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## **An Overview of Saturation State of Groundwater with Respect to Some Common Minerals in South Central Ontario**

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### **Abstract**

This study examines the saturation state of the groundwater within the South Central Ontario. An Excel Spread sheet methodology has been employed to calculate saturation states with respect to calcite, dolomite, gypsum and halite. Having revealed the different factors involved, the methodology was tested on some selected samples within laboratory error +/- 2%. When the results were compared with Langelier index (LI) and with the PhreeqC codes, the methodology was found to be consistently accurate for fixed electrical charges (not requiring Eh data), and with low to moderate ionic strengths. It can be understood from this study that, when saturation indices are extracted from large database and plotted on maps, they can be very useful in quickly observing spatial variability of saturation states that could be related to groundwater flow systems, including chemistry of formations (aquifers) and their variability with depth of wells or recharge/discharge conditions.

**Key words:** Solubility index; Langelier Index; activity coefficient; open system; closed system.

### **1. Introduction**

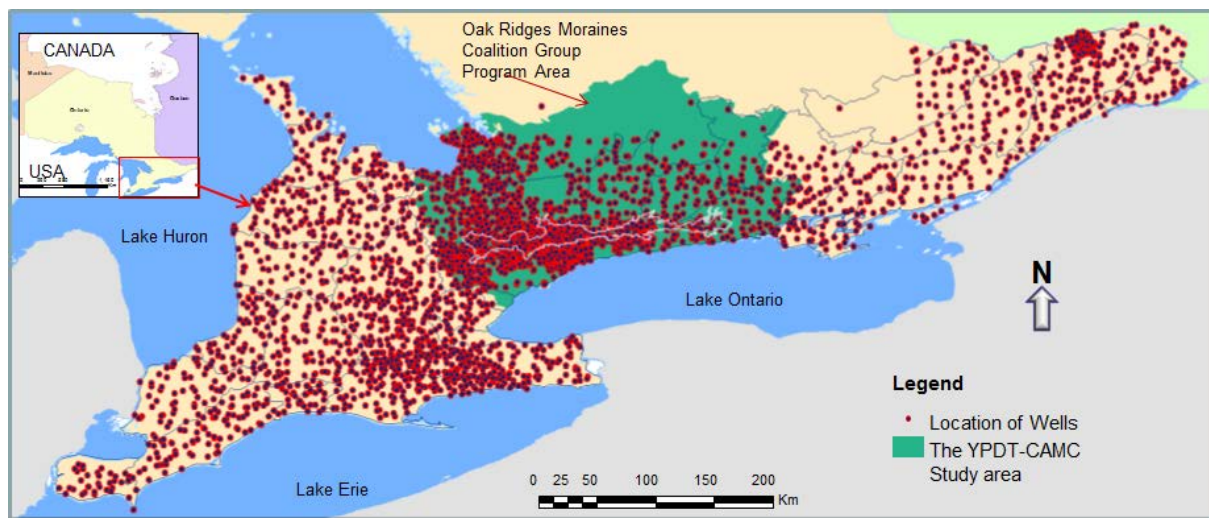
The purpose of this study is to augment the ongoing groundwater quality studies with an aspect of saturation states and integrating the results thus obtained with other detailed interpretations, in the Oak Ridges Moraine Groundwater Program (ORMGP) study area, (the greenish shaded area (**Figure 1**)).

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Data for this study has been acquired from the following different sources by the ORMGP: 1) the ORMGP; 2) the Ontario Geological Survey (OGS); 3) the Ontario Ministry of the Environment and Climate Change (MOECC) Provincial Groundwater Monitoring Network (PGMN); and 4) the MOECC Drinking Water Surveillance Program (DWSP). Amongst the 2888 well data information for the South Central Ontario that is being managed by the ORMGP, only 468 data points within  $\pm 2\%$  and with available Langelier Index (LI) and pH were used for the methodology, and 1714 data points within  $\pm 5\%$  were used for the application.

Groundwater quality changes occur due to natural processes through ion exchange and sorption, dissolution and precipitation of soluble minerals, acid-base reactions, oxidation-reduction reactions, evapotranspiration and weathering of minerals. During this process, certain ions are added or removed from the groundwater.



**Figure 1:** Location of the YPDT- CAMC study area

The saturation index (SI) for a mineral can be defined as the ratio of the activity product of the relevant ions in solution (in this case the major ions) to the respective thermodynamic reaction constants [1],[2],[3],[4], etc.. The solubility of minerals and the property of the water that comes into contact with the solid phases mostly depend upon temperature, pressure, pH, Eh and ionic strength. The total dissolved solids, salinity, chlorinity, etc., all reflect the overall concentration of solutes in groundwater at a given time and they are related to the saturation states of the respective water samples.

Some geochemical modeling tools, such as WATEQF, SOLMNEQ, PHREEQC are often used to calculate saturation state of minerals in water and, from the results obtained, it can be examined if a water sample has the potential to dissolve or precipitate with respect to the minerals considered. For example, the element barium can occur in barite mineral and the element fluorine can occur in fluorite minerals, etc. The release of such elements from the respective parent material and their concentrations in the groundwater system can be related to the equilibrium or dis-equilibrium situations that may have existed at the time of sampling. Hence, the output from the geochemical modeling tools can be used to speculate on the environmental significance of the observed species concentrations.

In this study, excel Spreadsheet has been used to calculate saturation state of the most common minerals (calcite, dolomite, gypsum and halite) from the groundwater of the monitored wells in Southern Central Ontario [10]. The output from the Excel Spreadsheet calculations has been used for a preliminary regional understanding of the saturation states of the groundwater with respect to calcite, dolomite, gypsum and halite, in the South Central Ontario.

