

**Modeling Cations in a Contaminant Plume in Saturated Zone**

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by

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Abstract of the Thesis

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Contaminant plumes from different sources have different cation compositions and corresponding concentrations. The cations in a plume are strongly sorbed on sediments in saturated zone which will influence the rate of their transport dependent on their valence states and atomic structure. We developed a multi-component interactive model to simulate the sorption and transport of cations in a contaminant plume in subsurface groundwater area using the MATLAB computer program.

High concentrations of nitrate in groundwater become more and more a concern for geologists in Suffolk County and wastewater from septic tank-cesspool system and turfgrass fertilizer are the two major sources of nitrate in this area. We applied our model to predict the fate of cations accompany nitrate in contaminant plumes from wastewater and turfgrass leachate. The results show that the cation chemistry of groundwater in monitoring wells which are sampling close to the source of contamination is more reliable in characterizing the source than the groundwater from public wells.

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**Link to MATLAB Users Guide and Program  
for Cation Transport in a Contaminant Plume  
<http://www.geo.sunysb.edu/reports/matlab/>**

## List of Symbols

$1/i, 1/j,$	coefficients of components in chemical reaction;
$[],$	symbol to show the concentration of the element or compound inside;
$a_i$	effective diameter of the ion
$a, b, c$	convertible factor between $K_d^{Na}$ and $K_d^I$ according to the relation of $K_{NaI}$
$A, B, C, D, E, F, G$	parameters in polynomial
AEC	anion exchange capacity
$C_0^I$	total concentration of element $i$ in system;
$C_L^I$	concentration of element $I$ in liquid;
$C_S^I$	concentration of element $I$ on solid;
$\Sigma C_{L0}^I,$	total concentration of cations in liquid at the initial state;
$\Sigma C_{Le}^I,$	total concentration of cations in liquid at the equilibrated state;
$\Sigma C_{S0}^I$	total concentration of cation sorbed on sediment at the initial state;
$\Sigma C_{Se}^I$	total concentration of cation sorbed on sediment at the equilibrated stage
CEC	cation exchange capacity
$F,$	fraction of the liquid;
$I$	ionic strength
$I^{i+}$	cation $I$ in $i+$ valence state;
$(^{mI/nI})_{f,0}$	initial isotope compositions of element $I$ of the fluid
$(^{mI/nI})_{s,0}$	initial isotope compositions of element $I$ of the solid.
$I-X_i,$	exchanger site hold by cation $I$ , $-X_i$ is surface function group with negative charge $i$ ;
$K_{I/J},$	equilibrium coefficient for exchange reaction between $I^{i+}$ and $J^{j+}$ , also known as exchange coefficient for cation pairs $I/J$ ;
$K_d^{S/L},$	distribution coefficient for one element between solid and water;
$M, N$	temperature dependent constants for Debye-Huckle equation
$P$	porosity in volume fraction;
$P$	density in mass of cation per unit pore volume;
$\rho_s$	density of solid ;

$\rho_L$	density of liquid;
$\text{pH}_{\text{PZC}}$	value of pH at the point of zero charge
$R_I$	retardation coefficient
S-OH	surface Hydroxyl
S- OH <sub>2</sub> <sup>+</sup>	positively charge surface complex;
S-O <sup>-</sup>	negatively charge surface complex;
subscripts L	concentrations of component I in liquid
subscripts S	concentrations of component I sorbed on the solid grains
$z_I$	charge of I ion
$\alpha$	activity
$\gamma$	activity coefficient

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## **Chapter I: INTRODUCTION**

