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Some Aspects of the Origin of the Naturally Occurring Sodium Chloride Waters in Eastern Ontario

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Abstract

This study examines the combined characteristics, as reflected by water types and similarity groupings, from major ion chemistry of groundwater samples collected by different agencies over a period of more than 60 years in the Southern Ontario. Based on the location of wells that have the same water types and similarity groups (particular characteristics within the sodium chloride waters), this study highlights a possible salinity impact upon the groundwater along the low lying areas of the St. Lawrence Platform, likely as a result of the deposition of sediments from the former Champlain Sea in this area.

Keywords: major ions; groundwater type; similarity groups; hydrochemical facies; Former Champlain Sea; Piper Diagram; recharge; discharge.

1. Introduction

This study provides an approach towards the characterization of the general hydro-chemical facies found in Southern Ontario **(Figure 1**).

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The main purpose of this study however, is to attain a general understanding of the uniqueness of groundwaters based on the combined water type and their similarity characteristics of the major ions, and to apply this uniqueness of waters in tracing the origin water quality impacts.

In particular, this study examines the effect of the former Champlain Sea on the groundwater of Eastern Ontario, based on the intrinsic variabilities that exist within the sodium chloride type waters.

Four data sets have been used in this study: i) the Oak Ridges Moraine Groundwater Program (ORMGP); ii) the Ontario Ministry of the Environment and Climate Change (MOECC) Provincial Groundwater Monitoring Network (PGMN); iii) the MOECC Drinking Water Surveillance Program (DWSP); and iv) the Ontario Geological Survey (OGS).

Out of the numerous chemical analyses (over 100) which the overall combined dataset consists, only the major ions (calcium, magnesium, sodium, potassium, bicarbonate, sulphate and chloride) in association with minor constituents (strontium, barium, boron, iron, manganese, zinc and aluminum) that were found to be important while studying groundwater quality in Ontario have been considered. The entire database consists of over 15,000 samples collected during various seasons over many years (1947 to 2015). The average values of the above mentioned constituents representing 4816 sample data points with co-ordinate locations are hereby analyzed. As shown on the greenish shaded area in Figure 1, more than half of these sample points have been managed by the Oak Ridges Moraines Coalition Group (**Figure 1**). It should also be noted that, out of the 4816 sample data points only 3853 fell within plus or minus 10% error. The discussion henceforth is based only on the average values from these 3853 sample locations.

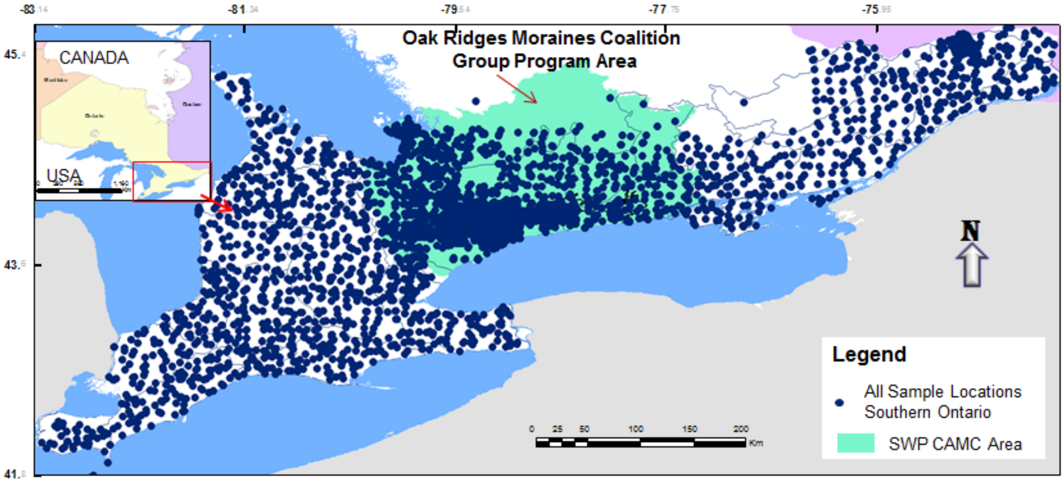


Figure 1: Location of the study area

The geochemical composition of groundwater continually evolves as water moves from recharge to discharge areas. According to Chebotarev's chemical sequence [1], groundwater in recharge areas is normally calcium or magnesium bicarbonate dominated. As it flows towards discharge areas, it dissolves more salts and evolves to become chloride or sulphate dominated. The total dissolved solids (TDS) also progressively increases towards discharge areas.

In this study, the concept of ratios between the major ions has been implemented. For example, the sodium to potassium ratio in sea water is 47, in rain water it is less than 10, and it is generally between 15 and 25 in most aquifers [2]. By simply comparing the ratio of sodium to potassium alone, the possibility of sea water influence on groundwaters can be assessed. Likewise, if all other major ion ratios are compared with one another, the resulting varieties of shapes of graphs (e.g. Schoeller diagrams) can be used to trace waters that may have a common origin. Once the samples are grouped, it becomes easier to further investigate the processes that might have influenced the geochemistry and the possible origins of the different water types.

2. Methodology

2.1. Extracting Water Types

Primarily, the groundwater types of the entire Southern Ontario have been investigated for a general understanding. The most commonly employed method of determining water types is plotting meq/L percentages of the major ions on the Piper Trilinear Diagram [3].

The position of a water sample on the Piper Diagram (**Figure 2**) indicates its hydro-chemical facies, from which general relationships between the chemical characteristics of the groundwater and lithology can be assessed. Plotting the analytical results on Piper Diagrams also provides insight into the evolution in water chemistry along a flow path [4].

The presence of contamination is not usually determined from water types, although certain waters (such as chloride type) could indicate possibility of chloride contamination, from road salt for example.

When too many samples are plotted on the Piper (or the related Durov diagram), it becomes difficult to identify individual water samples. To address this issue, a spreadsheet method, that can either supplement or replace the typical Piper approach, has been developed and applied.

This simple spreadsheet method can be applied where AquaChem (or similar trilinear plotting software) is not available, or in cases involving large databases.

The methodology employed stems from the fact that the four water types indicated on the upper left part of Figure 2 (type A, B, C, and D) reflect the proportion of the major cations and anions (in meq/L) with respect to one another. Hence the four water types were extracted by the spreadsheet method, based on the following set of logical expressions:

- If the ratio of (Na+K) divided by [(Ca+Sr) + (Mg+Ba)] is less than 1, then both Type A and Type B waters shown in Figure 2 (upper left) can be obtained.
- However, if the ratio of (HCO_3 divided by (Cl+F) + (SO_4)) is greater than 1, then only Type A water can be obtained.
- The rest of the water types (Types B, C & D) have been obtained by following similar logic (**Table 1**).