The findings in this study do not represent any particular time or season, since average values were used representing samples collected during various times. The explanations provided are for a regional understanding, aimed at applying the methodology for future more detailed investigations.

## 2. Methodology

A simple methodology to calculating saturation indices is hereby described and its application to the groundwater in the South Central Ontario briefly discussed.

### 2.1 A step by step procedure

- Convert concentrations (from the data) to concentrations in moles/Litre (molality).
- Calculate ionic strength of the individual samples.
- Calculate the activity coefficient from the Debye Hückel (1923) equation.
- Calculate the activity of the solute species from the activity coefficients.
- Find the dissociation constants and the equilibrium constants ( $K_{eq}$ ).
- Calculate the ionic activity product  $K_{iap}$

If  $K_{iap}$  is less than  $K_{eq}$ , then the water is under-saturated

If  $K_{iap}$  is equal to  $K_{eq}$ , then the water is in equilibrium

If  $K_{iap}$  is greater than  $K_{eq}$ , then the water is over-saturated

- Based on the above, determine the relative degree of saturation (results can be plotted on maps).

### 2.1 Necessary equations to be used in the Excel Spread sheet

- **Molality**

$$molality = \frac{meq / L}{valence} \bullet (10^{-3}) \dots\dots\dots(1)$$

- **Ionic strength**

$$I = 0.5 * \sum_{i=1}^{i=n} m_i Z_i^2 \dots\dots\dots(2)$$

• activities for the solute species involved

$$a_i = m_i \hat{a} \dots\dots\dots(3)$$

• activity coefficient and the Debye Hückel (1923) expression

$$\text{Log } \hat{a} = \frac{-AZ_i^2\sqrt{I}}{1+a_0B\sqrt{I}} \dots\dots\dots(4)$$

- For equation 2, *I* is the ionic strength, *m<sub>i</sub>* are the molalities of *n* species, and *Z<sub>i</sub>* are the respective valences;
- for equation 3, (*a<sub>i</sub>*) is the activities for the solute species involved; *m<sub>i</sub>* is the molality and  $\hat{a}$  is the activity coefficient;
- for equation 4, *a<sub>0</sub>* is ionic radius, *A* and *B* are constants that depend on temperature and pressure conditions and *I* is ionic strength.

The relevant constants (*A* & *B*) that can be extracted from various sources [4], [5], [6] etc. are provided (**Table 1**). Since it is known that most of the wells in Southern Ontario have temperatures ranging from 5 to 10<sup>0</sup>C, the averages of *A* and *B*, corresponding to a temperature of 7.5<sup>0</sup>C (*A* = 0.49405 and *B*= 0.32535 10<sup>-8</sup>) have been inserted in equation 4. All the corresponding ion size numbers (*a<sub>0</sub>*) have been inserted for the major ions, and the Debye Hückel equation (equation 4) solved for all the water samples.

**Table 1:** Parameters for the Debye Hückel equation at 1 atmosphere pressure [4]

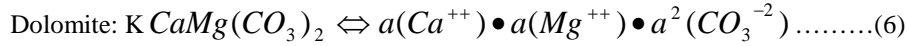
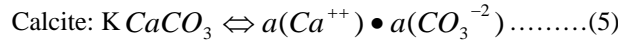
T	A	B	a <sub>0</sub>	Ion
0	0.4	0.324	6	Ca <sup>2+</sup>
5	0.4	0.324	8	Mg <sup>2+</sup>
1	0.4	0.325	3	K <sup>+</sup> , Cl <sup>-</sup> ,
1	0.5	0.326	4.0	SO <sub>4</sub> <sup>2-</sup>
2	0.5	0.327	4.25	Na <sup>+</sup> ,

The activity (*a*) of each species (calcium, magnesium, potassium, sodium, bicarbonate, sulphate and chloride)

can be obtained by multiplying the molality (from equation 1) by activity coefficient ( $\hat{a}$ ) as calculated from the Debye Hückel equation. At this stage, almost all the relevant parameters needed to calculate saturation state of any water sample with respect to calcite, dolomite, gypsum and halite are obtained. But, in order to calculate the ionic activity product *K<sub>iap</sub>*, the dissociation constants must be established for the minerals in question.

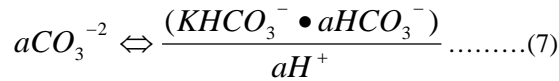
**2.2 Finding the necessary dissociation constants, ionic activity products and equilibrium constants**

The dissolution reactions can be written in terms of their respective dissociation constants as:

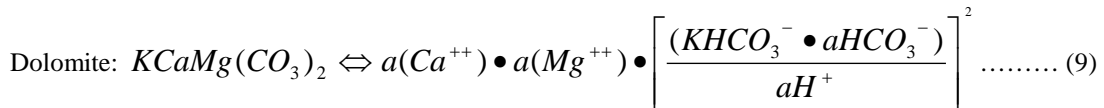
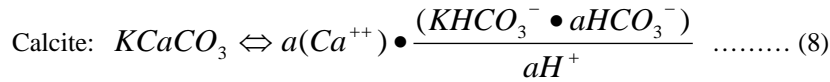


The left sides of the equations (5 & 6) represent the solubility of calcite and dolomite, respectively. The right sides of the equations are the products of the activities of their components (calcium and carbonate, in the case of calcite and, calcium, magnesium and carbonate in the case of dolomite).

