THE INFLUENCE OF CATION EXCHANGE ON THE CHEMISTRY OF LONG ISLAND GROUND WATER

Michael Lani and Martin A.A. Schoonen
Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100

ABSTRACT
The importance of cation exchange on the chemistry of Long Island ground water has been studied by comparing existing ground water chemistry data with cation exchange results obtained in this paper. Ground water chemistry data was obtained for the three major aquifers of Long Island - the Upper Glacial, Magothy, and Lloyd. In addition, analysis of effective cation exchange capacity (effective CEC) and exchangeable cations was performed on ten samples from the three major aquifers, as well as the Raritan clay, using a simple Barium Chloride ($BaCl_2$) method.

The ground water chemistry data show that the Upper Glacial and Magothy aquifers have ground waters with very similar chemical compositions. The Lloyd aquifer, on the other hand, has a very different chemical composition from both the Upper Glacial and Magothy aquifers. Results of the effective CEC and exchangeable cations analysis are very high for the Raritan clay, which acts as a leaky confining layer between the Magothy and Lloyd aquifers. Therefore, cation exchange taking place within the Raritan clay is believed to be the cause for the observed difference in the chemistry of Magothy and Lloyd ground water.

INTRODUCTION
The purpose of this research paper is to evaluate the importance of cation exchange on the chemistry of Long Island ground water. This has been carried out by comparing existing Long Island ground water chemistry data with effective cation exchange capacity (effective CEC) results of Long Island stratigraphic units obtained for this paper. The effective CEC is simply the CEC at the pH of the soil. An area of particular interest is the occurrence of cation exchange within the Raritan clay, and the effect that it has on the chemistry of the ground water as it passes through the Raritan clay and into the Lloyd aquifer. Apparently, there has not been any previous work published on this particular subject.

Cation exchange capacity (CEC) is defined as the sum of the exchangeable cations of a soil (Chapman, 1965). CEC's are generally low for silt and sand and very high for clays and organic matter (carbon). Consequently, the presence of even small amounts of clay or organic matter will significantly increase the CEC of the bulk soil. Due to this fact, an empirical formula has been established which relates CEC to percentage clay (<2 um) and organic carbon (Appelo and Postma, 1993).

LOCATION AND DESCRIPTION OF SAMPLES
The samples that were analyzed for effective CEC and exchangeable cations were obtained from the United States Geological Survey (U.S.G.S.) in Coram, N.Y. The samples are all from well # N3355, a test well at Nassau County Sanitarium, about 210 feet west of Round Swamp Road and 3160 feet south of Old Country Road, Plainview, Long Island, New York (Figure 1). Table 1 shows a geologic correlation for this well. Ten samples from the four major stratigraphic units of Long Island were analyzed. Table 2 shows the depth, stratigraphic unit, and grain size for each of the ten samples, and Table 3 shows the sample color and color code from a Rock Color Chart for each of the ten samples. Two samples were taken from the Upper Glacial aquifer, four from the Magothy aquifer, two from the Raritan clay, and two from the Lloyd aquifer.

RESEARCH STRATEGY AND METHODS
General Strategy
The research strategy for this paper involves a bi-faceted approach. Existing ground water chemistry data was obtained from the U.S.G.S. (Wat-Store Database) in Coram, N.Y. In addition, analysis of effective CEC and exchangeable cations was performed on ten samples from the four major stratigraphic units of Long Island. The method of analysis uses a $BaCl_2$ solution to displace the cations from the soil, yielding not only an effective CEC for the soil, but also the proportion of the exchangeable cations. The results of the effective CEC and exchangeable

cations analysis are used as a tool in evaluating the importance of cation exchange, as it relates to the chemistry of Long Island ground water.
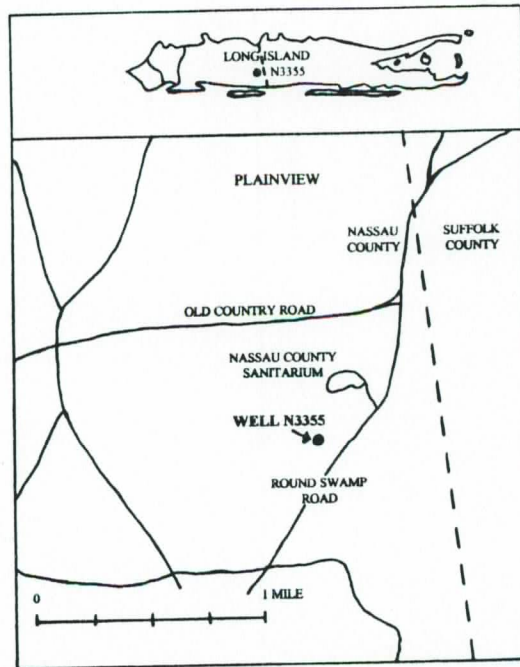

Figure 1. Map showing location of Well # N3355 at Plainview, Nassau County, Long Island, New York.

