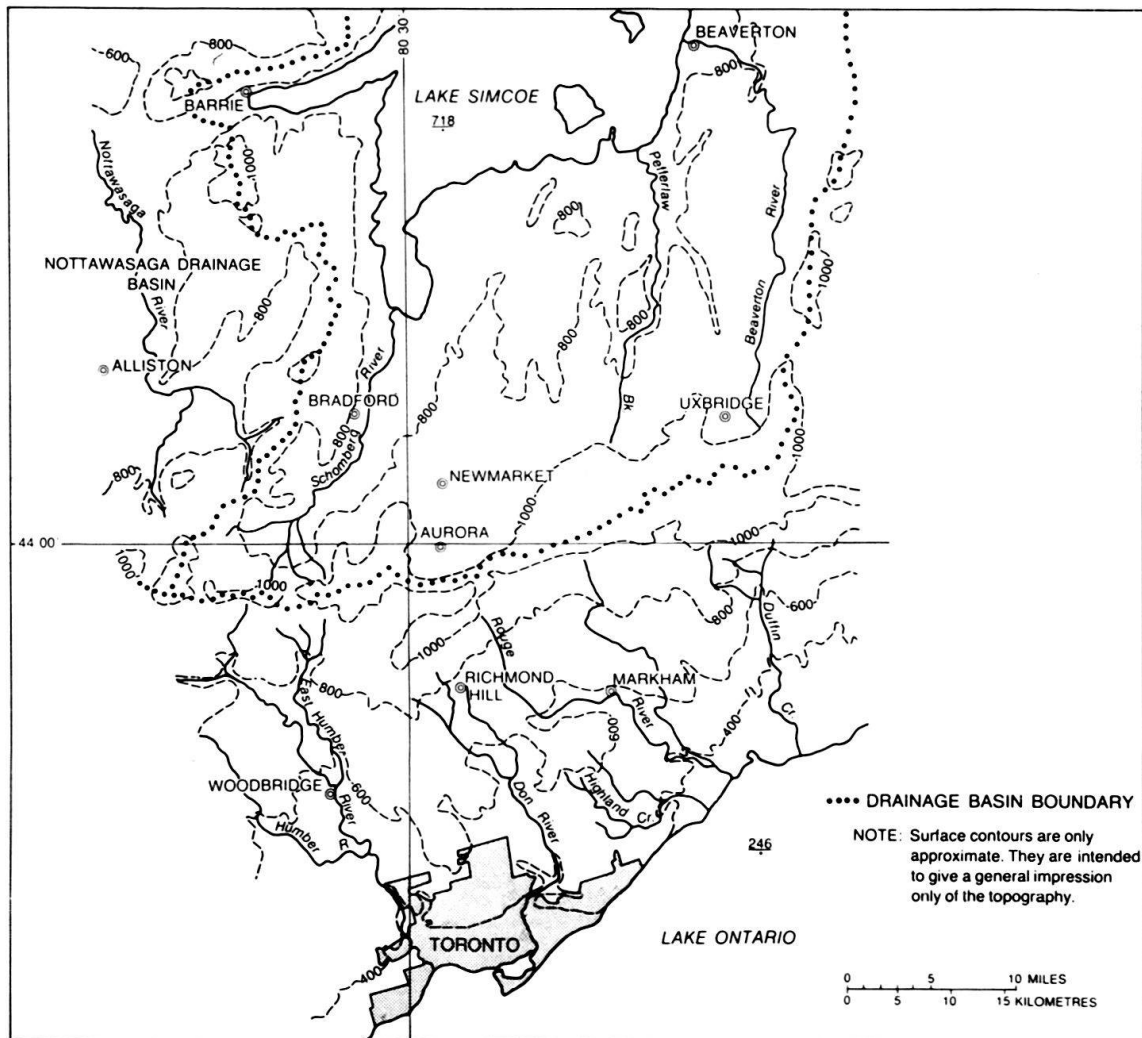


Fig. 1. Topography of study area.

compare them with other samples. The author believes that the most versatile method was developed by SCHOELLER (1935). SCHOELLER's semi-logarithmic plot, however, was perhaps considered too complicated and is therefore not applied often. A sub-objective of this paper is to show the advantage of this computation method which has been slightly modified.

Lake Ontario and its drainage basin have been selected as the type area to investigate for the International Field Year on the Great Lakes (IFYGL), a project for the International Hydrological Decade (IHD). In an attempt to determine if the terrestrial water balance of the Lake Ontario basin is affected by a major seepage from Lake Simcoe, the particular hydrogeological conditions between both lakes were investigated (Fig. 1). The relatively high elevation of the Lake Simcoe basin, the south dipping surface and bedding of the bedrock, and especially the north-south directed, buried, preglacial bedrock channels point to the possibility of a major southbound groundwater flow. To investigate the main groundwater flow systems, piezometric and mathematical analyses (HAEFELI 1970) were applied in addition to hydrogeochemistry.

The up to 700 ft (210 m) thick quaternary deposits between Lake Simcoe and Lake Ontario contain no extensive, well-defined aquifers. Over 70% of the overburden consists of till, clay and hardpan with inserted silt, sand and gravel lenses (Fig. 2). The general pattern is a low permeability body with enclosed high-permeability lenses of various sizes. The overall mean permeability of the entire quaternary deposits is approximately 10 gpd/ft² (4.72×10^{-4} cm/sec).