The activity of carbonate is given below:



Hence by substituting the activity of  $CO_3^{-2}$  into equations (5 & 6), the following two important equations are obtained:



In order to calculate the  $K_{sp}$  from the equations (8 & 9), the following must be used:

a) The activity of hydrogen ion ( $aH^{+}$ ) is obtained from the analytical results using the following equation, provided in many text books, eg. [1,2,3,4], etc.:-

$$aH^{+} = 10^{-pH} \dots\dots\dots(10)$$

b) From laboratory determinations at 22<sup>0</sup>C and 1 bar atmospheric pressure, the following are the rest of the equilibrium constants needed for the calculation :

- o the equilibrium constant (solubility) for calcite is  $K CaCO_3^{-} = 0.415 \cdot 10^{-8}$  ;
- o the equilibrium constant (solubility) for dolomite is  $K CaMg(CO_3)_2 = 0.117 \cdot 10^{-16}$
- o the equilibrium constant (solubility) for bicarbonate is  $K HCO_3^{-} = 0.439 \cdot 10^{-10}$

In order to make accurate SI calculation, the equilibrium constants (K values) must be converted from 22°C to aquifer water temperatures (about 7.5°C) using the following Van't Hoff's equation:

$$\frac{d \ln K}{dt} = \frac{\Delta H}{RT^2} \dots\dots\dots(11)$$

This equation relates the change in the K values to change in temperature, where  $\Delta H$  is the heat of reaction. K increases with increasing temperature. In order to correct equilibrium constant for temperature, the following equation derived from Van't Hoff's equation can be used [5]:

$$\text{Log}_{10} \frac{K_2}{K_1} = \frac{-\Delta H_R}{2.303R} \left( \frac{T_2 - T_1}{T_2 T_1} \right) \dots\dots\dots (12)$$

- Where  $K_2$  is the equilibrium constant at the desired temperature (average groundwater temperature of all wells being 7.5°C the new temperature  $T_2$  in degrees Kelvin = 273+7.5=280.5);
- $K_1$  = equilibrium constant at 22°C ( $T_1$  in degrees Kelvin = 273+22=295),  $R$  = gas constant = 1.987 calories/degree/mole, and  $\Delta H_R$  = change in enthalpy of the reaction (calories/mole).

The  $\Delta H_R$  value (kcal/mol) for  $\text{CaCO}_3^-$  = -288.57,  $\Delta H_R$  value (kcal/mol) for  $\text{CaMg}(\text{CO}_3)_2$  = -555.56, and the  $\Delta H_R$  value (kcal/mol) for  $\text{HCO}_3^-$  = -165.39 [4, pp. 351-355]. Substituting these values in the Van't Hoff's equation:

$$\text{Log}_{10} \frac{K_2}{0.415 \cdot 10^{-8}} = \frac{-(-288.57)}{2.303 \cdot 1.987} \left( \frac{280.5 - 295}{280.5 \cdot 295} \right) \dots\dots\dots (13)$$

$$\text{Log}_{10} \frac{K_2}{0.415 \cdot 10^{-8}} = -0.04363, \text{ whose antilog} = 0.904423225; \dots\dots\dots (14)$$

$$\text{Hence } K_2 \text{ for calcite} = 3.75336 \times 10^{-9}$$

$$K_2 \text{ for dolomite} = 9.64255 \times 10^{-18}$$

$$K_2 \text{ for bicarbonate} = 4.14438 \times 10^{-11}$$

### 2.3 Saturation State of the groundwater with respect to Calcite and Dolomite

At this stage, all the relevant parameters needed to calculate saturation state of the water sample with respect to calcite and dolomite are obtained. Having substituted all the activities and equilibrium constants for calcite dolomite and bicarbonate into the right parts of equations (8 & 9), the ionic activity products ( $K_{iap}$ ) of calcite and dolomite were calculated. The results were then compared with the respective equilibrium constants ( $k_{eq}$ ), from

which it was possible to know the degree of saturation (saturation index) of the groundwater with respect to calcite and dolomite.

Thus, the Saturation Index (SI) can be expressed in any of the following ways:-

$$\text{➤ } SI = \frac{K_{iap}}{K_{eq}} > 1 \rightarrow \textit{oversaturated}; SI = \frac{K_{iap}}{K_{eq}} < 1 \rightarrow \textit{undersaturated}$$

(this can also be expressed in

percentage by multiplying by 100). Or,

$$\text{➤ } SI = LOG \frac{K_{iap}}{K_{eq}} > 0 \rightarrow \textit{oversaturated}; SI = Log \frac{K_{iap}}{K_{eq}} < 0 \rightarrow \textit{undersaturated}$$

#### 2.4 Saturation State of the groundwater with respect to gypsum

Since the activity of the major ions has already been calculated, it is worth looking into the saturation state of the groundwater with respect to gypsum and halite as well.

The only extra data needed to calculate gypsum and halite saturations are their respective equilibrium constants. The saturation state of the groundwater with respect to gypsum has been calculated based on the following equations:

$$K_{eq} \Leftrightarrow \frac{aCa^{+2} \cdot aSO_4^{-2} \cdot a^2H_2O}{aCaSO_4^{-2} \cdot 2H_2O} \dots\dots\dots (15)$$

When activity of  $H_2O$  is 1, and considering pure solid of  $CaSO_4 \cdot 2H_2O$ , the ion activity product for gypsum becomes activity of calcium times activity of sulphate [4]. The solubility product of gypsum at 25°C, is  $10^{-4.61}$ , or 0.00002455

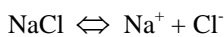
Substituting the known values in Van't Hoff's equation, the new solubility product at 7.5°C = 0.0000200785

$$\text{Therefore, } SI_{(gypsum)} = LOG \frac{aCa^{+2} \cdot aSO_4^{-2}}{0.0000200785} \dots\dots\dots (16)$$

The saturation state of the groundwater with respect to gypsum has been calculated based on the above equation.

