

AN ANALYTICAL TRANSPORT MODEL  
OF THE CARBONATE SYSTEM  
IN THE SUBSURFACE ENVIRONMENT

A Thesis Presented

By

David John Popielarczyk

Submitted to the Graduate School of the  
University of Massachusetts in partial fulfillment  
of the requirements for the degree of

MASTER OF SCIENCE

February 1987

Department of Civil Engineering  
Environmental Engineering Program  
University of Massachusetts at Amherst



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January 21, 1987

Arthur Screpetis  
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Dear Art:

Here is a copy of a Master's Thesis "An Analytical Transport Model of the Carbonate System in the Subsurface Environment," by David Popielarczyk. David received partial support for this work on MDWPC Project No. MDWPC 87-01. We intend to publish the research in the referred literature, and I'll keep you posted on its progress.

Sincerely,

David Ostendorf, Sc.D.  
Associate Professor

enclosure

cc: M.S. Switzenbaum

DO:ld

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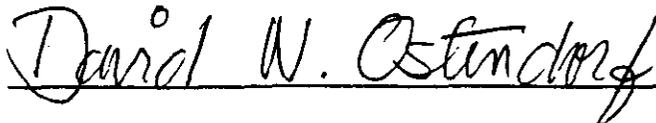
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## ABSTRACT

An analytical contaminant model is developed in this study to model the transport of the carbonate system in the subsurface environment under constant pH conditions. This model describes the transport of bicarbonate and carbon dioxide in the horizontal x-direction and in the vertical z-direction. Once the model is developed, it is calibrated and tested using data from a contaminated aquifer in Babylon, New York with reasonably accurate results. The source of this contamination is a municipal landfill serving the town of Babylon. The vertical transport model yields an independent, physically based estimate for the loss of gaseous carbon dioxide to the atmosphere. The degassing rate is explicitly related to the vertical dispersivity of the aquifer, and is in agreement with the empirical behavior noted by prior investigators.

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## NOTATION

- a activity coefficient.
- A Debye-Hückel constant.
- b unsaturated zone thickness, m.
- B landfill width, m.
- c transported contaminant conc., moles/liter or  $\text{kg/m}^3$ .
- c' depth averaged contaminant conc., moles/liter or  $\text{kg/m}^3$ .
- c1 carbon dioxide conc., moles/liter or  $\text{kg/m}^3$ .
- c2 bicarbonate conc., moles/liter or  $\text{kg/m}^3$ .
- D vertical hydrodynamic dispersion coefficient in the aquifer,  $\text{m}^2/\text{s}$ .
- $D_a$  vertical hydrodynamic dispersion coefficient in the unsaturated zone,  $\text{m}^2/\text{s}$ .
- $D^*$  vertical molecular diffusion,  $\text{m}^2/\text{s}$ .
- F mass flux,  $\text{kg/m}^3$ .
- g gravitational acceleration,  $\text{m/s}^2$ .
- G population growth rate, cap/s.
- h aquifer thickness, m.
- I ionic strength.
- k permeability,  $\text{m}^2$ .
- k1 equilibrium coefficient, moles/liter.
- $K_H$  Henry's law constant, moles/liter-atm.
- L mass of carbon lost from the aquifer,  $\text{kg/m}^3$ .
- n porosity.
- p partial pressure of carbon dioxide, atm.

P user population, cap.  
 q discharge of water per unit of aquifer width,  $m^2/s$ .  
 r constant reflecting a variation in hydrated radius.  
 R ideal gas constant, atm-l/mole- $^{\circ}K$ .  
 S contaminant loading factor, kg/s-cap.  
 sc specific conductance, micromhos/cm.  
 t time, s.  
 T temperature,  $^{\circ}C$  or  $^{\circ}K$ .  
 U Debye-Hückel constant.  
 v average linear velocity, m/s.  
 w ion charge.  
 x far field horizontal distance downstream of pollutant source, m.  
 z vertical distance, m.  
 $\alpha$  transverse dispersivity, m.  
 $\beta$  underlying aquiclude slope angle.  
 $\delta$  error.  
 $\delta'$  mean error.  
 $\epsilon$  recharge velocity, m/s.  
 n water table elevation below source position, m.  
 $\gamma$  velocity modification factor.  
 $\lambda$  first order decay constant, 1/s.  
 $\nu$  kinematic viscosity,  $m^2/s$ .  
 $\rho$  gaseous carbon dioxide conc., moles/liter or  $kg/m^3$ .