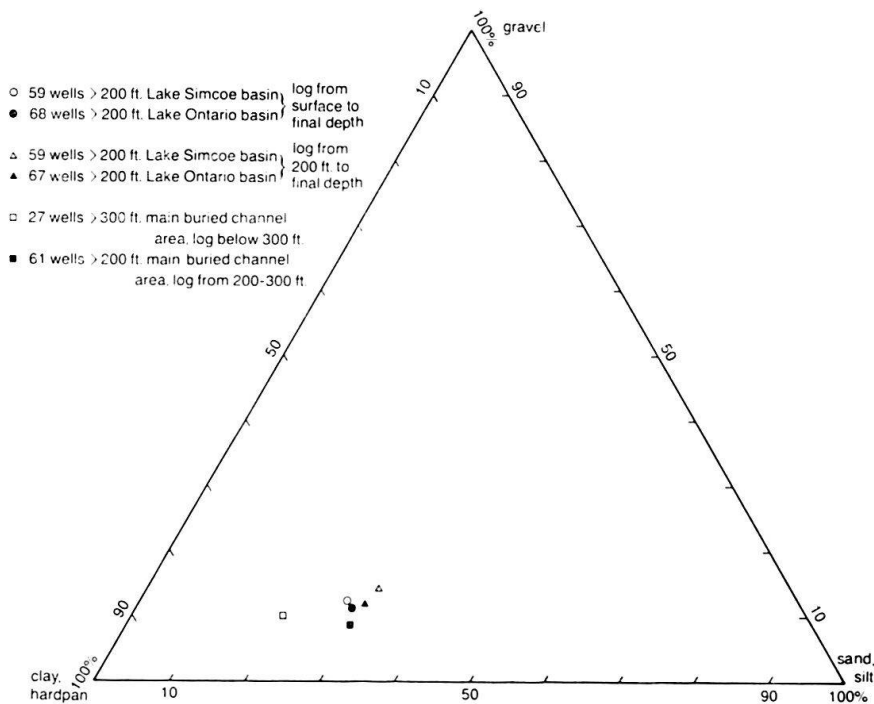


Fig. 2. Composition of the quaternary deposits (after drillers logs).

2. Sampling

The selection of water wells to be sampled requires special attention. Any immediate or short connection with the surface water would falsify the chemical composition of the groundwater of the deeper flow system and has to be avoided. To obtain reliable results, only wells below a certain depth and with no pollution indication should be considered for region-wide, groundwater-flow studies. It is preferable to choose a small number of wells rather than to include wells of questionable value. Nitrates, nitrites and other nitrogen-containing compounds may be used as pollution indicators. Since nitrate is the most convenient and stable compound to analyze, it was chosen as the pollution criterion. To illustrate the relation of the nitrate content with the well depth, average nitrate values of 30 samples studied are as follows:

- 10 wells < 200 ft (61 m): NO₃ content 14.9 ppm.
- 20 wells > 200 ft (61 m): NO₃ content 2.9 ppm.

The smaller nitrate content in the deeper wells might have been caused not only by an initial low concentration but also to some degree by the gradual reduction of NO_3 in the saturated zone. Samples from wells reaching below the level of Lake Simcoe and deeper than 175 feet (53 m) with a nitrate content of less than 12 ppm – limits which were set rather arbitrarily – were considered in the evaluation. Eleven had to be rejected because they did not meet the requirements. Four main characteristics were used to derive the main groundwater-flow direction: concentration, zonation, base exchange and saturation.

3. Concentration

To evaluate the relation between the location of the wells and their chemistry it is an advantage to choose a reference location which may represent an assumed hydrologic boundary. Since the Lake Simcoe shore as our most distinct location has a very irregular shape, the basin divide was taken as reference line instead (Fig. 1).

Chloride is one of the most important pointers to the time of contact of the groundwater with the rock and to the length of its passage. The chloride content was plotted against the distance of the well from the basin divide. This was done separately for the wells of the Lake Simcoe and Lake Ontario basins. In both cases, the chloride content increases with the distance from the divide, indicating a general recharge area around the basin divide (Fig. 3). The total concentration of dissolved solids and

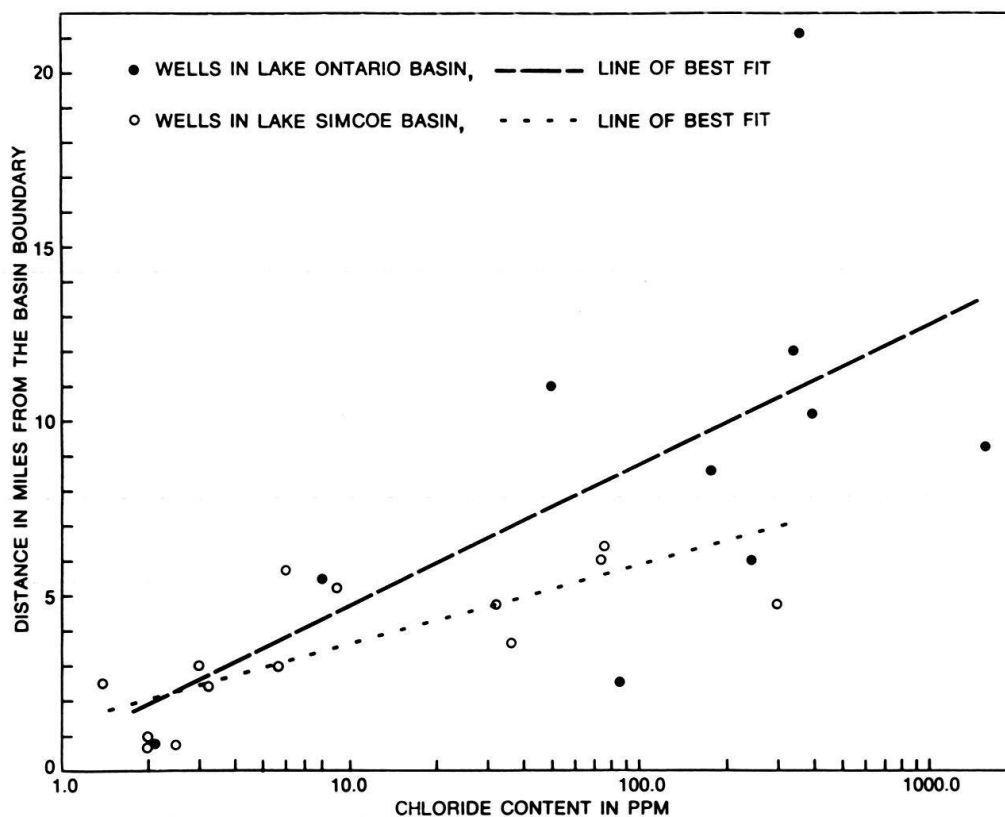


Fig. 3. Chloride content versus distance from the basin boundary.

the closely related electrical conductivity show the same direction of groundwater flow. Table 1 represents the average concentration for groups of wells versus their distance from the basin divide. The total dissolved solids and the conductivity are approximately three times smaller in the group situated within 6 miles (9.6 km) of the divide than in the group 6–21 miles (9.6–33.6 km) distant. The difference in the chloride content is even more distinct. Unfortunately, there were not enough samples from which to draw chemical contour maps.