Table 1: Ratio criteria for extracting water types by the spreadsheet method

Ratio - (Na+K) Divided by [(Ca+Sr)+(Mg+Ba)]	**Ratio - HCO_3 Divided by [(Cl+F)+(SO_4)]**	**Water Type (from the Piper diagram - Fig. 2a)**
IF <1	AND >1	Type A - Ca+Mg - (HCO_3)
IF <1	AND <1	Type B - Ca+Mg - SO_4-Cl
IF >1	AND <1	Type C - Na+K - SO_4-Cl
IF >1	AND >1	Type D - Na+K - HCO_3

Initially, the water types of southern Ontario were obtained using the AquaChem software and the results plotted on the Piper diagram to compare and test the validity of the spreadsheet method. Subsequently, the four water types were extracted from the spreadsheet method, and when these water types were plotted using the AquaChem software, all the dots fell exactly within the expected area within the Piper diagram, proving the Spreadsheet method to be accurate (**Figure 2**).

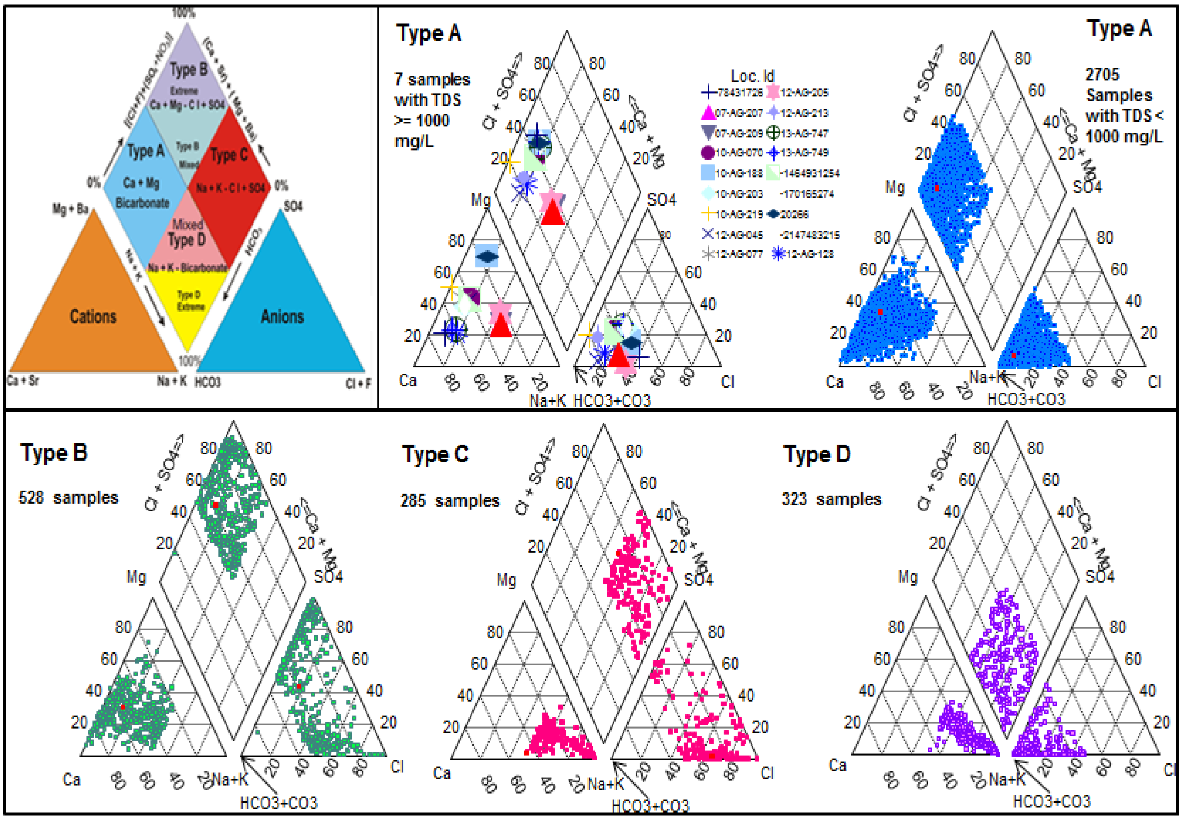


Figure 2: Piper Diagram showing the four different water types upper left and plots using AquaChem, after the water types were first extracted by the spreadsheet method

The results thus obtained from the 3853 samples were used in ArcGIS for further analysis and mapping. This procedure has proven effective in analyzing the geochemistry of Ontario's wide ranging water types. The spreadsheet method provides much more flexibility by allowing any minor constituent to be readily brought into the analyses along with the major ions. Minor constituents are typically excluded from ion balance calculations. However, the concentration of some ions in some groundwater samples from across southern Ontario was found to exceed the "minor constituents" criteria of 1 mg/L [5]. Although these minor constituents are not found in high enough concentrations to alter the water type (e.g. from Type A to Type C), they are often found in high enough concentrations that they do deserve to be considered when interpreting Ontario's groundwater quality. Within the spreadsheet analyses, these constituents have been incorporated into the ion balance calculations, which also allowed correcting for small ion balance errors associated with their exclusion. Hence, on the cation side, strontium (found in concentrations greater than 20 mg/L in some waters), has been considered together with calcium; barium has been considered with magnesium; and potassium has been considered with sodium. Although boron could have also been considered with calcium due to its similar ionic radius, within the current analyses it has been left with the metal group. The most commonly found metals (iron, manganese, zinc, aluminum and boron), which constituted up to 2% of the total ions in some samples, were also brought into the ion balance calculations. On the anion side F has been considered with Cl. Further investigation, beyond the scope of this study, would be needed to identify the sources of the above mentioned individual "minor constituents".

From the number of samples indicated on figure 2, it can be seen that most (70.5%) of the Ontario samples plot as Type A waters (i.e. a calcium/ magnesium bicarbonate dominated). As shown in the upper middle part of figure 2, only 0.3% of this Type A waters has their total dissolved solids (TDS) greater or equal to 1000 mg/L. Next to Type A, 13.7% samples plot as Type B (Ca+Mg - SO_4-Cl); few waters (7.4%) of the Ontario samples plot as Type C (Na+K - SO_4-Cl); and (8.4%) plot as Type D (Na+K - HCO_3).

2.2. Extracting Similarity Groups from the Water Types

There are various methods and procedures of summarizing and presenting water quality data that assist in understanding the geochemistry of groundwaters [7]. Each method depicts some aspect of its quality. More common and standardized methods, for example the Piper Plot or the Schoeller diagram are effective tools for characterizing water samples. However, in terms of trying to differentiate individual samples, and when the number of samples to be reviewed approaches the levels seen in this regional study, these tools prove to be cumbersome.