Depth (feet)	Mean Sea Level (feet)	Formation
0 to 77	+183 to +106	Upper Glacial
77 to 155	+106 to +33	Upper Glacial and Manetto Gravel(?)
155 to 787	+33 to -604	Magothy
787 to 955	-604 to -772	Raritan Clay
955 to 1218(?)	-772 to -1035(?)	Lloyd

Table 1. Composite log for Well #N3355 based on data from two test holes spaced about 25 feet apart, a driller's log, electrical log, and field observation of the drilling (Craig Brown, written communication, U.S.G.S. in Coram, N.Y., 1995).

Sample#	Geologic Unit	Depth (feet)	Grain Size
1	Upper Glacial	75 to 77	Sand, fine to coarse, and gravel
2	Upper Glacial	148 to 150	Sand, medium to coarse, and gravel
3	Magothy Formation	168 to 170	Fine sand to sandy clay
4	Magothy Formation	209 to 211	Clay, sandy, very fine to fine
5	Magothy Formation	347 to 349	Sand, fine to medium
6	Magothy Formation	596 to 598	Medium to coarse sand
7	Raritan Clay	794 to 796	Clay
8	Raritan Clay	854 to 856	Clay
9	Lloyd Sand	1020 to 1022	Fine sand
10	Lloyd Sand	1112 to 1114	Fine sand

Table 2. Description of samples. Grain size is from a supply well log (Craig Brown, written communication, U.S.G.S. in Coram, N.Y., 1995), as well as personal observation.

Sample#	Sample Color	Color Code
1	Light brown	5YR6/4
2	Light brown	5YR6/4
3	Moderate yellowish brown	10YR5/4
4	Pale yellowish brown to very light gray	10YR6/2 to N8
5	Moderate yellowish brown	10YR5/4
6	Pale yellowish brown to very light gray	10YR6/2 to N8
7	Very light gray	N8
8	Medium light gray	N6
9	Light gray	N7
10	Pale yellowish brown to very light gray	10YR6/2 to N8

Table 3. Color of samples, as well as color code (from a Rock Color Chart).

Ground Water Chemistry Strategy

Long Island ground water chemistry data was obtained for all three major aquifers - the Upper Glacial, Magothy, and Lloyd. The data chosen for this paper had to include Na, K, Ca, and Mg analyses. To avoid using data from contaminated wells, data were not used for waters with $NO_3 + NO_2$ more than 1.0 mg/l, specific conductance more than 75 uS/cm, and Na or Ca with more than 10 mg/l.

The normalized values of the cations were determined by converting concentrations in mg/l to meq/l. This was done in order to be consistent with the units obtained in the effective CEC and exchangeable cations analysis. Also, Na and K were grouped together (Na+K), and, since Na is the dominant cation, when (Na+K) values in mg/l were converted to meq/l, the gram formula weight of just Na was used.

Effective CEC and Exchangeable Cations Method

The CEC of agricultural soils is commonly measured using the ammonium acetate (NH_4OAc) method buffered at pH 7; however, due to the steep slope to the CEC-pH curve, measuring CEC at a pH other than that in the field gives misleading results (Hendershot and Duquette, 1986). Hendershot and Duquette (1986) therefore recommend that a simple Barium Chloride method, which measures the effective CEC and exchangeable cations, be used in routine analysis of acidic soils, especially when nonagricultural lands are under investigation.

Effective CEC was therefore determined by a sum of cations displaced by 0.1 M $BaCl_2$. The following method is slightly modified from Hendershot and Duquette (1986). The samples were oven dried and the fraction < 2 mm was used for analysis. Samples of between 1 and 5 grams, depending on their probable effective CEC, were weighed into 50 ml centrifuge tubes. 20 ml of 0.1 M $BaCl_2$ was added and the tubes placed in an ultrasonic bath for 15 minutes. The samples were then centrifuged at 2000 rpm for 15 minutes. The supernatant solutions were then filtered through 0.45 um filter paper. The solutions were collected in polyethylene bottles for analysis of Ca, Mg, Na, K, and total Fe. The effective CEC was then determined by a sum of the above cations, expressed in the appropriate units, milliequivalents per 100 grams of dry soil (meq/100g).