Due to the nonexistence of region-wide, homogeneous, “impermeable” layers, infiltrations into the groundwater body not only occur in a well defined recharge region but also in adjacent areas. Consequently, the continuous mineralization process from the recharge to the discharge area is disturbed. One effect of the disturbance is the scattered distribution of the points in the distance/chloride diagram (Fig. 3).

4. Zonation ($rCl/rHCO_3$, $rSO_4/rHCO_3$, rSO_4/rCl , rMg/rCa)

The milli-equivalents per litre of the Ca, Mg, Na + K, Cl, SO_4 and HCO_3 ions were plotted on the semi-logarithmic graph developed by SCHOELLER (Fig. 4). Line I represents the average of 10 samples originating from wells situated within 6 miles (9.6 km) of the basin divide; line II shows the average of 9 samples from wells located 6–21 miles (9.6–33.6 km) from the same reference location. The relative ratios of the main dissolved elements can be determined directly from the inclination of the connecting lines in the semi-logarithmic plot. The obvious difference between the two lines is the previously mentioned entire mineralization. The average values of the ratios considered to be characteristic in the progressive change of the chemical composition of the groundwater are also presented in Table 2 versus their distance from the basin divide. The most distinguishable feature is the relation between the main anions tending to change as follows from the recharge to the discharge area:

- (1) $rCO_3 > rCl$ or rSO_4
- (2) rSO_4 or $rCl > rCO_3$
- (3) $rCl > rSO_4 > rCO_3$

which is basically the zonation described by CHEBOTAREV (1955) and SCHOELLER (1962). Once the infiltrated water has reached the zone of saturation, it normally would not pick up CO_2 which combines with water to form H_2CO_3 , the agent dis-

Table 1. Average concentration versus distance from basin divide.

Distance of well groups from basin divide	Group 1 (10 wells) 6 miles	Group 2 (9 wells) 6–21 miles
Content of Ca, Mg, Na, K, SO_4 , HCO_3 in ppm	389.3	900.8
in epm	10.6	30.1
Conductivity in micromhos at 25 °C	554	1646
Cl-content in epm	1.61	10.1

Table 2. Zonations, average ratio versus distance from basin divide.

Distance of well groups from basin divide	Group 1 (10 wells) 6 miles	Group 2 (9 wells) 6-21 miles
$rCl/rHCO_3$	0.41	2.30
rSO_4/rCl	0.046	0.059
$rSO_4/rHCO_3$	0.02	0.13
rMg/rCa	0.49	0.50