#### 2.5 Saturation State of the groundwater with respect to halite

Although it is known that halite could hardly become oversaturated, the “saturation state” of the groundwater with respect to halite has been calculated based on the following equations:





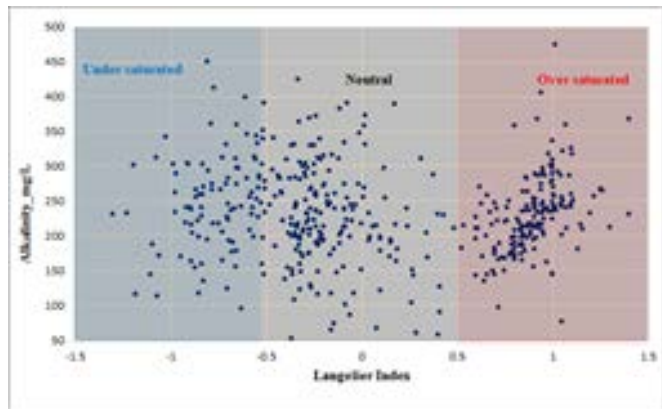
The solubility product of halite at 25<sup>0</sup>C is 10<sup>-1.52</sup>, or 0.0301995172040201. Substituting known values in Van't Hoff's equation, the new solubility product at 7.5<sup>0</sup>C = 0.031459676

$$\text{Hence, SI}_{(\text{Halite})} = \text{LOG} \frac{aNa^{+} \bullet aCl^{-}}{0.031459676} \dots\dots\dots (17)$$

The saturation state of the groundwater with respect to halite has been calculated based on the above equation.

**3. Discussion of results**

Before using all the calculated results from the Excel Spreadsheet method, an idea of the saturation states were envisaged from existing database. Most analytical results usually provide the Langelier Index (LI), which indicates the degree of saturation of water with respect to calcium carbonate (calcite). The variables normally used in the calculation of LI are alkalinity, hardness, total dissolved solids, the actual pH, and the temperature of the water. In order to have an idea of the saturation state of the groundwater with respect to calcite, the average LI values were compared against the respective average alkalinity values (**Fig. 2**).



**Figure 2:** The Average Langelier Index (LI) plotted against average alkalinity

The different coloured plots in figure 2 indicate extreme cases of under saturation, neutral zone and over saturation. In general, if LI is greater than zero, then the respective water sample is over-saturated with respect to calcium carbonate, and it may have tendency to scaling.

If the LI is less than zero, then the respective water sample is under-saturated and it may have a tendency to dissolve calcium carbonate. However, alkalinity values and the corresponding LI values could significantly change over time, which means that if LI is close to zero (between - 0.5 and + 0.5) the respective water sample would be close to being neutral, in which case the water sample will have no tendency to scaling or to dissolve calcium carbonate.

The various factors that account for LI, such as alkalinity, pH and TDS change in time. Therefore, what has been observed on figure 2 may not necessarily be true for all wells and for all the time. However the LI results indicated in figure 2 can be used for comparing the results obtained from Excel Spreadsheet method.

The reasonableness of the solubility index (SI) calculated from Excel Spreadsheet methodology was verified, first by checking if the interrelated parameters make sense, and then verifying the SI values by the PHREEQC



codes.

In accordance with the step by step procedure discussed earlier, it would be better to check the calculated results for ionic strengths first. In most cases, total dissolved solids, salinity, chlorinity and ionic strength reflect the overall concentration of solutes in groundwater at a given time, and are therefore directly related to one another. This was confirmed by plotting the average TDS values of all wells against their respective ionic strengths (IS) that was calculated from the Excel Spread sheet (Fig. 3). As shown on figure 3, a strong correlation ( $R^2 = 0.89$ ) prevailed between IS and TDS, indicating the calculated IS to be accurate.

One way of checking if the results are reasonable is also to compare ionic strengths with activity coefficients ( $\hat{a}$ ), not activity (a) of the ions within the respective samples considered; these ( $\hat{a}$ ) values are within the IS sheet [10]. Plots of the calculated activity coefficients of both calcium and chloride showed very good correlation ( $R^2=0.99$ ), confirming that activity coefficient ( $\hat{a}$ )

decreases as IS increases (Fig. 4). As ionic strength increases, the activities calculated by different methods (Debye Hückel, extended Debye Hückel, Davies and Pitzer equations) differ from one another [2].

It can then be concluded from this that the calculation of activity coefficient from the Debye Hückel equation becomes more reliable only for fresh to slightly brackish groundwater (ie. those with ionic strength less than 0.1).

Thus, having calculated all SI values for calcium, dolomite, gypsum and halite, the accuracy of the method employed was again verified by comparing the LI data provided by the different laboratories with the corresponding calculated saturation states (SI) of calcite and dolomite expressed as  $\text{Log } K_{i\text{ap}}/K_{\text{eq}}$  (Fig. 5).