Effective CEC and Exchangeable Cations Analysis

Triplicate analyses were performed on samples #1 (Upper Glacial aquifer) and #7 (Raritan clay), and a duplicate analysis was performed on sample #6 (Magothy formation). Cations were analyzed simultaneously by Direct Current Argon Plasma Emission Spectrometry (DCP-AES) using a SpectraSpan SSVB instrument with multi-element capability. The detection limits for the cations were based on three times the standard deviation of the blank analyzed 15 times in succession at the conclusion of the analyses. Each solution was analyzed four times, resulting in an analytical uncertainty of less than 5%, on average, for concentrations well above the detection limits. For Ca, Mg, K, and Fe, the detection limits are 0.02 ppm, 0.09 ppm, 0.0014 ppm, 0.12 ppm, and 0.035 ppm, respectively. For Na, Ca, and Mg, the solutions of every sample are well above the detection limits for these cations. However, for K and Fe, several solutions approach the detection limits for each cation. For K, the solutions for sample #'s 4, 6, and 8 are each about four to five times the detection limit, which, based on the analysis of the standards, suggests an analytical uncertainty of approximately 10%. For Fe, the solutions for sample #'s 6, 7, and 9 range from the detection limit to two times the detection limit, which suggests an analytical uncertainty of between 10 and 15%.

Iron was analyzed as total Fe. However, it is reported as milliequivalents of ferrous iron. Also, by using results for the analysis of the standards in comparison to the theoretical concentrations of the standards, slight adjustments were made to some of the solution results. This was accomplished by preparing graphs of the ratio of the observed results of the standards to the theoretical values of the standards vs. the theoretical values of the standards.

RESULTS AND DISCUSSION
Ground Water Chemistry

Table 4 shows average concentrations, as well as normalized values of Ca, Mg, and (Na+K) for precipitation, the Upper Glacial aquifer, the Magothy aquifer, and the Lloyd aquifer (uncertainties represent one standard deviation). For the Upper Glacial aquifer, data from 13 wells were used, ranging in depth from 30 feet to 193 feet. For the Magothy and Lloyd aquifers, data from 14 and 36 wells were used, respectively, ranging in depth from 144 feet to 962 feet and 303 feet to 1395 feet, respectively.

According to Table 4, even though average concentrations are much higher for ground water than they are for precipitation (due to evapotranspiration), the normalized values show that the Upper Glacial and Magothy aquifer's cations are in almost the same ratio as for that of precipitation. The ratio of the Lloyd aquifer's cations are clearly different from precipitation. Average Lloyd ground water is richer in Ca and Mg than both Upper Glacial and Magothy ground water. Ca and Mg concentrations in the Lloyd are both approximately double what they are in the Upper Glacial and Magothy aquifers, while (Na+K) concentrations are only about 20% higher in the Lloyd aquifer. The explanation for this change in ground water chemistry from the Magothy aquifer to the Lloyd aquifer must be found in the Raritan clay, which behaves as a leaky confining layer between the two.

	Ca (mg/l)	Mg (mg/l)	Na+K (mg/l)	%Ca	%Mg	%(Na+K)
Precipitation	0.48	0.19	1.27	25.3	16.8	57.9
Average Upper Glacial	1.76+-1.05	0.98+-0.33	4.65+-0.69	23.7+-9.3	21.8+-5.8	54.4+-8.2
Average Magothy	1.58+-0.87	0.85+-0.80	4.35+-1.02	23.4+-8.7	20.7+-10.8	55.9+-13.6
Average Lloyd	3.48+-2.05	1.82+-1.21	5.55+-1.72	**30.8+-10.8**	**26.5+-8.2**	**42.7+-15.9**

Table 4. Average concentrations and normalized values (based in milliequivalents) for precipitation (from Schoonen & Brown, 1994), the Upper Glacial aquifer, the Magothy aquifer, and the Lloyd aquifer. The ground water chemistry data was obtained from Craig Brown, written communication (from the U.S.G.S. Wat-Store database), 1995. For the Upper Glacial aquifer, data from 13 wells were used, ranging in depth from 30 feet to 193 feet. For the Magothy and Lloyd aquifers, data from 14 and 36 wells were used, respectively, ranging in depth from 144 feet to 962 feet and 303 feet to 1395 feet, respectively. Uncertainties represent one standard deviation.