In this study, only the major ions are considered to almost fully define sea water. Hence, understanding the inherent characteristics within the water type C (sodium chloride waters), with an additional knowledge on topography (or DEM), geological history, sediment thickness, well depth and TDS, was considered to be satisfactory for the intended purpose. Hence, the Piper Plot and accompanying spreadsheet analyses have been used to classify the groundwater samples into four distinct types (A, B, C and D). But, there is still room to further sub-divide these water types, by considering similarity or uniqueness of waters.

Two waters can be considered similar if the major ionic proportions (ratios) between major ions are close to one another. Even if two waters may have very different total ion concentrations (TDS), they can still be similar provided that the ratios between their major ions are similar.

For example, a rain water sample mixed with one gram of salt would be similar to the same rain water mixed with ten or more grams of salt; because both waters are similarly influenced by the salt while the proportion of the remaining ions remains constant (assuming constant saturation). This simple concept has various applications, such as determining the possibility of dilution or mixing of waters, which can lead to better understanding of processes such as the interaction between surface water and groundwater, for example.

The most common method for determining the similarity of waters is with the use of a Schoeller diagram [8]. From such diagrams, where the major ions (in meq/L) are plotted on a semi-logarithmic scale, the relative differences in major ion concentrations can be observed.

As in the case with the use of the Piper Plot, the use of Schoeller diagrams in identifying similar waters is relatively straight forward when only a few samples are evaluated. However, it becomes very cumbersome if many water samples are considered. Other than visual inspection, the Schoeller diagram does not provide an easy way of segregating similar waters. In this study however, the basic shapes (representing the ratios between different ions) found on Schoeller diagrams have been replicated using the spreadsheet approach.

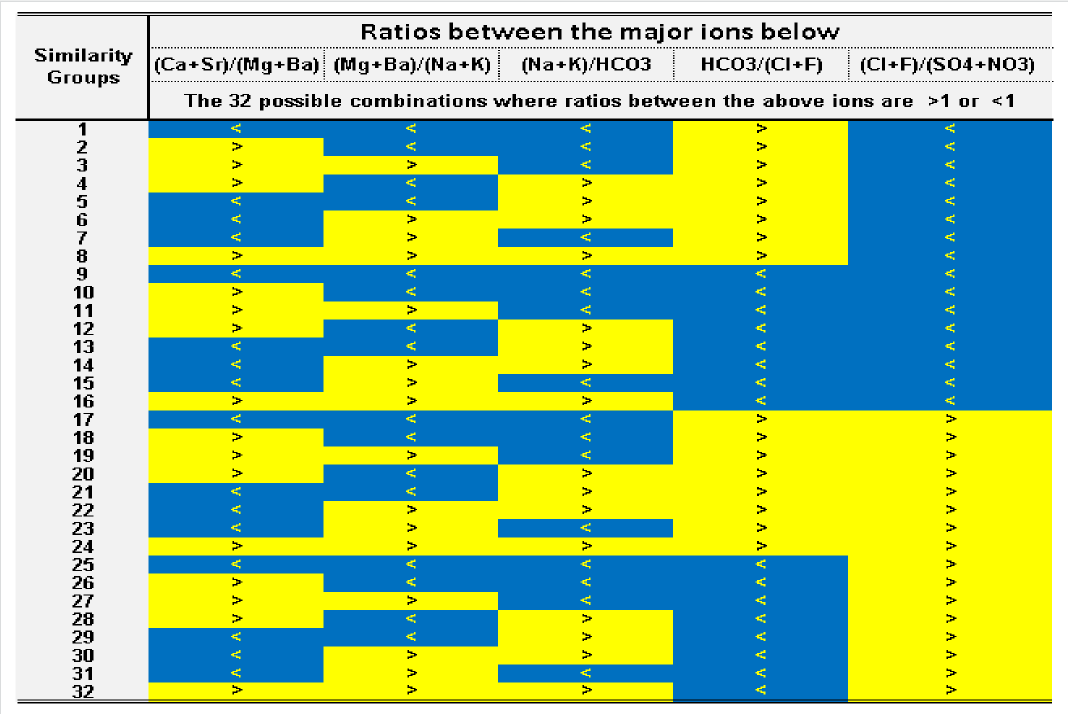
In order to facilitate extraction of similar waters, the possible ionic ratios between the six major ions/ion groups, have been established (**Table 2a**). The methodology evaluates the two possibilities (greater or less) for each ion comparison indicated on the top part of Table 2a. Each ratio comparison has only two possibilities and they can be combined in exactly 2^5 or 32 different ways.

This spreadsheet approach allowed for the easy management of the large dataset and facilitated grouping of similar waters that may not otherwise be possible by visual inspections from the Schoeller diagram. Having determined the 32 possible similarity groups indicated in Table 2a, the next step was to determine how many samples from each of the four water types (Type A, Type, B, Type C and Type D) fall in any one of those groups. Thus, having established all of the possibilities within the spreadsheet, each sample was tested to see to which of the 32 different similarity groups it belongs.

Hence from the spreadsheet that incorporates the greater or lesser comparisons as indicated in Table 2a, the well names corresponding to each water type and similarity groups were obtained (**Table 2b**). The number of groupings observed varied from one water type to the other. Although 32 theoritical similarity groupings are possible, only 24 similarity groups were detected to occur out of the 3853 groundwater samples that were evaluated in this current investigation (**Table 2b**).

The rest possible similarity groups (9, 10, 15, 22, 24, 25, 30 & 32) do not appear to exist in the groundwater characteristics of the Southern Ontario (*some or all these similarity groups may or may not exist in other parts of the world*).

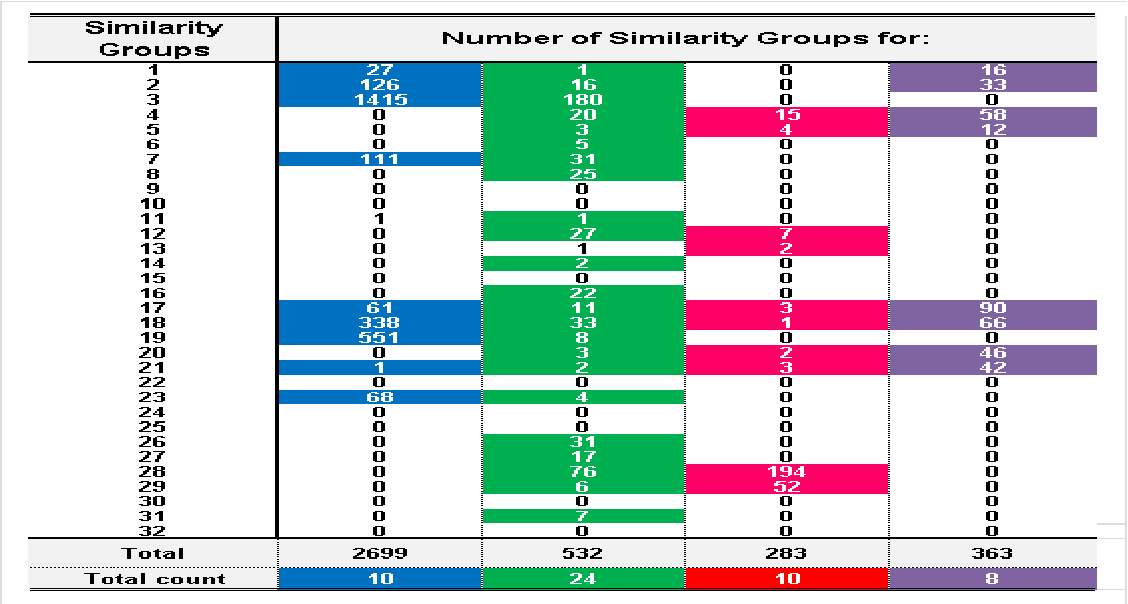
Table 2a: Ratios used in order to extract groups of waters that are similar