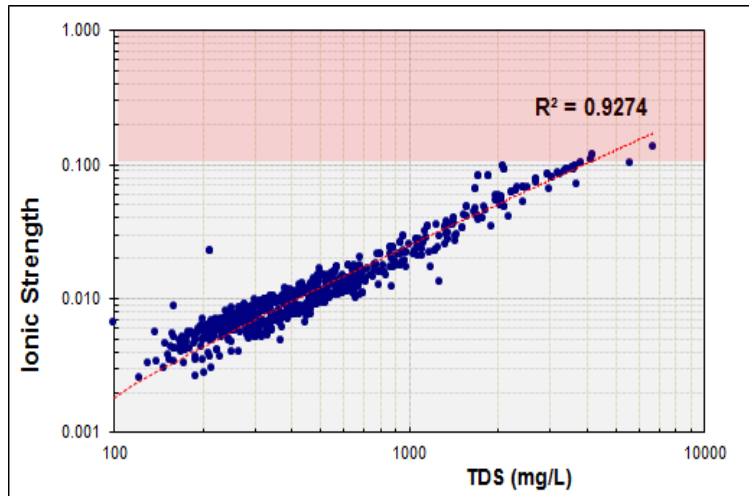


Figure 3: Relationship between TDS and the calculated ionic strength of the groundwater from all wells

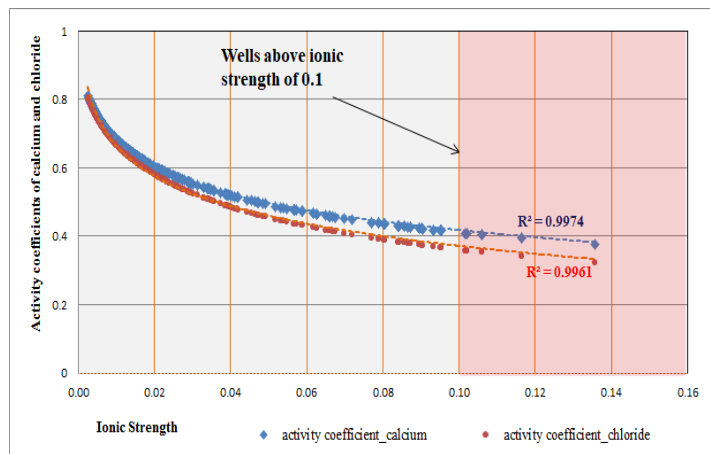
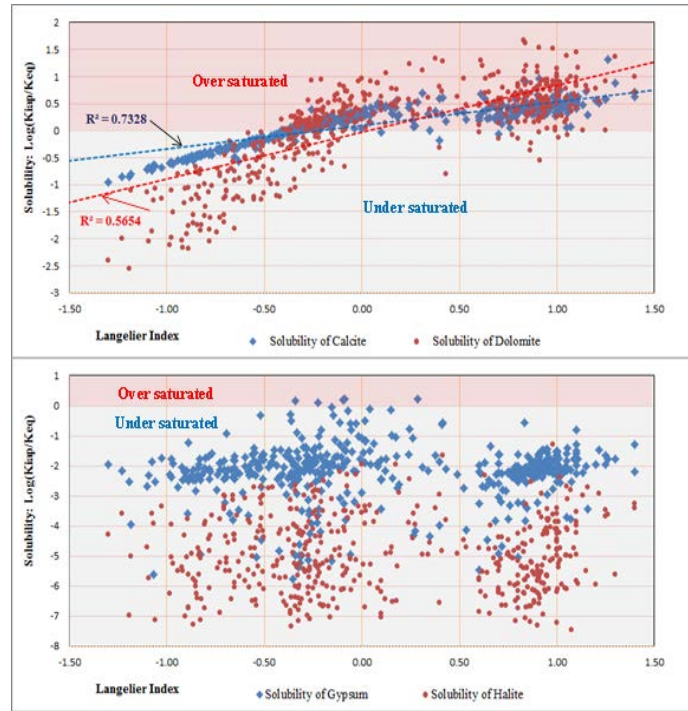


Figure 4: Relationship between the calculated activity coefficients and ionic strength

As shown in the figure, a very good relationship ( $R^2 = 73$ ) has been observed for calcium carbonate, and a less perfect relationship ( $R^2 = 0.56$ ) for dolomite. The wider range of dolomite saturations as LI increases may reflect the relatively complex nature of the aquifers in mineral compositions.

It worth noting the similarity of data populations between figure 2 and figure 5 (upper part), which confirms again the reliability of the Excel method employed. Both figure 2 and figure 5 indicate that slightly more of the water samples (above 50%) are under saturated with respect to both calcite and dolomite. For gypsum and halite, only few samples (out of the 468 samples, with 2% accuracy) were over saturated with respect to gypsum (**Fig. 5**, lower part).



**Figure 5:** Relationship of LI with the saturation state of the groundwater with respect to calcite and dolomite (upper figure), and gypsum and halite (Lower figure)

Again, in order to reaffirm the validity of the Excel Spreadsheet method, the PHREEQC code was executed using an option of only major ions. Slight differences were observed between the two methods.

This can be explained by the fact that equilibrium calculations for a particular species are influenced by the ionic concentrations of not only major ions, but also other species where the interaction taking place is between groundwater and multitude of minerals.

The PHREEQC code uses, not only the major ions, but also those other species. Regardless, the spreadsheet method can still be used for a general understanding of the groundwater saturation state with respect to these limited minerals (not affected by redox potential), and it can be helpful to quickly evaluate these minerals from a large database and to plot the results on GIS maps.

### 3.1 Saturation state of the groundwater of the different groundwater types

An understanding about the saturation state of the groundwater becomes even more evident when such understanding is augmented from a knowledge of water types (hydrochemical facies). Water type maps are usually used to indicate the groundwater facies related to specific aquifer type (natural) and/or any other anthropogenic effect [11].

The saturation states within each water types has been examined from the water types of the South Central Ontario, by plotting graphs and finding relations. A summary of the relations between LI and the calculated SI with respect to calcite, dolomite, gypsum and halite for the four water types is presented on a Table (**Table 1**).