Effective CEC and Exchangeable Cations

The effective CEC and exchangeable cations results, as well as the exchange pH's, are shown in Table 5. The analytical uncertainties displayed are based on one standard deviation of the solution analyses, whereby each solution was analyzed four times by the DCP-AES instrument. The results appear to be higher than one would initially expect for the types of soils analyzed; however, it must be kept in mind that what has been analyzed is an effective CEC, rather than a classical CEC.

Table 5 shows that the exchange pH's generally range from 3.5 to 5.5, which demonstrates why a classical CEC method (measured at pH 7) would not give a true indication of the exchange capacity of the soils, as it exists in the field. As further proof of the reliability of the results obtained, two samples were re-tested using DI water as the displacing solution, instead of $BaCl_2$, and, as expected, the exchange that took place was negligible. This shows that the $BaCl_2$ method is actually yielding a true effective CEC.

A comparison of the effective CEC results obtained in this paper to CEC results obtained by others for similar soils demonstrates the difference that field pH can have on CEC determinations for acidic soils. Faust (1963) determined the CEC's of sediments from the vicinity of Brookhaven National Laboratory in Upton, Long Island, New York and found that they generally ranged from 1 meq/100g to 11 meq/100g. In addition, Douglas and Trela (1979) determined the CEC's of Pine Barrens soil horizons in New Jersey and found an average CEC of 5.8 meq/100g, with a range from approximately 2 meq/100g to 17 meq/100g. The effective CEC results obtained in this paper are generally an order of magnitude higher than the above classical CEC results, which shows the importance of determining the effective CEC when analyzing acidic soils.

Sample#	Na	K	Ca	Mg	Fe	Effective CEC	Exchange pH
1	35.7 +- 0.7	2.4 +- 0.1	12.2 +- 0.5	10.3 +- 0.2	<0.1	60.6 +- 1.5	5.2
1 duplicate	31.0 +- 0.5	2.2 +- 0.2	11.2 +- 0.4	8.9 +- 0.1	<0.1	53.3 +- 1.2	5.4
1 triplicate	35.2 +- 1.4	2.2 +- 0.1	12.4 +- 0.7	10.3 +- 0.4	<0.1	60.1 +- 2.6	5.3
2	25.8 +- 0.4	3.8 +- 0.1	14.6 +- 0.8	9.9 +- 0.3	<0.1	54.1 +- 1.6	5.1
3	15.0 +- 0.4	2.4 +- 0.1	13.5 +- 0.9	12.3 +- 0.4	<0.1	43.2 +- 1.8	5.5
4	10.2 +- 0.3	1.5 +- 0.1	9.4 +- 0.6	7.0 +- 0.2	<0.1	28.1 +- 1.2	4.5
5	16.6 +- 0.7	2.1 +- 0.2	15.4 +- 0.6	10.9 +- 0.3	24.6 +- 1.4	69.6 +- 3.2	3.6
6	1.5 +- 0.1	1.2 +- 0.2	3.8 +- 0.6	1.6 +- 0.1	0.6 +- 0.1	8.7 +- 1.1	4.1
6 duplicate	3.0 +- 0.2	1.2 +- 0.1	4.2 +- 0.3	1.6 +- 0.1	0.2 +- 0.1	10.2 +- 0.8	4.3
7	36.4 +- 1.5	17.2 +- 0.7	19.4 +- 1.0	13.4 +- 0.4	0.4 +- 0.3	86.8 +- 3.9	3.5
7 duplicate	32.5 +- 0.5	14.2 +- 0.4	18.4 +- 0.6	12.1 +- 0.1	0.5 +- 0.1	77.7 +- 1.7	3.6
7 triplicate	32.0 +- 0.8	15.0 +- 0.1	17.6 +- 0.6	11.1 +- 0.2	0.5 +- 0.1	76.2 +- 1.8	3.5
8	5.5 +- 0.1	4.8 +- 0.1	17.6 +- 0.2	79.2 +- 1.6	130.9 +- 2.0	238.0 +- 4.0	2.7
9	10.1 +- 0.2	11.4 +- 0.3	8.0 +- 0.2	5.8 +- 0.3	0.4 +- 0.1	35.7 +- 1.1	4.2
10	34.1 +-0.6	6.3 +- 0.1	15.6 +- 0.2	16.9 +- 0.2	<0.1	72.9 +- 1.1	4.6

Table 5. Results of effective CEC and exchangeable cations analysis, as well as exchange pH's. All values are given in units of meq/100g. Uncertainties represent one standard deviation of the solution analyses, whereby each solution was analyzed four times.