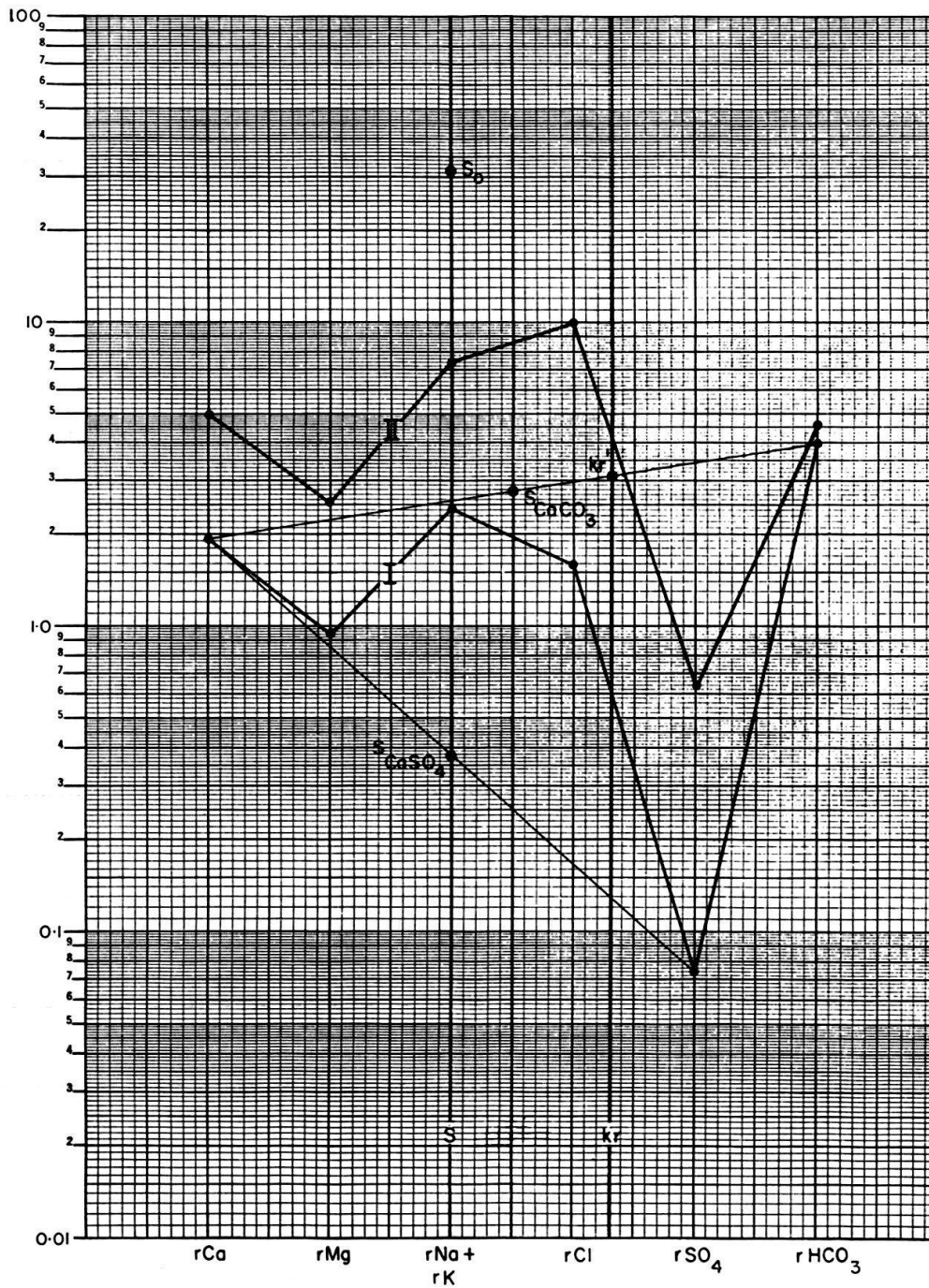


Fig. 4. Chemical analyses: Average values in epm for group I (10 wells) and group II (9 wells) with calculated S_0 , S_{CaSO_4} , S_{CaCO_3} , kr' for group I.

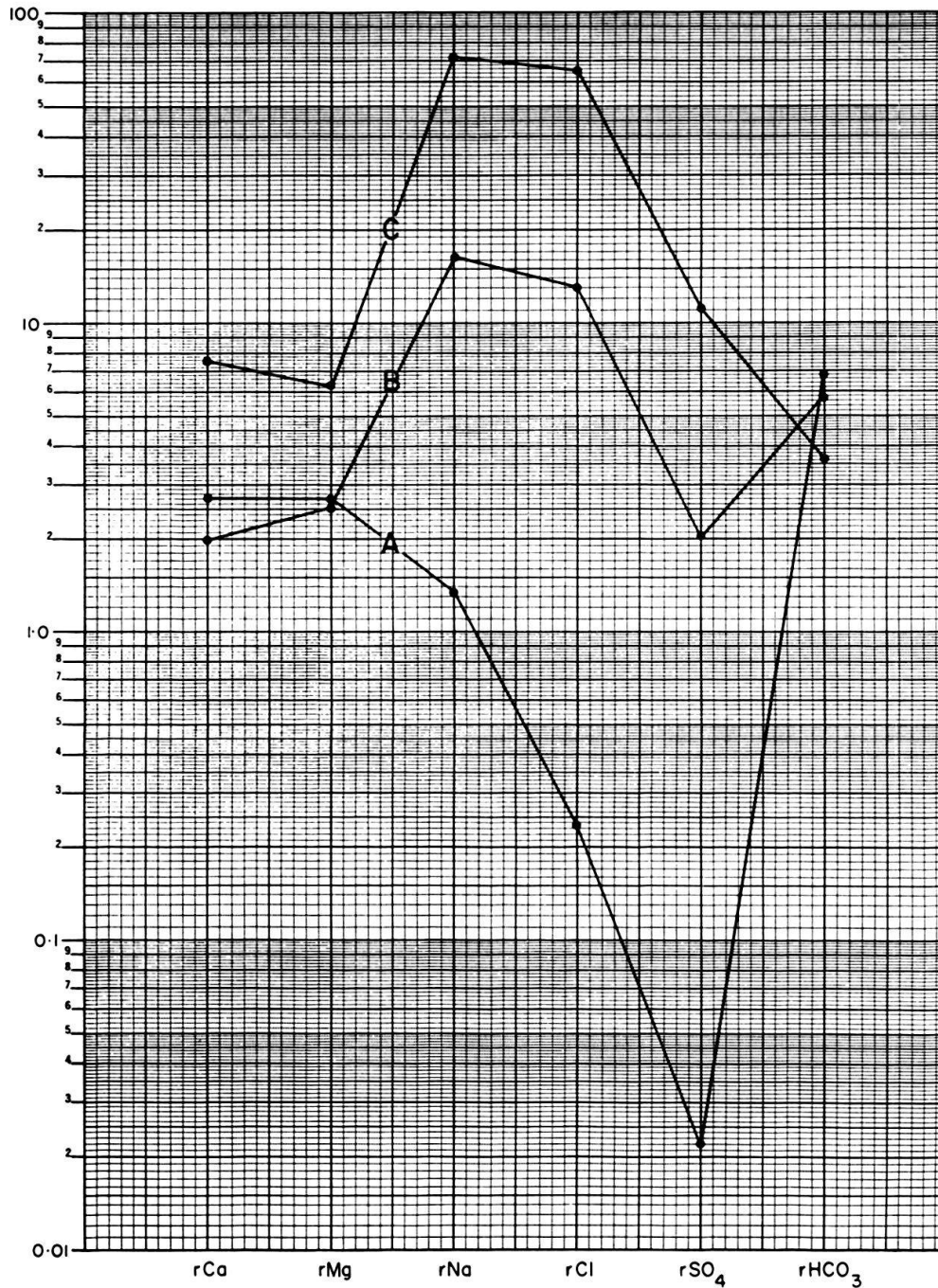


Fig. 5. Chemical analyses: Average values in epm for group A (6 wells), group B (4 wells), and group C (3 wells) from Winnipeg area.

solving carbonates. Therefore the carbonate content usually remains rather steady, whereas the chlorides and to a minor extent the sulphates are dissolved continuously by the groundwater during its passage, very seldom reaching the saturation point.

The wells from the first group distinctly represent the recharge zone (1), and those from the second group represent zone (2). Although the $rSO_4/rHCO_3$ ratio is increasing with distance, rSO_4 remains smaller than $rHCO_3$; the pattern of zone (3) has not been reached yet.

For comparison, average values from a hydrochemical survey by CHARRON (1969) in the prairie south of Winnipeg, Manitoba, were computed and are plotted in Figure 5. The sampled wells are drilled in glacial deposits, mainly till, and are situated in an almost flat area with an inclination of a few feet per mile. The mid-points of the three different well groups A, B and C are approximately 7.5 miles (12 km) apart. Due to the small hydraulic gradient from A to C, a less humid climate and low permeability, the complete sequence from zone (1) to (3) was reached within a short distance.