Similarity Groups	Ratios between the major ions below				
	(Ca+Sr)/(Mg+Ba)	(Mg+Ba)/(Na+K)	(Na+K)/HCO3	HCO3/(Cl+F)	(Cl+F)/(SO4+NO3)
	The 32 possible combinations where ratios between the above ions are >1 or <1				
1	<	<	<	>	<
2	>	<	<	>	<
3	>	>	<	>	<
4	>	<	>	>	<
5	<	<	>	>	<
6	<	>	>	>	<
7	<	>	<	>	<
8	>	>	>	>	<
9	<	<	<	<	<
10	>	<	<	<	<
11	>	>	<	<	<
12	>	<	>	<	<
13	<	<	>	<	<
14	<	>	>	<	<
15	<	>	<	<	<
16	>	>	>	<	<
17	<	<	<	>	>
18	>	<	<	>	>
19	>	>	<	>	>
20	>	<	>	>	>
21	<	<	>	>	>
22	<	>	>	>	>
23	<	>	<	>	>
24	>	>	>	>	>
25	<	<	<	<	>
26	>	<	<	<	>
27	>	>	<	<	>
28	>	<	>	<	>
29	<	<	>	<	>
30	<	>	>	<	>
31	<	>	<	<	>
32	>	>	>	<	>

As shown at the bottom of Table 2b, from the most abundant water type A samples, only 10 number of similarity groupings were obtained. This shows the relatively conservative nature (not showing much variabilities within). Type B waters have the most variable internal characteristics (24 variable types). It could be misleading to compare this number with the total sample, since this variability may not reflect the total number of samples analyzed. Type C waters showed 10 variable types and Type D waters showed only 8 variable types.

Table 2b: Number of similarity groups per water type



Similarity Groups	Number of Similarity Groups for:			
1	27	1	0	16
2	126	16	0	33
3	1415	180	0	0
4	0	20	15	58
5	0	3	4	12
6	0	5	0	0
7	111	31	0	0
8	0	25	0	0
9	0	0	0	0
10	0	0	0	0
11	1	1	0	0
12	0	27	7	0
13	0	1	2	0
14	0	2	0	0
15	0	0	0	0
16	0	22	0	0
17	61	11	3	90
18	338	33	1	66
19	551	8	0	0
20	0	3	2	46
21	1	2	3	42
22	0	0	0	0
23	68	4	0	0
24	0	0	0	0
25	0	0	0	0
26	0	31	0	0
27	0	17	0	0
28	0	76	194	0
29	0	6	52	0
30	0	0	0	0
31	0	7	0	0
32	0	0	0	0
Total	2699	532	283	363
Total count	10	24	10	8

Also following the upper half and lower half of the the right column of Table 2a, it would be interesting to particularly identify water samples whose sulphate is relatively low or high, respectively. Since the main objective in this exercise is to understand the sodium chloride waters, the make-up of the Type C waters was further investigated in making use of Group 4 (high sulphate low TDS) and Group 28 and Group 29 (low sulphate and high TDS) out of the 10 similarity groups observed in Table 2a (the red coloured rows). Although there are 10 varieties of Group C, only these three similarity groups represent 92% of the entire water sample. Thus, the milli-equivalent values of the major ions from these three similarity groups associated with the Type C waters were plotted on Schoeller diagrams (**Figure 3**).

For the sake of comparison, a text book example of typical sea water composition, river water and rain water [9] were also plotted (the lower right part of Figure 3).   As shown on all graphs with the exception of the one on the lower right of Figure 3, all water samples within each group (one sample is represented by one line) have a more or less similar ratio between their major ions. This is reflected by the fact that, within each of the three graphs, the lines resemble each other in shape although plotted at a different level along the Y axis. Hence, it can be seen that the ratio comparisons of the three Similarity Groups in Table 2a corresponds exactly as shown on the three graphs in Figure 3. For example, Group 29 waters (upper left part of Figure 3), representing 52 water samples, can be characterized as follows: calcium plus strontium is less than magnesium plus barium, which is less than sodium plus potassium; bicarbonate is less than chloride plus fluoride, which is again greater than sulphate. Likewise, other groups can be identified by the relative differences in their major ion ratios. Group 28, representing 194 samples is different from Group 29 by its higher calcium; Group 4, representing 15 samples is different from the others due to its relatively high sulphate, like the rest of Similarity Groups 12 &13 of the same water type C (**Tables 2a & 2b**).