As one would expect, the two Raritan clay samples have the highest effective CEC's, while the lowest values are found in the Magothy aquifer. The Raritan clay results are of the most interest, since the ground water chemistry changes so markedly after passage through the Raritan clay. The two highest Ca exchangeabilities are found in the Raritan clay, and two of the three highest Mg exchangeabilities are found there also. On the simplest of levels, what appears to be happening is the following: (Na+K)-rich waters are entering the Raritan clay from the Magothy aquifer, at the ground water divide, and while passing slowly through the Raritan clay, Na and/or K are exchanging with Ca and/or Mg on the clay surface. The result is a ground water that, as it enters the Lloyd aquifer, has higher Ca and Mg concentrations, which actually is the case (Table 4).

Geochemical/ Geological Importance

A question that should be looked at is whether or not it can be determined if the aquifers have retained a "signature" of their original depositional environments. The general idea postulated here is that ground water cation ratios (based in meq) tend to display the water types of their depositional environments. The reasoning behind this belief is the following: at the time of deposition, exchangeable sites on the accumulating sediments will become occupied by the dominant cations of the depositing water solution. Consequently, the occurrence of cation exchange within the aquifer releases the cation(s) into the ground water.

The Raritan Formation, which consists of both the Lloyd aquifer and the Raritan clay, was deposited under fluviodeltaic conditions in early Late Cretaceous time (Trapp, 1987). From observing the ground water chemistry data (Table 6), the Lloyd aquifer displays cation ratios which more closely resemble those of a continental "signature" than the other two aquifers. The (Na+K):Mg and (Na+K):Ca ratios for average Lloyd ground water are 1.6:1 and 1.4:1, respectively, which compare favorably with ratios that would be expected for an aquifer that was deposited under continental conditions (Table 6). Therefore, it appears that the Lloyd aquifer has retained a "signature" of its original depositional environment. However, it should be kept in mind that cation exchange taking place within the Raritan clay has a large impact on the chemistry of Lloyd ground water, and this effect may be masking any depositional "re-setting" that may have occurred.

The Magothy aquifer, which is of marine origin, has (Na+K):Mg and (Na+K):Ca ratios which more closely resemble those of a marine depositional environment than the ratios which were present for the Lloyd aquifer; however, they are not as high as one might expect. This is possibly due to a "re-setting" of the original "signature" by ground water passing through the Magothy aquifer, which had its origin as precipitation. Indeed, when one observes (Na+K):Mg and (Na+K):Ca ratios for the Magothy aquifer (Table 6) they are very close to those of both precipitation and the Upper Glacial aquifer.

	Ca:Mg	(Na+K):Mg	(Na+K):Ca
Continental	2.4	**1.0**	**0.4**
Marine	0.2	4.5	23.3
Precipitation	1.5	3.5	2.3
Average Upper Glacial	1.1	2.5	2.3
Average Magothy	1.1	2.7	2.4
Average Lloyd	1.2	**1.6**	**1.4**

Table 6. Cation ratios (based in milliequivalents) showing continental "signature" of the Lloyd aquifer. Continental figures are taken from data of world average river water (unpolluted) from Berner & Berner, 1987. Marine figures are taken from data of average seawater from Berner & Berner, 1987. Precipitation figures are taken from data from Schoonen & Brown, 1994.

CONCLUSIONS

Ground water chemistry data for Long Island shows that the Upper Glacial and Magothy aquifers have ground waters with very similar chemical compositions, while the Lloyd aquifer clearly has ground water with a different chemical composition. The explanation for this change in ground water composition lies in the Raritan clay, which acts as a leaky confining layer between the Magothy and Lloyd aquifers.

The Raritan clay has a very high effective CEC (Table 4), and, as a result, ground water passing from the Magothy aquifer to the Lloyd aquifer undergoes a change in composition. While passing slowly through the Raritan clay, Na and/or K in the water are exchanging with Ca and/or Mg on the clay surface, producing a ground water that as it enters the Lloyd aquifer has higher Ca and Mg concentrations.

In addition, ground water ratios (based in meq) of (Na+K):Mg and (Na+K):Ca for both the Upper Glacial and Magothy aquifers are very close to each other, as well as those for Long Island precipitation (Table 6). This most likely shows that the two aquifers no longer show a "signature" of their original depositional environments. Instead, it has been "re-set" by ground water passing through the aquifers, which originated as precipitation. The Lloyd aquifer, on the other hand, displays cation ratios which suggest that a "signature" of the original continental depositional environment has been at least partially preserved (Table 6).

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