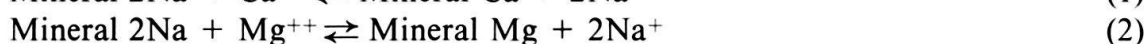
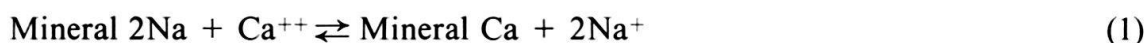
The rMg/rCa and rSO_4/rCl ratios have been proposed for a different type of zonation (SCHOELLER 1955, 1961, 1962). However, in the glacial deposits of our study area as well as in the example of Manitoba, there is no significant trend for these ratios between the sample groups.

Table 3. Base exchange, average ratio versus distance from basin divide.

Distance of well groups from basin divide	Group 1 (10 wells) 6 miles	Group 2 (9 wells) 6–21 miles
rNa/rMg	2.57	2.96
rNa/rCa	1.22	1.49
b.e.i. $(Na^+, K^+) = r \frac{Cl - (Na + K)}{Cl}$	-6.69	-0.76
b.e.i. $(Ca^{2+}, Mg^{2+}) = r \frac{Cl - (Na + K)}{SO_4 + HCO_3 + NO_3}$	-0.43	+0.53
c.r. $= r \frac{Na + K}{Ca + Mg}$	0.85	1.05
a.r. $= r \frac{Cl}{HCO_3 + SO_4}$	0.21	1.09
c.r./a.r.	4.05	0.96

5. Base exchange

Groundwater has the ability to exchange cations which are held by minerals either by the rather weak physical or Van der Waals adsorption, or by the strong valency bond. With regard to the quaternary deposits of the area under study, the exchange takes place mainly at the surface of the argillaceous minerals. The following principal exchanges between the alkalines and earth alkalines occur:



The Na/Ca and Na/Mg ratios change, therefore, with the travel time of the groundwater and might indicate to some extent which exchanges occur. From Figure 6 and Table 3, it can be seen that Na increases in relation to Ca and Mg , which would indicate a base exchange as described in equations (1) and (2) to the right. However,

the higher solubility of the alkaline chlorides, compared to the earth alkaline compounds, might have a similar cause and change the cation relations. Therefore, in order to determine which base exchanges occur, we have to eliminate the dissolution effects. The content of K is always very small in comparison to Na, and is difficult to exchange because it is bound strongly to illite; nevertheless, it was included in the computations below. The following two assumptions can be made, that is, a) rCl and $r(Na + K)$ are equal in the original water entering the saturated zone and b) all alkalines obtained through the dissolution process were bound to Cl and the earth alkalines to the other anions. With these assumptions it would be possible to determine from one sample if any base exchanges occurred and which ones, by comparing:

$$rCl - r(Na + K). \quad (3)$$

These assumptions might be invalid in most cases, but when different samples of the same groundwater stream in a rather uniform geological area are compared, it is possible to tell which base exchanges occurred. The term (3) is then divided by rCl to obtain a relative value and to make a comparison between different samples possible:

$$\text{b.e.i. (Na}^+, \text{K}^+) = r \frac{Cl - (Na + K)}{Cl}. \quad (4)$$

If the alkaline base exchange index (b.e.i. (Na⁺, K⁺)) tends to become positive moving downstream, Na⁺ and K⁺ of the water are exchanged with Mg and Ca of the minerals. If it is negative, the opposite interaction takes place, but in this case, the term, $r(SO_4 + HCO_3 + NO_3)$ may be introduced as the denominator (SCHOELLER 1962) as an indication of the amount of earth alkaline obtained through dissolution:

Both base exchange indices are distinctly negative in the vicinity of the basin divide (Table 3 and Fig. 4) and tend to become positive with increasing distance, indicating

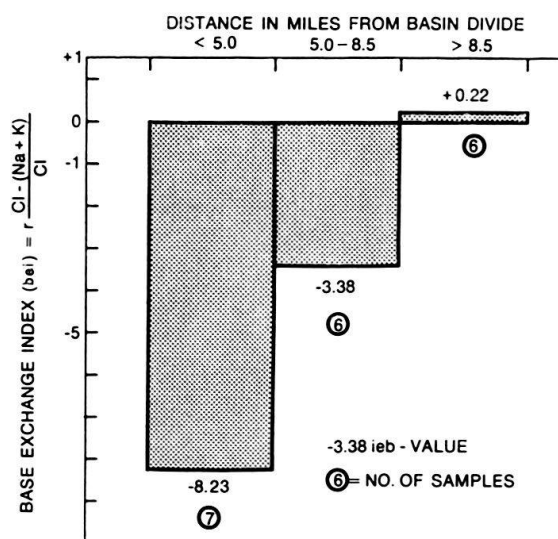


Fig. 6. Average values of base exchange indices versus distance from basin divide.

$$\text{b.e.i. (Ca}^{++}, \text{Mg}^{++}) = r \frac{\text{Cl} - (\text{Na} + \text{K})}{\text{SO}_4 + \text{HCO}_3 + \text{NO}_3} \quad (5)$$

that the exchange mineral $(\text{Ca} + \text{Mg}) + 2(\text{Na}^+ + \text{K}^+) \rightarrow (\text{Ca}^{++} + \text{Mg}^{++}) + \text{mineral } 2(\text{Na} + \text{K})$ becomes predominant. Figure 6 shows the clear relationship to the length of the groundwater trajectory. The same trend can be observed by comparing $r\text{Na}$ and $r\text{Cl}$ in the example south of Winnipeg (Fig. 5). Similar observations were made by CHARRON (1967, 1969) in other areas of Manitoba consisting of glacial deposits.

Another way to reveal the base exchange processes between different samples is by comparing the anion (a. r.) and cation (c. r.) ratios:

$$\text{a. r.} = r \frac{\text{Cl}}{\text{HCO}_3 + \text{SO}_4} \quad (6)$$

a. r. is a measure of the alkalines and earth alkalines originating from the dissolution process. Since any possible sulphate reduction is neglected, the denominator represents the minimum amount of dissolved earth alkalines and gives a maximum value for a. r.