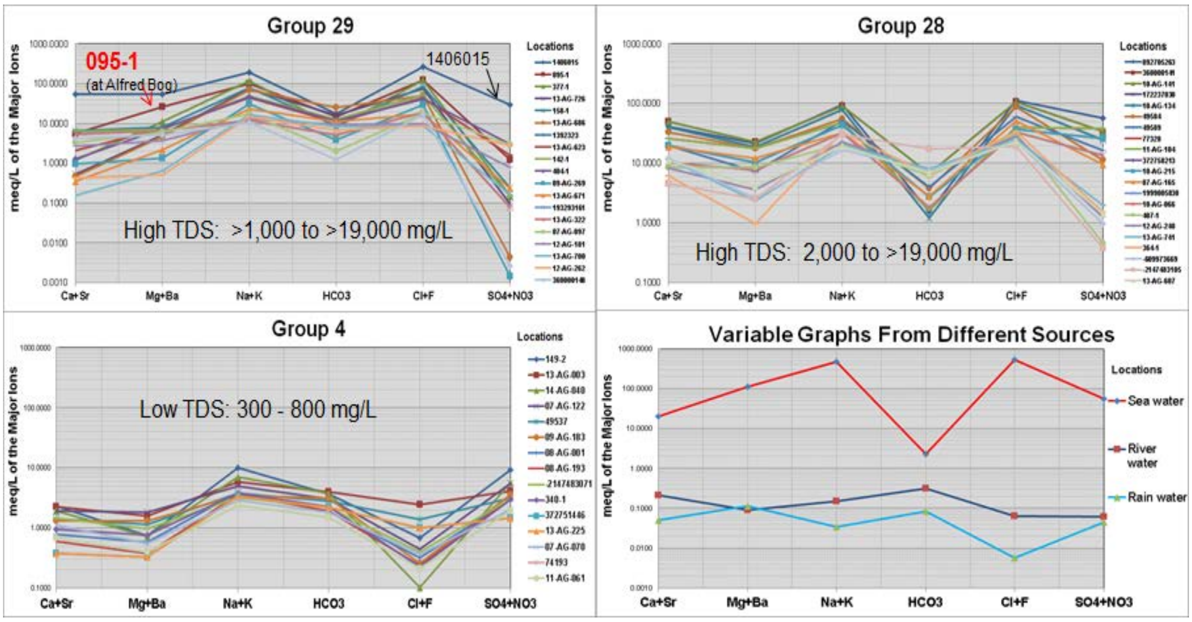


Figure 3: Type C waters from different similarity groups compared to typical sea water, rain water and river water (lower right)

What is most important to note in this exercise is that, it is only Similarity Group 29 waters (52 samples) that are exactly similar in all their ionic ratios to that of sea water (the red line lower right of Figure 3).

3. Discussion

3.1. Groundwater Types in Southern Ontario

Water Types from the averages of 3853 groundwater samples, were extracted using the spreadsheet method mentioned in section 2.1 and plotted on a map. Figure 4 shows the distribution of the Water Types across Southern Ontario. The size of the dot on this map is proportional to well depths. Figure 5 also shows the distribution of water types with the size of the dot being proportional to TDS. Based on these maps, only a general overview of water types in Southern Ontario is hereby provided. In future more detailed studies, these same maps can also be used for a better understanding of the relationships between water type and geology (formations) or other related hydrogeological factors (e.g. transmissivity, groundwater movement, age, etc.).

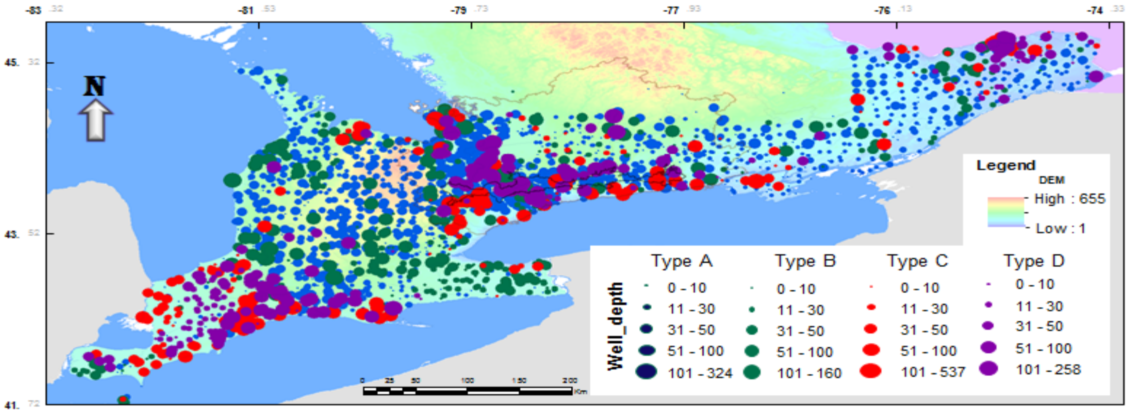


Figure 4: Distribution of Water Types across Southern Ontario (Note: size of dot is proportional to well depth; DEM is shown in the background)

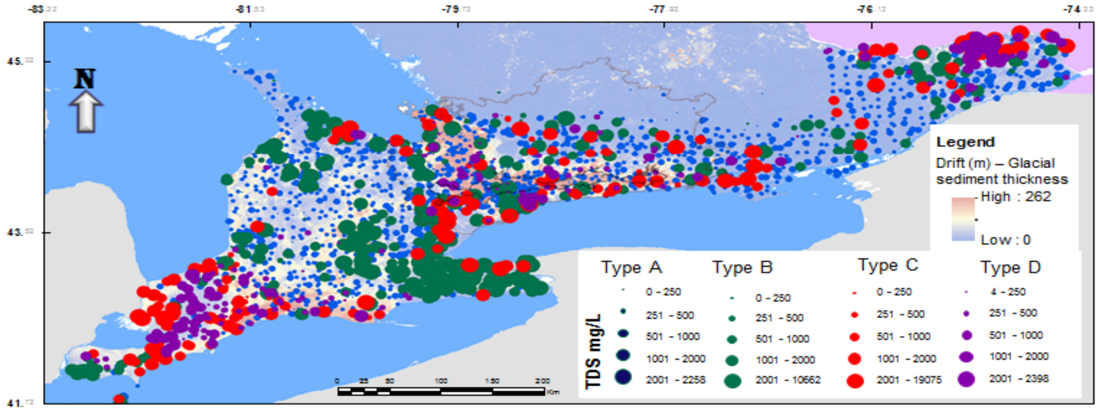


Figure 5: Distribution of Water Type across southern Ontario (Note: size of dot is proportional to TDS; glacial sediment thickness is shown in the background)

Although all water types are discussed in a general way through the following sections, a particular focus has been placed on Type C waters. The inherent characteristics within the Type C waters and their significance in understanding their origin are further examined in the next sections.

As shown on Figure 4 and Figure 5, there seems to be a relation between water type and well depth as well as TDS. Figure 4 depicts that most of the wells in southern Ontario are generally drilled to shallow depths as evidenced by the large number of smaller dots from Type A waters. Type C waters, particularly in the central part of the study area, north of Lake Ontario, tend to be associated with relatively deeper wells (as evidenced by the relatively larger red dots). This central area contains a thick (up to 200 metres) package of glacial materials (Laurentian bedrock valley infill sediments and Oak Ridges Moraine sediments). In Eastern Ontario, where the glacial sediments are relatively thinner (generally less than 50 metres), Type C waters are obtained from wells that are shallower.

The two depth ranges within these two different areas for the Type C waters raises the possibility that the origins of sodium and chloride in their respective water samples may also differ. Usually shallow wells when compared to deeper wells are more susceptible to local surface contamination due to sources such as road salt, water softeners, landfills or septic system effluent. Where it is known that there is no human impact on the environment, then other natural explanations must be provided, as will be discussed further.