As may be expected, a very good relation ( $R^2$  ranging from 0.63 to 0.87) was observed between the LI and SI for calcium in all the water types, while a slightly weaker relation was observed for dolomite in all the water types. For gypsum and halite, no relation was observed between the LI and SI of all the water types. This does not mean that the chemical composition of most of the aquifers in the studied is devoid of gypsum and halite. In fact it is known from water

**Table 1:** The relationship between the Langelier index (LI) and the groundwater saturation states (SI) with respect to calcite, dolomite, gypsum and halite for the different water types

Water Type	Coefficients of regression between Langelier Index and the Saturation States for the corresponding minerals below			
	Calcite	Dolomite	Gypsum	Halite
Type A - Ca+Mg - (HCO <sub>3</sub> )	0.75	0.58	0.001	0.009
Type B - Ca+Mg - SO <sub>4</sub> -Cl	0.75	0.48	0.07 (-)	0.01
Type C - Na+K - SO <sub>4</sub> -Cl	0.63	0.56	0	0.18
Type D - Na+K - HCO <sub>3</sub>	0.87	0.83	0.25 (-)	0.04 (-)

type studies [11], and other regional hydrogeochemistry studies of Southern Ontario [12], [13], etc. that a number of wells in Southern Ontario are rich in gypsum and halite. What Table 1 shows is that LI provided by laboratories cannot be used to assess the presence or absence of gypsum and halite, or their saturation states.

It is also worth considering regional flow system and changes in chemistry. According to Chebotarev's sequence [14], groundwater tends to evolve chemically toward the composition of sea water; bicarbonate and non-bicarbonate waters are segregated through time and distances travelled, as follows:



Only the South Central Ontario may not be enough to visualize Chebotarev's sequence in terms of regional flow and changes in chemistry.

However, assuming the central Oak Ridges area as recharge area, and the surrounding peripheries as discharge areas, the observed information (figure 5 and Table 1) could suggest that the carbonate (calcium and magnesium carbonates from calcite and dolomite) waters represent aquifer recharge areas, whereas the non-carbonate waters (sulphates and chlorides from gypsum and halite) represent discharge areas. This becomes evident with spatial analysis (see also next section).

### 3.2 Application of results

The chemical composition of the geologic units in Ontario is provided in many books and reports dealing with the geology of the studied area [15,16,17,18,19] etc.. In Ontario, the bedrock aquifer types are carbonate (Paleozoic) and non carbonates (Precambrian), as well as sediments derived from glacial deposition (Pleistocene) that are mostly composed of clay, silt, sand and gravel.

The Oak Ridges Moraine forms the most central parts of the studied area. Up to 300 metres of glacial sediment can be found in the South Central Ontario [16]. Based on the SI results thus obtained, this study attempts to investigate the reason why certain groundwater samples are under saturated and why others are over saturated within the South Central Ontario.

Prior study on the geology of the studied area has revealed eight formations that are of glacial sediment origin and one formation that is of undifferentiated bedrock origin (Table 2). Since groundwater in the different geologic formations exhibit different chemical characteristics, it is thought to be interesting to examine existing variations in the calculated SI groundwater samples within the nine formations. Although it is not intended to discuss this in detail, this paper will highlight some statistical and GIS mapping approach.

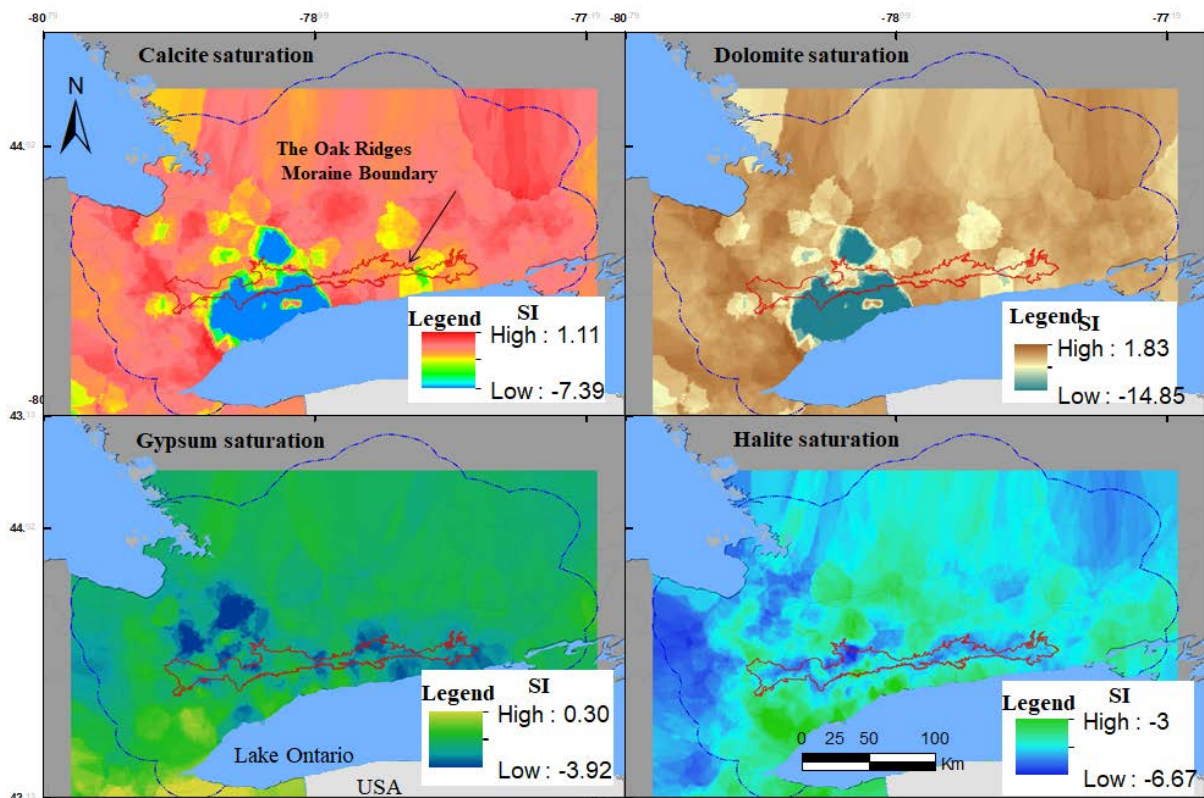
**Table 2:** Statistical summary of SI for groundwater per geologic formation