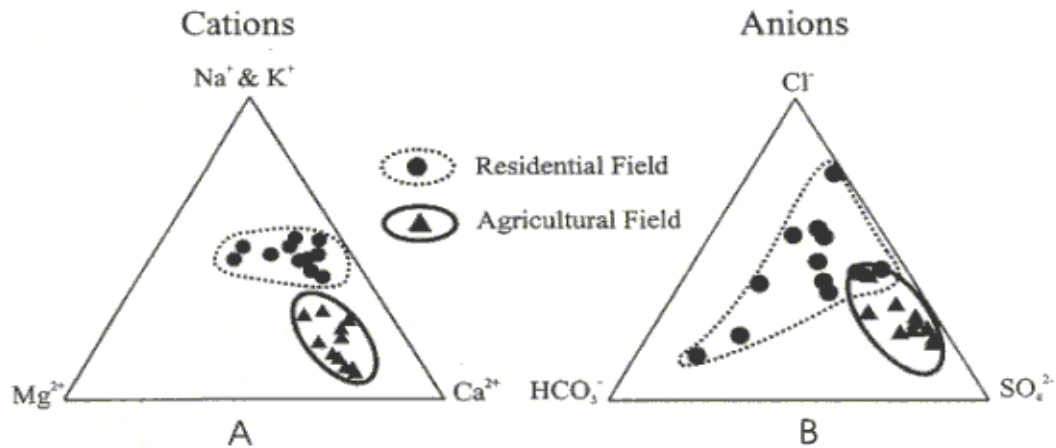
Groundwater is the only source for drinking water on Long Island outside of New York City. So water quality control is one of the major concerns. Along with development in Suffolk County, almost 70 percent of public water supply wells were rated as high, or very high for susceptibility to nitrates. By the standard of Environmental Protection Agency (EPA), if nitrogen as nitrate concentration is higher than 10 ppm, it may induce the occurrence of blue baby syndrome, a disease causing infants deprived of oxygen in blood.

The two main sources of nitrate in developed areas of Suffolk County are wastewater from septic tank-cesspool system and turfgrass fertilizer (Bleifuss, 1998; Boguslavsky, 2000; Hanson & Schoonen, 2001). Our original purpose for this study is to find a way to determine whether wastewater or turfgrass fertilizer is the major contributor to the high nitrate level in Suffolk County groundwater.

A previous study on Long Island (Bleifuss, 1998) suggested that the major ion chemistry of groundwater is affected by the land use of the recharge zone (Figure 1).

Groundwater recharged in residential and agricultural areas was found to have distinct fields. Agricultural area produced a calcium-enriched water while residential area produced water contained more sodium.

These results suggested that both cation chemistry and anion chemistry may be used to distinguish the land use type of their source areas. I doubted the validity of this conclusion because, as we know, anions are good tracers of groundwater, especially for Cl, because they are conservative in saturated zone while cations are always useless due



**Figure 1. Ternary diagrams of the major cations and anions in groundwater according to land use (Bleifuss, 1998)**

to the intensive sorption by the sediments in aquifer. Most of cations are retarded and their velocities in saturated zone are consequently much slower than those of anions. So anions and cations can not show similar information. The goal of this study was to evaluate whether the cation chemistry in nitrate contaminant plumes can be used to distinguish the land use type of their source areas in Suffolk County.

Groundwater is recharged mainly by rain. The composition of groundwater can be viewed as that of rain plus any constituents added as the rain water infiltrates into the aquifer. In our study we are interested in the effects of the addition of wastewater and leachate from turfgrass fertilizer application area.

To predict the fate of cations from the contaminant plume along the flow line, we developed a model using MATLAB to simulate the non-linear, multi-component sorption and one-dimension transport of cations in the contaminant plume in saturated zone. The program neglected the effects of dispersion and diffusion which caused dilution or

mixing between rainwater and any contaminant plume, because groundwater collected from the public supply well is a product of mixing between modified rainwater and the contaminant plumes. The contaminant flow model is evaluated by comparison with previous results from some soil column experiments (Voegelin, et al. 2000).

Before I created my own model, I considered popular software used in hydrology to see if I could have used these existed tools, for instance, MODFLOW, MT3D and RT3D. I found that none of them could simulate competitive sorption for multicomponent with transport of the plume simultaneously.