By comparing a. r. with the cation ratio

$$\text{c. r.} = r \frac{\text{Na} + \text{K}}{\text{Ca} + \text{Mg}} \quad (7)$$

a measure for the magnitude of the base exchanges is obtained (Table 3). The data presented in Table 3 show an increase in a. r. in downstream direction. Consequently it may be supposed that more Na- and K-ions are liberated by dissolution than Ca and Mg. As, however, a corresponding increase in c. r. is not observed (indicated by the fall in c. r./a. r. ratio), base exchange processes have been active, through which Na-ions were fixed and Ca- and Mg-ions liberated.

6. Saturation of CaSO_4 and CaCO_3

Definitions:

$$rC = \frac{\text{equivalents per million (e.p.m. or milliequivalents per litre}^2) \text{ of C}}{\text{weight in milligrams} \times \text{valence}} \times \text{formula weight}$$

$$[C] = \text{concentration of C in mol/litre} = \frac{\text{weight in grams}}{\text{formula weight}}$$

$$rC = [C] Z_c 10^3$$

$$\langle C \rangle = \text{activity, applied instead of } [C]$$

$$\langle C \rangle = \gamma_c [C]$$

$$\log \gamma = -0.505 Z^2 \sqrt{\mu} \quad (3)$$

$$\mu = \text{ionic strength} = \frac{1}{2} \sum m_n Z_n^2$$

$$\text{or } \mu = \frac{1}{2} ([C_1] Z_1^2 + [C_2] Z_2^2 + \dots + [C_n] Z_n^2)$$

$$\text{or } \mu = 0.5 \cdot 10^{-3} (rC_1 Z_1 + rC_2 Z_2 + \dots + rC_n Z_n)$$

$$Z = \text{valence, } [C] = m = \text{molality, } \gamma = \text{activity coefficient}$$

²⁾ Since the density of ordinary groundwater is very close to 1, it was neglected.

³⁾ May be computed also after the Debye-Hückel expression (GARRELS and CHRIST 1965) for more concentrated solutions, taking into account the ionic radii.

Table 4. Solubility – and ion – product and saturation index versus distance from basin divide.

Distance of well groups from basin divide	Group 1 (10 wells) 6 miles	Group 2 (9 wells) 6–21 miles
μ	$6.78 \cdot 10^{-3}$	$19.08 \cdot 10^{-3}$
$S_{CaSO_4} = \sqrt{(rCa)(rSO_4)}$	0.37	1.75
$\mu_{S_0} = 0.062 + (\mu - rCaSO_4 \cdot 10^{-3})$	$66.78 \cdot 10^{-3}$	$75.49 \cdot 10^{-3}$
S'_0	31.8	33.4
$S_0 = S'_0 + S'_0 \cdot \alpha / 31$ ($\theta = 9^\circ C$)	30.2	31.7
$S_{CaCO_3} = \sqrt{(rCa)(rHCO_3 + rCO_3)}$	2.7	4.7
pH measured	7.76	7.63
pH eq.	7.37	6.88
$pH_s = pH \text{ eq.} + .1 \text{ pH}$	7.71	7.43
s.i. = pH – pH _s (after Schoeller)	+0.05	+0.20
s.i. = pH – pH _s (after Langelier)	+0.05	+0.40
$k'_r = \sqrt[3]{(rHCO_3)^2 (rCa)}$	3.05	4.6

The relation between the ion product $S = \sqrt{(rA) \cdot (rB)}$ used in the SCHOELLER semi-logarithmic graph method and the corresponding common term $K = [A] \cdot [B]$ is:

$$S = 10^3 \sqrt{Z_A \cdot Z_B \cdot K}$$

Computations:

The ion product of $CaSO_4$ is:

$$S_{CaSO_4} = \sqrt{(rCa)(rSO_4)}$$

$$\text{or } \log S_{CaSO_4} = \frac{1}{2} \log (rCa)(rSO_4)$$

which is solved graphically using the semi-logarithmic plot (Fig. 4). S_{CaSO_4} is halfway along the straight line joining the points rSO_4 and rCa . To see how far the water is saturated, the solubility product for $CaSO_4$, S_0 , which depend on μ and the temperature θ , is computed. First the ionic strength μ_{S_0} for the water sample is calculated under assumed $CaSO_4$ saturation conditions:

$$\mu_{S_0} = 0.062 + (\mu - rCaSO_4 \cdot 10^{-3})$$

$$0.062 = \mu \text{ for } S_0 \text{ in pure water at } 20^\circ C$$

and the uncorrected solubility product S'_0 is computed from curve a) in Figure 7. The temperature correction factor α is taken from curve b). Since, in turn, the total temperature correction depends on the value of S'_0 , the actual saturation point, S_0 , is determined from the formula