The highest TDS waters are those of Type C (red coloured) followed by Type B waters (turquoise coloured). Type A (blue) and D (purple) waters are seen to generally have lower TDS concentrations. Although the delineation of groundwater flow systems is beyond the scope of this regional study, by looking at the regional digital elevation model (DEM), from the background of Figure 4, and the glacial sediment thickness, from the background of Figure 5, it can be surmised that some of the sodium chloride dominated Type C waters, particularly in the deeper wells, may be related to long residence times, whereas those found in recharge areas are related to short subsurface residence times, with a possibility of being influenced by any one or more of the above indicated sodium chloride sources. However, no conclusive remarks can be drawn from this study without further investigation.

In the absence of any known evidence for any of the above mentioned contamination sources, it can be speculated that the elevated sodium and chloride in the deeper wells (greater than about 100 metres) towards the western and central parts of Southern Ontario may have been derived from brines that are related to the original Paleozoic Era sediment deposition [6]. On the other hand, the elevated sodium and chloride concentrations within the relatively shallow (less than 100 metres) wells towards the eastern parts of Southern Ontario might be related to salt water leakage from marine clay sediments; it is unlikely (particularly for the sampled wells located within the large wetland and in the other naturalized (i.e. undeveloped) areas that these wells have been impacted by surficial contamination source. To further investigate the Type C waters, the percentages of the major ion composition (in meq/L) was mapped across southern Ontario as pie charts (**Figure 6**).

For discussion purposes, the water samples can be grouped into three areas: i) those to the west, that are north of Lake Erie; ii) those in the central area, north of Lake Ontario; and iii) those in the east, that are north of the St.

Lawrence River. In Figure 6, the sizes of the pie charts are made to vary according to their respective TDS values.

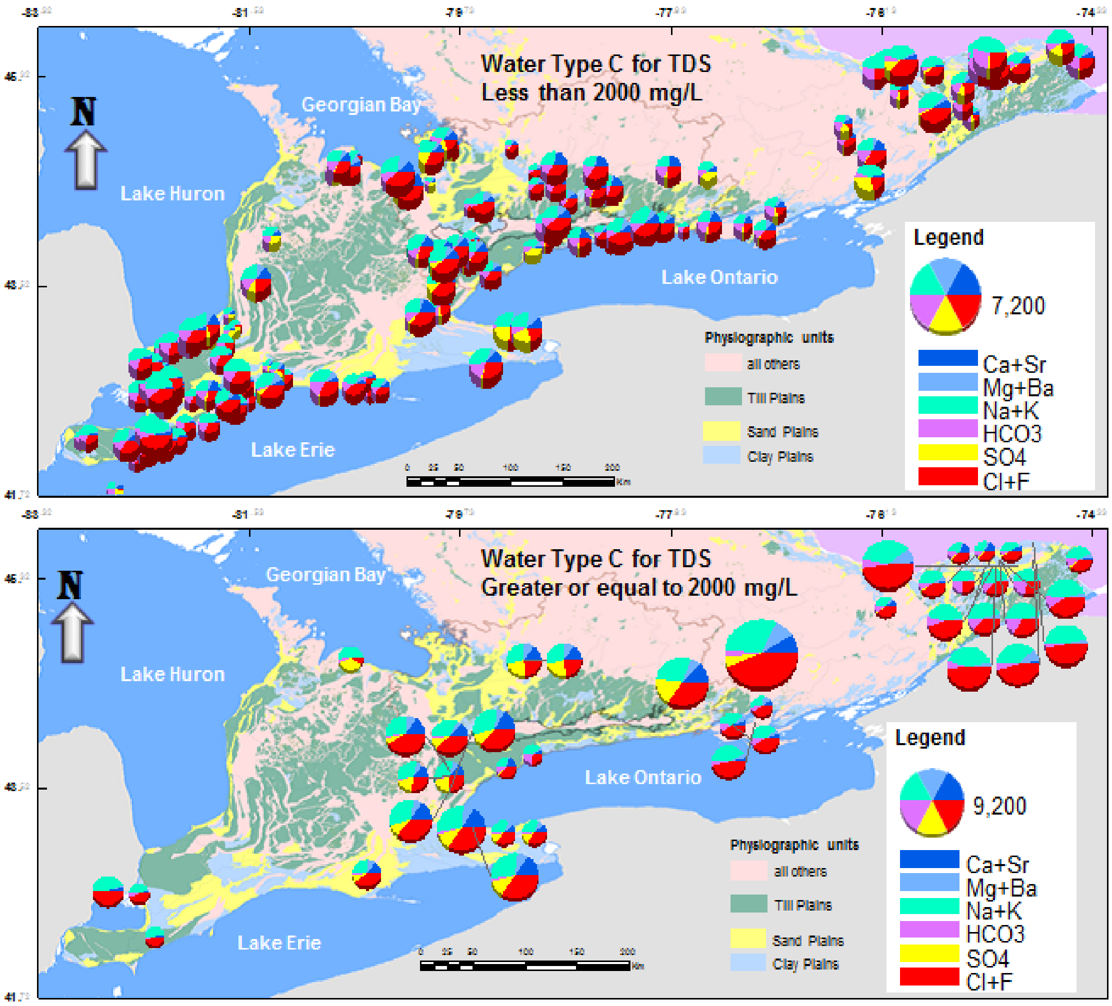


Figure 6: Pie Chart for major ion characterization of the Type C waters of Southern Ontario

The upper part of Figure 6 shows those samples where TDS is less than 2000 mg/L, whereas the lower part of Figure 6 represents those with relatively high TDS (greater than or equal to 2000 mg/L). Some of the notable features that can be readily observed from Figure 6 are provided below:

- There are only 3 Type C samples in the southwest (north of Lake Erie) with TDS concentration that exceeded 2000 mg/L, compared to the numerous Type C waters in the same area with TDS less than 1000 mg/L (upper part of Figure 6).
- In both the upper and lower parts of Figure 6 the predominant cation for the Type C waters is sodium (green), with calcium and magnesium being of lesser significance.
- Although chloride (red) is most frequently the dominant anion in the Type C waters, there are some samples in samples with lower TDS, where sulphate (yellow colour) is also significant (upper part of Figure 6).

- The proportion of bicarbonate is also more prominent in the low TDS samples than in high TDS samples.
- For the high TDS samples, those in the east are characterized by an absence of sulphate and calcium, with sodium and chloride being the most significant ions.
- Of the Type C waters that have greater than TDS of 2,000 mg/L (lower part of Figure 6), none of the samples north of the St. Lawrence River in the east, have any significant sulphate levels. Calcium (in blue) is also almost totally absent from the samples in the east.
- The proportion of ions, North of Lake Ontario, appears to be different from that of the east and west.

As indicated above, the Type C waters show different characteristics across the span of Southern Ontario, suggesting different origins. In this study however, particular attention is given to Eastern Ontario, and the situation is further scrutinized through additional investigation of the Type C waters.