## **Chapter II: THEORY**

### **2.1 Chemical Background**

During the movement of cations in a contaminant plume in saturated zone, the plume will go with the groundwater in the same direction at the same speed. However, owing to sorption effects, most cations in the plume are not transported at the same speed as groundwater, which is called as retardation.

Sorption influences the transport of cations in the saturated zone. It involves mass exchange between the plume and the sediment. There are two separate types of sorption: if the cation is held primarily at the sediment surface, it is known as adsorption; or if the cation is incorporated into the mineral structure, it is known as absorption. The process in which a cation in solution replaces a sorbed cation is known as cation exchange.

In a groundwater system that has been stable for a significant period of time, the cations in groundwater and those sorbed on sediments are in equilibrium. When the contaminant plume enters the groundwater (figure 2), the plume displaces the groundwater and the cations in the plume exchange with those sorbed on the sediments (figure 3). In our model the flow line of the plume is assumed to be made up of multiple sequential cells and the fluid volume filled in the vacancies of the whole flow line is supposed to be one pore volume. The cells had the same unitless configuration. When the solution enters a cell, cation exchange occurred between the contaminant plume and the sediment. After reaction, the fluid from the first cell with a new composition will move into the next cell and the cation exchange process is repeated until the fluid pass through the whole pore volume. The plume and cells have no linear dimension, volume, or time scale except those parameter described by pore volume, porosity, cation exchange

capacity and the composition of the cations sorbed on the sediments and in the modified contaminant plume. When the water along the flow line all gains the composition of the initial contaminant, the plume and sediments are in equilibrium and their compositions will be stable.

To simulate the sorption process of multi-cations in a contaminant plume with equilibrated sediments in groundwater, the following factors must be known:

- a. Cation exchange capacity-----CEC
- b. Selectivity coefficients
- c. Rate of exchange reaction
- d. Cation composition and concentration of cations in groundwater, on sediments and in contaminant plume

### **2.1.1 Cation exchange capacity-----CEC**

The cation exchange capacity of sediments is a measure of the quantity of cations sorbed onto or within sedimentary particles that can be easily exchanged. The value of the cation exchange capacity is dependent on the type of material and pH (Table 1). Boguslavsky (2000) found that the glacial sand on Long Island consists primarily of quartz. Quartz contributes about 3% to CEC, whereas the grain coatings which make 0.8 to 13% of the sediment weight contribute about 97% to the CEC. The grain coatings consist of variable fractions of illite, kaolinite, and chlorite, with minor organic matter and iron compounds. Consequently, the value of CEC varies as a function of grain size and weight percentage of the coating.

Wastewater from cesspool, as an example, comes through the open bottom of cesspool into the vadose zone and then enters the saturated zone, where it forms a plume moving with groundwater. During this process, the cations in the plume exchange with those on sediments.