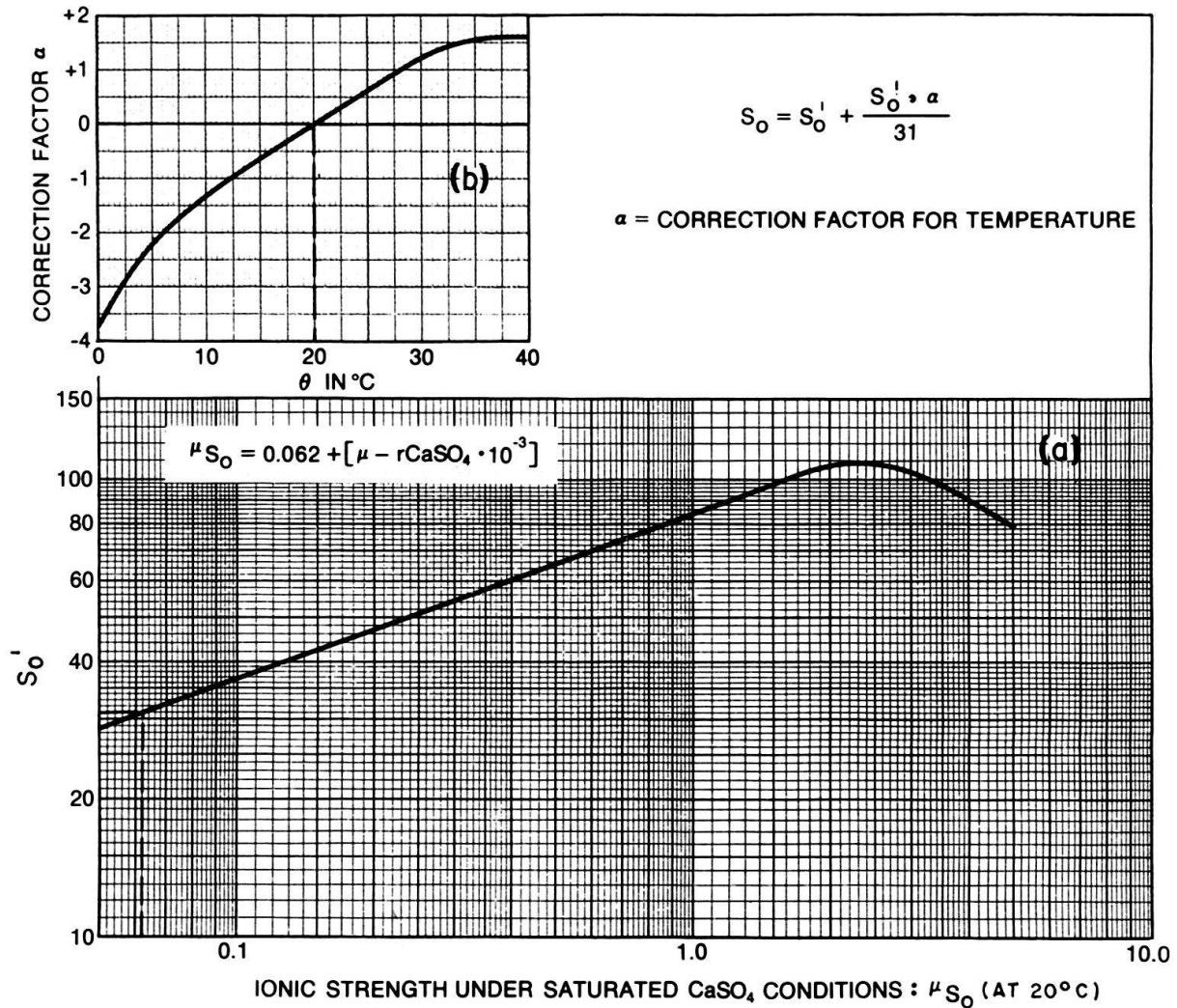


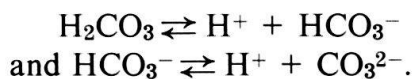
Fig. 7. Computation of the saturation point S_0 of CaSO_4 .

$$S_0 = S'_0 + \frac{S'_0 \cdot \alpha}{31}$$

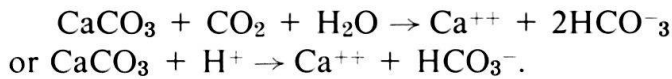
$$S_0 = 31 \text{ e.p.m. in pure water at } 20^\circ\text{C.}$$

Moving toward the discharge region of our study area the ionic strength μ and especially S_{CaSO_4} grow rapidly (Table 4). The dissolution of sulphates increases approximately twice as much as the total mineralization or the ionic strength. The saturation point S_0 is, however, far from being reached (Fig. 4).

The pH eq. is the pH of the water when saturated with CaCO_3 . It corresponds to the CO_2 of equilibrium which regulates the equilibrium with the dissolved CaCO_3 . If the actual pH is less than the pH eq., it means that free H_2CO_3 still exists which isn't needed to keep the CaCO_3 in solution:



The water is in this case unsaturated in CaCO_3 and has an aggressive tendency, especially toward carbonates:



The pH eq. may be computed by different methods e.g. according to SCHOELLER (1962):

$$S_{\text{CaCO}_3}^2 = 4K'_c \cdot (< \text{H}^+ > \text{eq.} / 2K'_2 + 1)$$

where the equilibrium constants are at 25°C:

$$K'_c = [\text{CO}_3^{2-}] [\text{Ca}^{2+}] = 4.78 \cdot 10^{-9} - 4\sqrt{\mu}$$

$$K'_2 = [\text{H}^+] [\text{CO}_3^{2-}] / [\text{HCO}_3] = 5.61 \cdot 10^{-11} - 0.382\sqrt{\mu}$$

$$(\text{p}K'_c = 8.32 - 4\sqrt{\mu}, \text{p}K'_2 = 10.25 - 0.382\sqrt{\mu}).$$

The ion product of CaCO_3 is:

$$S_{\text{CaCO}_3} = \sqrt{(r\text{Ca}) (r\text{HCO}_3 + r\text{CO}_3)}$$

$$\text{or } \log S_{\text{CaCO}_3} = \frac{1}{2} \log (r\text{Ca}) (r\text{HCO}_3 + r\text{CO}_3).$$

S_{CaCO_3} is obtained in the same way as S_{CaSO_4} , it is halfway along the straight line joining the points $r\text{HCO}_3$ and $r\text{Ca}$ on the semi-logarithmic plot (Fig.4). For the sake of simplicity the pH eq. is computed directly from Fig.8; after the necessary adjustments have been made for θ and μ , the corrected pH of equilibrium pH_s is computed.