3.2. Origin of the Naturally Occurring Sodium Chloride Waters

In order to examine if indeed groundwater quality from all samples belonging to Similarity Group 29 (upper left part of Figure 3) might represent rain and/or glacial melt water mixed with sea water, further consideration was focused on a single sample (095-1) from Similarity Group 29 (upper right part of Figure 3).

The sample was obtained from a PGMN well that is 26 metres deep, situated within a vast area covered by thick (over 100 metres) marine clay sediment (Champlain Sea related) in the middle of the Alfred Bog - a large natural wetland in Eastern Ontario.

Based on the fact that this well (095-1) draws water from these marine sediments and no contamination from road salt or other sources within the Alfred Bog is known to occur in this area, it is inferred that the groundwater from this well reflects a sea water origin. In order to examine possible sources of the other Group 29 waters it becomes necessary to spatially locate them on maps (**Figure 7 and Figure 8**), and further examine other causes for their unique characteristics compared to the other similarity groups.

An examination of Figure 7 shows that Group 29, Group 28 and Group 4 waters are randomly distributed throughout Southern Ontario, but their density varies from place to place.

Particular attention was given to Group 29 waters, because of their relatively higher density towards the east and towards the low lying areas up to Lake Ontario. Also these waters exactly resemble sea water (lower right of Figure 3).

However, both Group 28 & Group 29 waters have very high total dissolved solids (TDS), mostly ranging from 1000 to over 19,000, and they are both spatially close to one another in some parts. Since Group 28 also shows almost similar characteristics, with the exception of its relatively higher calcium content, it can then be surmised that Group 28 waters also may have had the same origin as Group 29 waters, although they may have gained more of their calcium through more residence time and interaction with calcium rich aquifers. In contrast to these two groups, Group 4 waters are characterized by their relatively high sulphate, and they have very low

TDS (300 to 800 mg/L).

They occur mostly towards the west. Other Similarity Groups within Type C water, such as Group 12 and 13 are not considered here, since they are not much different from Group 4.

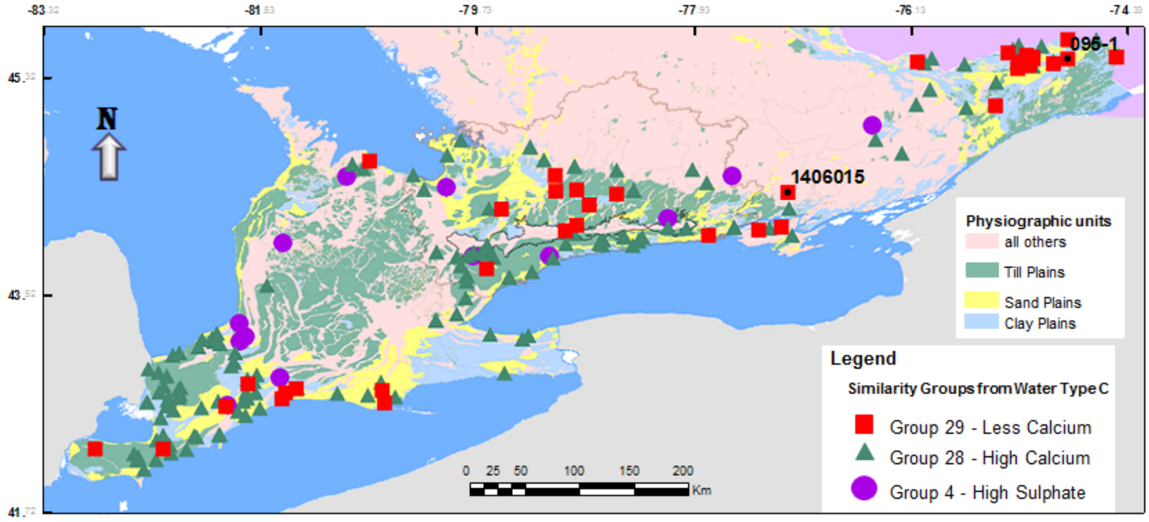


Figure 7: Map showing distribution of the three similarity Groups from Type C waters

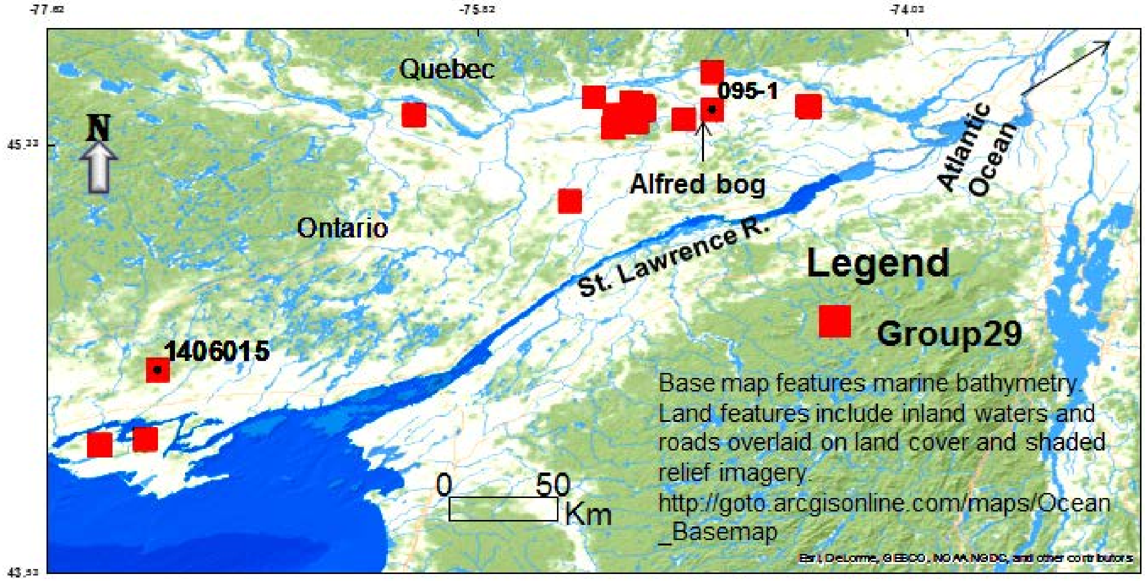


Figure 8: Map showing approximate area (low areas in marine blue) covered by the former Champlain Sea and Similarity Group 29 waters

Although it is not known whether or not all Group 29 groundwater samples that were obtained from wells situated outside of Alfred bog are impacted by road salt, or any other source of NaCl, it can be speculated that the other Type C, Similarity Group 29 waters, especially those situated in Eastern Ontario, may also have a sea water origin. Given such spatial differences in the location of the different Type C waters, it can be questioned as to whether there might be a common origin to the Type C, Group 29 waters, and possibly some of the Group 28 waters found in eastern and central southern Ontario. Another interesting aspect, in particular Group 29 waters is their occurrences towards Lake Ontario. For example, a 43.6 metres deep bedrock well (1406015), which has a very high TDS (over 19,000 mg/L) plots north of Lake Ontario (**Figure 7**).