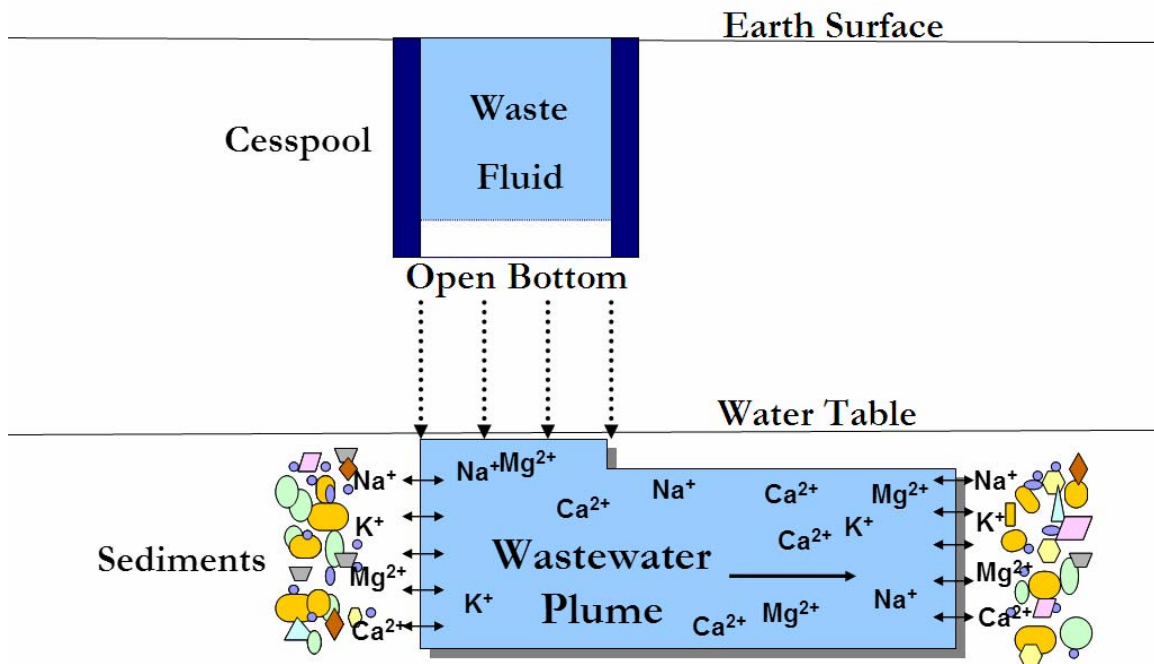
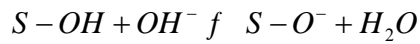
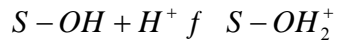


Figure 2. Transport and sorption of cations in a wastewater plume

Table 1. Published cation exchange capacity of different types of material (<sup>2</sup>Appelo and Posma, 1999 and <sup>1</sup>Boguslavsky, 2000)

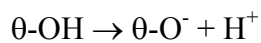
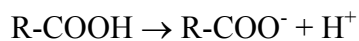
<i>CEC, meq/100g</i>	
Sand without coating on Long Island <sup>1</sup>	0.27
Kaolinite <sup>2</sup>	3-15
Illite <sup>2</sup>	20-50
Chlorite <sup>2</sup>	10-40
Goethite & Hematite <sup>2</sup> ;	up to 100
Organic matter <sup>2</sup>	150-400 (at pH=8)

For cations, the fraction sorbed is a function of pH. At different pH values, the  $H^+$  or  $OH^-$  in solution will react with the surface hydroxyls, inducing the variation in CEC of the sediments (Kehew, 2001), according to the following reaction:

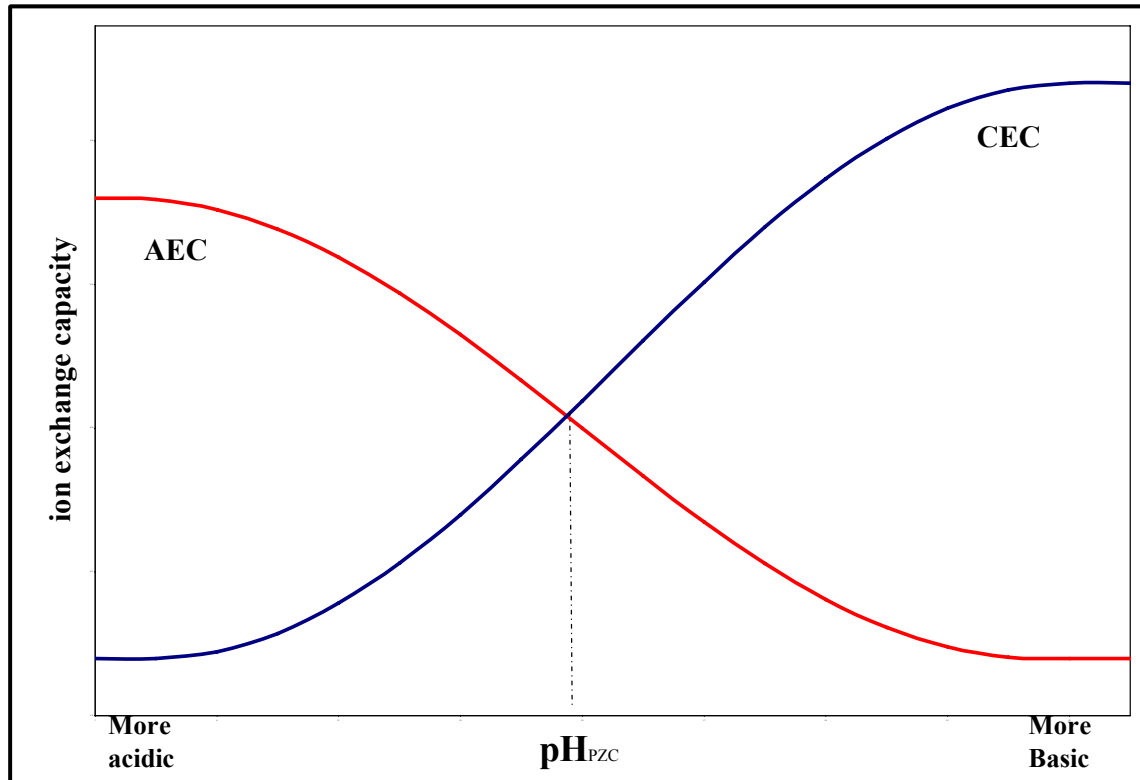


At lower pH, the net surface charge is positive; and as pH rises, the net charge becomes negative. There is some pH value at which the net charge is zero, known as pH at point of zero net charge,  $pH_{PZC}$ . The value of  $pH_{PZC}$  is a property of the material. The magnitude of the ion exchange capacity depends on the relation between the solution pH and the  $pH_{PZC}$  of the material as shown in figure 3. When the pH is greater than  $pH_{PZC}$ , the material has a negative surface charge and cation exchange capacity dominates. At pH less than  $pH_{PZC}$ , the value of anion exchange capacity (AEC) will be greater.

The  $pH_{PZC}$  of the most common materials making up the sands and coatings in Suffolk County (Table 2) is mostly lower than the average pH value of about 5 in this area (Stoeber and Dean, 1999; Boguslavsky, 2000), Organic matter dissociates in groundwaters with pH of 4 to 8 and are negatively charged (Aiken and Kuniandy, 2002; Carling and Gustafsson, 1998).



These minerals therefore behave generally as cation exchangers. The  $pH_{PZC}$  of iron oxides is higher than the pH in groundwater. However, the fraction of iron oxides on grains is extremely low and so they can be ignored (Boguslavsky, 2000).



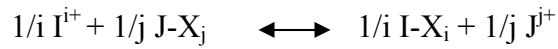
**Figure 3. Relationship between pH and  $pH_{PZC}$  and their effects on CEC and AEC**

**Table 2.  $pH_{PZC}$  of clay minerals and common soil matter (Davis and Kent, 1990; Parks, 1967; Hussain, et al. 1996; Stumm and Morgan 1981).**

	$pH_{PZC}$
Quartz, $SiO_2$	2.9 (Davis and Kent)
Kaolinite	4.6 (Parks)
Illite	2.5 (Hussain)
Chlorite	3 (Hussain)
Hematite, $\alpha-Fe_2O_3$	8.5 (Davis and Kent)
Goethite, $\alpha-FeOOH$	7.3 (Davis and Kent)
$Fe(OH)_3$	8.5 (Stumm and Morgan)

### 2.1.2 Selectivity coefficients

Cation exchange is described by:



(see list of symbols for the definitions)

The selectivity coefficient is:

$$K_{i/j} = \frac{[I - X_i]^{1/i} [J^{j+}]^{1/j}}{[I^{i+}]^{1/i} [J - X_j]^{1/j}}$$

For example, the selectivity coefficient with respect to sodium is shown in Table 4. The lower the value of  $K_{Na/I}$ , the less easily the cation  $I^{i+}$  on the exchanger site will be replaced by  $Na^+$ .