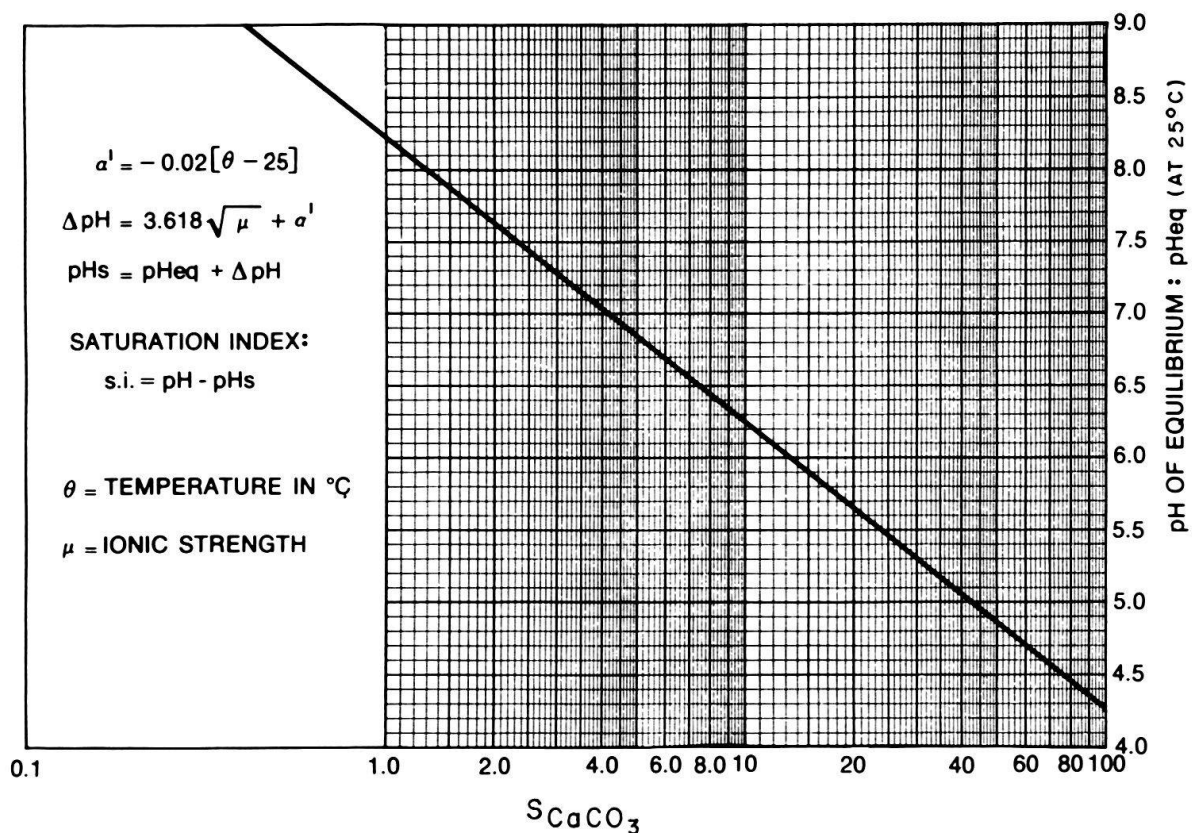


Fig. 8. Computation of pH of equilibrium and saturation index.

The saturation index, s. i., is negative if the water is unsaturated in CaCO_3 and positive if it is supersaturated. The index may also be calculated after the method of LANGELIER (1946). The saturation indices in Table 4 show that the water in the first group is nearly saturated, and in the second group supersaturated, indicating the expected groundwater-flow direction despite the influence of μ (see below).

The ion product of $\text{Ca}(\text{HCO}_3)_2$, kr' is computed again in the same manner as

S_{CaSO_4} :

$$kr' = \sqrt[3]{(r\text{HCO}_3)^2 \cdot (r\text{Ca})}$$

$$\text{or } \log kr' = 1/3 \log (r\text{HCO}_3)^2 \cdot (r\text{Ca}).$$

kr' is at 1/3 the distance from $r\text{HCO}_3$ on the straight line joining $r\text{Ca}$ and $r\text{HCO}_3$ (Fig. 4). Since the saturation point of CaCO_3 increases with the ionic strength (valid for $\mu < 1$) the groundwater as it moves downstream is able to dissolve more CaCO_3 without becoming oversaturated (Fig. 9). In this study, the well group more than 6 miles from the groundwater divide shows an increase in kr' of approximately 50% compared with group 1, but only a slight supersaturation (Table 4).

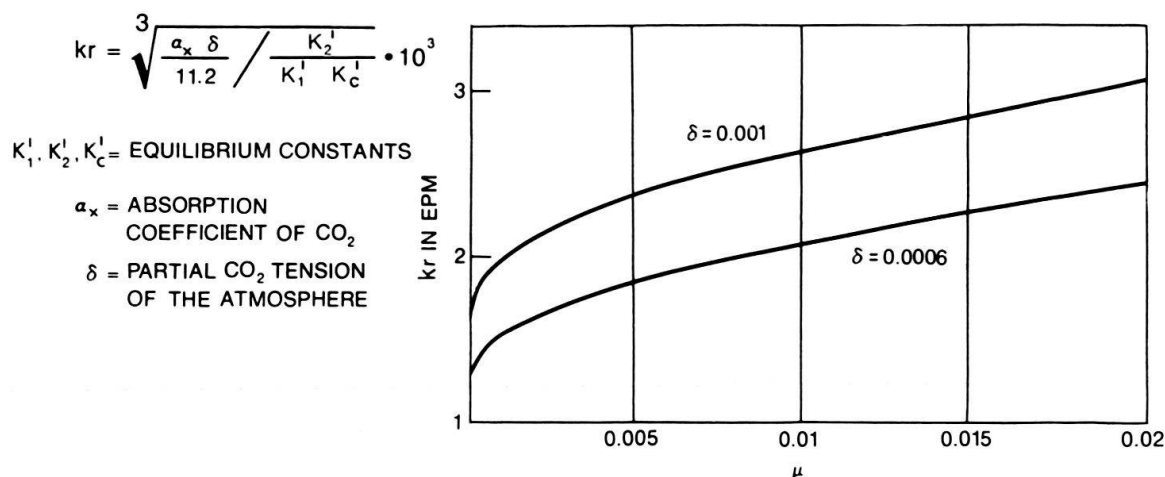


Fig. 9. Saturation point of CaCO_3 , kr as a function of the ionic strength μ (SCHOELLER 1962).

GENERAL CONCLUSIONS

All four hydrogeochemical criteria used in this study, in particular the concentration, zonation and base exchange, point to a general recharge area situated in the region of the basin divide between Lake Simcoe and Lake Ontario, and consequently to a north- and south-bound groundwater-flow. The result corresponds with previous piezometric and numerical analyses.

The author believes that the described hydrochemical method can be applied with success either independently or as an auxiliary means of regional groundwater-flow interpretations in deep glacial deposits.

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