The unique groundwater quality signature that has been uncovered in wells throughout Southern Ontario is an interesting observation. Given the strong likelihood of the sea water related origin to the Type C waters in the east, and similar waters with high TDS towards the west, the question arises: is the groundwater in the wells north of Lake Ontario also resulting from a sea water origin? In order to provide answer to this question, some aspect of the historical Quaternary geology has also been considered.

As has been explained by different authors [10,11,12,13], the Champlain Sea advanced from the Atlantic Ocean in the east into the low lying parts of Quebec and Eastern Ontario after partial deglaciation when the land was still isostatistically depressed about 12,500 years ago. At this time, saline to brackish sea water of the Atlantic Ocean spread into the Ottawa and Upper St.Lawrence valleys leading to the deposition of marine clays in the Ottawa area. The Champlain Sea withdrew due to uplift after de-glaciation, about 8700 BP.

An approximate area thought to have been occupied by the former Champlain Sea can be speculated from the whitish area shown on the combined bathymetry and land map (**Figure 8**). The locations of the Type C, Group 29 waters are plotted on this map. From a DEM map, it has been observed that the lowermost regions along the St. Lawrence river reaches a maximum of only 75 metres above sea level, up to Lake Ontario

Evidence to support the presence of Champlain Sea related marine conditions has been well documented as far inland as the Brockville area in Ontario [14]. However for the wells exhibiting Type C, Group 29 groundwaters that are situated north of Lake Ontario, any direct linkage to sea water due to the invasion of the former Champlain Sea could be tenuous.

Groundwater quality in Eastern Ontario has been previously studied [15, 16, 17]. These past studies have commented upon the impact of salt within the groundwater in Eastern Ontario, and have considered its source to be related to the Former Champlain Sea. According to one groundwater quality study [18] that sampled deep piezometers set into the Champlain Sea clay sediments near Montreal: “Concentrations of ^{18}O, Na^{+}, and Cl^{-} in water from the deepest piezometer suggest that the deep clay was deposited in a mixture of about 33% seawater and 67% freshwater”. According to the results from this study, it is obvious that sea water the Former Champlain Sea had an impact on the low lying areas of Quebec. Exactly how far westward, in Ontario, the Champlain Sea advanced has been debated over the years. It was initially considered to have advanced into the Lake Ontario basin when a large marine basin, the “Gilbert Gulf”, was proposed to have occupied parts of the current-day Lake Ontario [19]. More recent researchers have also considered the Champlain Sea to have reached into the Lake Ontario basin [13, 20, and 21]. Others [22] who searched for evidence of marine fossils within the Lake Ontario bottom sediment cores and [14] have documented that no evidence has been found to support the existence of marine conditions within the Lake Ontario basin. If marine conditions had occurred, some authors [22] surmised that the marine waters would have been short-lived and so diluted by fresh glacial melt waters, that marine-like conditions could not have become established.

As discussed above and from the spatial distribution of the two similarity groups, and in particular Group 29, it can be asserted that the effect of the Former Champlain Sea clay sediments near Montreal must have extended further to Eastern Ontario. What remains to be known is its exact effect towards the west, and if it reaches Lake Ontario. Also, the possibility of sea water penetration into deeper wells through fractured bedrocks at the lower sediment contact should not be out ruled.

In Eastern Ontario, groundwater quality within the aquifers that are vertically connected to the Champlain Sea sediments, including groundwater from wells that terminate at the overburden bedrock contact or within the upper fractured bedrock, frequently exhibit poor quality, which may have been caused due to leakage from the overlying marine sediments. Since this study is limited to only finding out the origin of sodium chloride waters in Eastern Ontario, all other water quality problems retated to or not to sodium chloride needs further investigation.

It should also be noted that all those waters that show similar characteristics as sea water do not necessarily mean that they have originated from the Former Champlain Sea related sea water. For the wells north of Lake Ontario, for example the previously mentioned well (1406015), other possible origins for the groundwater can be put forward. It may be that very old sea water (not Champlain Sea) was entraped within the Paleozoic rocks at their time of deposition and has resided in the rocks with only minimal geochemical changes for a significant period of time. Brine waters are commonly found in deeper sedimentary basins, often in association with petroleum exploration [6].

4. Conclusions

This study was focused on detailed analysis of sodium chloride groundwater types (Type C) in Southern Ontario, with an intention of finding out if this is related to sea water composition. The water types were classified and mapped with particular emphasis in understanding groundwater quality impact from the Former Champlain Sea. The Spreadsheet methodology utilized in this study has proven effective for the identification of any one sample into a particular water type as well as the respective similarity groupings within each water type. The results obtained from such method was analysed in conjunction with other important parameters, such as total dissolved solids, DEM, sediment thickness and quaternary geological history of the Eastern Ontario area. It is believed that same methodology can be applied for other water types for various other purposes.

In this study, about 4000 Ontario groundwater samples, from an area spanning southern Ontario were analysed. The results indicate that waters of Type A (i.e. calcium/magnesium bicarbonate water types) are by far the most prevalent. This water type is commonly found in shallow groundwater systems where it is only slightly evolved beyond infiltrating precipitation.   Based on the density and distribution of the four water types, it can be concluded in general, that there is a relationship between particular water types and geographic locations; Southern Ontario has varied geology, topography and land use from east to west.

The study has found that a unique subset of groundwater samples can be found in the area extending from

Ottawa in the east through to near the western end of Lake Ontario. These waters are broadly characterized by elevated sodium and chloride, but also in that the relationship of the major ions to one another is very similar to sea water. When found in Eastern Ontario, these waters have been interpreted to be related to the Former Champlain Sea which inundated parts of Quebec and Ontario some 12,000 years ago. The origin of the brackish waters in the east (i.e. within the South Nation and the Raisin River watersheds) is likely to have been caused by leaching of sodium and chloride from the Post glacial Champlain Sea deposits (mostly clay, silt, and silty clay sediments). Although the bicarbonate in wells from these areas is higher compared to that of the sea water, this can be explained by mixing with infiltrating rain water over time.

Further investigation will be required to fully resolve the exact origin of the Type C, Group 29 waters to the north of Lake Ontario. Other methods of tracking groundwater sources, such as stable isotopes of oxygen ^{18}O, and deutorium ^{2}H, as well as the radio active isotopes of tritium ^{3}H and carbon ^{14}C could also be helpful to further determine groundwater characteristics and their respective origins in Southern Ontario.

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