Formations	Formation Name	Criteria	Calcite	Dolomite	Gypsum	Halite	Remarks
f1	YPDT - Late Stage Glaciolacustrine-Glaciofluvial	SI>=0	25.00	24.00	0.00	0.00	37 samples, mostly oversaturated with respect to calcium and dolomite. . All samples undersaturated with respect to gypsum and halite Average SI show both calcite and dolomite are oversaturated Percentages and averages show moderate to high oversaturation of calcite & dolomite
		SI<0	12.00	13.00	37.00	37.00	
		Average	0.41	0.51	-2.11	-4.86	
		%	67.57	64.86	0.00	0.00	
f2	YPDT - Halton/Kettleby Till	SI>=0	34.00	34.00	2.00	0.00	59 samples, mostly oversaturated with respect to calcium and dolomite. . 62 samples, all except 2 samples, undersaturated with respect to gypsum and halite Average SI for dolomite indicate close to neutrality Percentages show close to neutrality and few gypsum (3%)
		SI<0	25.00	24.00	60.00	62.00	
		Average	0.10	0.09	-1.62	-4.49	
		%	57.63	57.63	3.39	0.00	
f3	YPDT - Mackinaw/Oak Ridges (MIS/ORAC)	SI>=0	83.00	79.00	0.00	0.00	121 samples, mostly oversaturated with respect to calcium and dolomite. . 123 samples, all undersaturated with respect to gypsum and halite Average SI for both calcite and dolomite show undersaturation Percentages show moderate oversaturation of calcite and dolomite
		SI<0	38.00	42.00	123.00	123.00	
		Average	-0.02	-0.26	-2.12	-5.41	
		%	68.60	65.29	0.00	0.00	
f4	YPDT - Channel - Silt/sand	SI>=0	4.00	4.00	0.00	0.00	8 samples, half oversaturated with respect to calcium and dolomite. . All undersaturated with respect to gypsum and halite Average SI show undersaturation Percentages showsaturation close to zero
		SI<0	4.00	4.00	8.00	8.00	
		Average	-0.64	-1.27	-2.33	-5.07	
		%	50	50	0	0	
f5	Newmarket (all) including Lower Sediment Lower Unit	SI>=0	149.00	134.00	0.00	0.00	208 samples, mostly oversaturated with respect to calcium and dolomite. . All samples (216,217), undersaturated with respect to gypsum and halite Average SI for both calcite and dolomite indicates moderate over saturation Percentages show high oversaturation of calcite and dolomite
		SI<0	59.00	72.00	216.00	217.00	
		Average	0.13	0.18	-1.27	-2.96	
		%	71.63	64.42	0.00	0.00	
f6	YPDT - Thorncliffe	SI>=0	49.00	43.00	0.00	0.00	85 samples, mostly oversaturated with respect to calcium and dolomite. . All samples (90), undersaturated with respect to gypsum and halite Average SI for both calcite and dolomite indicates under saturation Percentages show close to neutral saturation
		SI<0	36.00	42.00	90.00	90.00	
		Average	-0.23	-0.56	-2.49	-5.02	
		%	57.65	50.59	0.00	0.00	
f7	YPDT - Sunnybrook	SI>=0	2.00	1.00	0.00	0.00	9 samples, mostly under saturated with respect to calcium and dolomite. . All samples (10), undersaturated with respect to gypsum and halite Average SI for both calcite and dolomite indicates moderate under saturation Percentages show under saturation
		SI<0	7.00	8.00	10.00	10.00	
		Average	-0.17	-0.30	-2.98	-4.51	
		%	22.22	11.11	0.00	0.00	
f8	YPDT - Scarborough	SI>=0	24.00	24.00	0.00	0.00	42 samples, mostly oversaturated with respect to calcium and dolomite. . All samples (35,41), undersaturated with respect to gypsum and halite Average SI for both calcite and dolomite indicates under saturation Percentages show close to neutral saturation
		SI<0	18.00	18.00	35.00	41.00	
		Average	-0.08	-0.08	-3.17	-4.70	
		%	57.14	57.14	0.00	0.00	
f9	YPDT - Bedrock - Undifferentiated	SI>=0	91.00	84.00	2.00	0.00	137 samples, mostly oversaturated with respect to calcium and dolomite. . All samples (139,144), except 2 for gypsum are undersaturated Average SI for both calcite and dolomite indicates moderate over saturation Percentages show moderate to high over saturation of calcite & dolomite
		SI<0	46.00	53.00	139.00	144.00	
		Average	0.12	0.11	-2.14	-3.88	
		%	66.42	61.31	1.46	0.00	
f0	Not Identified	SI>=0	505.00	471.00	89.00	0.00	963 samples, mostly oversaturated with respect to calcium and dolomite. . 89 samples are super saturated with respect to gypsum Average SI for both calcite and dolomite indicates moderate slight undersaturation Percentages show close to neutral saturation
		SI<0	458.00	491.00	880.00	937.00	
		Average	-0.44	-0.89	-0.13	-0.28	
		%	52.44	48.91	9.24	0.00	