**Table 3. Selectivity coefficients for  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  based on the exchange with  $Na^+$  (Appelo and Postma, 1999)**

Ion $I^{i+}$	$K_{Na/I}$ Typical value (Range)
$K^+$	0.20 (0.15-0.25)
$Mg^{2+}$	0.50 (0.4-0.6)
$Ca^{2+}$	0.40 (0.3-0.6)
$Sr^{2+}$	0.35(0.3-0.6)
$NH_4^+$	0.25(0.2-0.3)

### 2.1.3 Rate of exchange reaction

Voegelin, et al.(2000) reported that at the general temperature and pressure of most groundwater, it takes only minutes to achieve equilibrium between cations in aqueous solution and cations sorbed on sediment surfaces.

#### **2.1.4 Cation compositions and concentrations in groundwater, on sediments and in contaminant plume**

During the passage of the contaminant plume through the aquifer, I assumed that the CEC value of sediment did not change either with time or along the flow line. The proportion of CEC, however, was allowed to vary both in time and space for each cation. In a plume containing a variety of inorganic metal cations, interactive competition was allowed between them for the available charged sites on sediments. Ionic potential, i.e. the charge of a cation over its ionic radius was one of the most significant factors that determined the affinity of a particular cation to the soil surface. The relative ionic potentials of major cations in a contaminant plume is  $\text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+}$ , reflecting preferential sorption sequence.

The cations in a contaminant plume changed along the flow line due to sorption. Before the contaminant plume enters the aquifer, the cations it carries exchange with those on sediments and eventually come to equilibrium. So in fact, the composition of cations in groundwater determines the proportion of CEC for the cations on the sediment. When the contaminant plume enters the aquifer, the composition of cations in plume is different from that in groundwater, so the former equilibrium is destroyed and the charged sites on sediment will be redistributed. After new equilibrium is established, the proportion of CEC for the cations on the sediment will reflect the composition of cations in the plume this time. However, because the number of charged sites on given sediments is fixed, the total equivalent concentration of cations sorbed on the sediment and those in the plume will not change.

## 2.2 Cations of Interest

The major cations in both contaminant plumes from septic tank-cesspool system or turfgrass area and ambient groundwater were  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (Munster, 2004). In this case, due to my special interests in  $\text{NO}_3^-$  and isotopes in groundwater, I also considered sorption of  $\text{NH}_4^+$ , for it is an important form of N which is readily to be transformed into  $\text{NO}_3^-$  and  $\text{Sr}^{2+}$ . The model, however, was not restricted to these cations. It can be applied to any cation assemblage of interest.

## 2.3 Chemical Equations

The plume has no actual physical length and can consist of any number of cells. Increasing the number of cells allows more resolution in describing the composition of the cations along the path of the plume. A cell is defined by a porous solid phase and a liquid occupying the available porosity. Like the plume, the cell has no physical dimensions except for its proportion of the plume. Every cell in our model is an individual unit for reaction. As the contaminant enters the plume, the cations in the liquid and solid within a cell are equilibrated with each other. The liquid passes through the cells in sequence and the cation exchange and equilibrated process are repeated. The reaction in a cell can be described by following mathematical equations:

The model relies on mass balance for each cation I;

$$C_0^I = FC_L^I + (1-F)C_S^I \quad (1)$$

F is the mass fraction of liquid in one pore volume, and  $C_0^I$  is the total concentration of a particular ion I in the system interested. F is given by:

$$F = \frac{P\rho_L}{P\rho_L + (1-P)\rho_S} \quad (2)$$



































