Since the methodology discussed is found to be fairly accurate, analytical results from 1714 wells (instead of 468) from the South Central Ontario, that are within +- 5% error, has been applied for this purpose. Accordingly, a statistical summary of the SI's calculated for water samples in wells from each formation are presented (Table 2). As indicated on the last column of Table 2, most samples within the different aquifers (geologic formations) showed significant variations between themselves. For example, the SI average and percentages of the uppermost aquifer (Formation 1: YPDT, Late stage Glaciolacustrine/Glaciofluvial) indicate moderate to high over saturation, as well the SI average and percentages of the lowermost aquifer (Formation 9: YPDT, bedrock undifferentiated) indicate moderate to high over saturation. The high oversaturation in the

bedrock aquifers could be due to high calcium and dolomite content of the bedrock aquifers, whether in an open (confined) or closed (confined) system. On the other hand, it is known that wells in Formation 1 are mostly unconfined, and are open to the atmosphere. In this situation, carbonic acid could form easily due to interaction between groundwater and atmospheric carbon dioxide, thus leaching any available carbonate in the aquifer.

As indicated on Table 2, only two formations (f2 & f9) showed over saturation with respect to gypsum. However, as also indicated on Table 2, 89 samples showed oversaturation of gypsum in the unidentified formations (f0, last row in Table 2). At this point it will be interesting to examine spatial variations of SI, since aquifer recharge/discharge conditions too, that vary spatially indicate variability in the flow system and if aquifers are confined or unconfined. Moreover, it is known from OMCG investigations that one formation in one area could differ in mineralogical composition from the same formation in another area [16]. Hence, in order to understand better which variables play most in which area, it would be necessary to see spatial variability of groundwater characteristics in each formation. However, this is beyond the scope of this paper. Instead, the spatial variations of SI calculated by the Excel Spread sheet are applied for the groundwater samples of all wells from all formations, including those that are not identified (**Fig. 6**).



**Figure 6:** Spatial presentation of the calculated saturation indices (Log (Kiap/Keq)) with respect to calcite, dolomite, gypsum and halite of the groundwater in South Central Ontario

As shown on figure 6, the general pattern in all the four maps indicates areas where SI values are relatively low

(representing under saturation), and areas where SI values are relatively high (representing over saturation). In general, the areas where SI values are relatively low are the recharge areas along the ridges of the Oak Ridges Moraines, and where SI values are relatively high are the discharge areas away from the ridge.

From the spatial maps alone (**Fig. 6**), it can be concluded that the under saturation of most formations may be due to the non-carbonate origin of these waters. However, direct recharge in unconfined aquifers, within the recharge areas (mostly along the Oak Ridges Moraines) could increase the SI from under saturation to neutrality or even to over saturation.

With the exception of the halite saturation map (lower right figure), indicating under saturation only, the other three maps (**Fig. 6**) indicate significant spatial coverage of some over saturation somewhere. It is suspected that most of these over saturated waters are within the unidentified formations (f0 in Table 2). Since most of these high SI values occurred away from the flanks of the Oak Ridges Moraines(**Fig. 6**), it is also suspected that most of these, especially those indicating oversaturation of gypsum, are from bedrock aquifers. This, in accordance with Chebotarev's sequence, could suggest the predominance of non carbonate waters away from recharge areas. However, taking into account the complexity in the geology of the area, such a simplistic approach may not be satisfactory, unless the situation for each geologic formation is considered.

#### **4. Conclusions**

The saturation state, or solubility index (SI) with respect to calcite, dolomite, gypsum and halite, of the groundwater within the South Central Ontario has been calculated using an Excel Spread sheet methodology discussed in this paper. This methodology has been verified, mostly by comparing the relations between the different components that account for the saturation states of groundwater. Results of the calculated SI were then statistically analyzed and spatially mapped, using a GIS platform. This study has tried to explain reasons for the differences in saturation indices in different areas, but due to the regional nature of this study, it has not been possible to distinguish which one of the factors plays a major role in creating those differences. However, it is believed that an ongoing study with an application of such simple and useful method to existing large database would reveal some important information, such as variations in SI's due to geologic formations, well depth, recharge/discharge conditions and groundwater flow. Few groundwater samples from unidentified formations happened to be oversaturated with respect to gypsum. All groundwater samples, even those with known high salt (NaCl) content, are under saturated with respect to halite, thus proving the conservative nature (not getting easily oversaturated) of sodium and chloride. A better analysis of calcite saturation has been possible by segregating water types into bicarbonate and non-bicarbonate waters. This can be especially helpful in order to relate groundwater flow systems in large basins, conferring to Chebotarev's sequence of regional changes in dominant anion species. In general, groundwater is less acidic than surface waters hence the ratio between the bicarbonate to calcium content in surface water will be greater than in groundwater. Therefore, by studying the spatial and chemical proximity of certain surface water samples to groundwater samples, it could be possible to verify if there is an interaction between the two. Atmospheric and land surface variables are prone to change in time. Therefore, by studying the saturation state of groundwater from analytical data collected at various times from monitoring programs, it could be possible to explore the consequences of carbon dioxide production and

the effects of global warming [20]. The variability of groundwater rise and decrease in ion concentration (decrease in ion activity product, increased or decreased saturation index over time) and vice-versa would be another very important factor that helps in understanding the interrelated aspects of climate change, land use, surface water and groundwater chemistry.

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