$\sigma$  standard deviation.

$z$  landfill length, m.

#### SUBSCRIPTS

$c$  characteristic quantity.

$Cl$  chloride property.

$H^+$  hydrogen ion property.

$HCO_3$  bicarbonate property.

$i$  population growth segment condition.

$s$  conditions at far field source.

$sd$  shutdown condition.

## CHAPTER I

### INTRODUCTION

#### Objective

An analytical model will be developed in this study to describe the transport of the components of the carbonate system under constant pH conditions in the subsurface environment. Once developed, this model will be tested using data available from a United States Geological Survey (USGS) study performed on a contaminated plume located in Babylon, New York. The source of this contaminated plume is a municipal landfill that serves the town of Babylon.

#### Background

There is a growing concern over the widespread groundwater contamination problems facing practically every area in the country. The severity of the groundwater contamination problem is magnified by the fact that groundwater use has been growing faster than population in the recent past from 12.4 trillion gallons per year in 1950 to almost 30 trillion gallons per year in 1975 (Sharefkin et al., 1984). Murray and Reeves (1977), in a study of water use in the United States in 1975, determined that groundwater use accounts for 39 percent of the total water

use in the country. Also, between 40 and 50 percent of the population in the United States depends on groundwater as its primary source of drinking water (United States Water Resources Council, 1980). Thus, groundwater contamination is a problem that has the potential to affect a large portion of the population in this country.

Legislation reflecting environmental concern during the past several decades has focused mainly on attempting to restrict air and surface water pollution. This legislation has led to an increase in disposal to the subsurface environment (National Academy of Sciences, 1984). Estimates by the National Academy of Sciences (1984) suggest that 0.5 to 2 percent of groundwater in the conterminous United States may be contaminated. This study also suggests that this contamination often occurs in areas where the water is relied upon the most heavily. A study by the United States Environmental Protection Agency (1980) lists the following sources of groundwater contamination:

1. landfills
2. surface impoundments
3. septic systems
4. agriculture
5. underground injection
6. accidental leaks and spills
7. mining
8. artificial recharge
9. highway de-icing
10. salt water encroachment

The most widely used means of solid waste disposal are landfills (National Academy of Sciences, 1984). The Environmental Protection Agency (1980) estimated that

200,000 landfills and dumps receive 150 million tons per year of municipal solid wastes and 240 million tons per year of industrial wastes. Due to poor design and/or management landfills are major contributors of groundwater contamination (Javandel et al., 1984). Water percolating through the landfill comes into contact with refuse and subsequently becomes contaminated. This contaminated water, or leachate, is a potential health and environmental hazard.

Only recently have the impacts of landfill pollution been felt. As a result, the newer landfills are designed to reduce the risk of groundwater contamination. However, the design of the majority of existing landfills does not reflect a concern over potential groundwater contamination problems. Of the 18,500 municipal land disposal sites operating in 1974, only about 20 sites were lined and only 60 sites had leachate treatment facilities (United States Environmental Protection Agency, 1977).

In order to effectively deal with groundwater contamination an understanding of its fate is essential. By developing a transport model of a contaminant spatial and temporal predictions may be made of future contamination as well as of the history of existing contamination. This type of information is an important prerequisite for the proper design, impact assessment, and regulation of present and future landfill facilities.

### Approach

Prior to model development a literature review will be performed so that the work done in this study may be placed in an appropriate perspective in relation to past work. Following a review of past work in this area a one dimensional conservative contaminant model will precede the development of the more complex, depth varying carbonate system species model. Once the carbonate system model has been developed the model will be calibrated and tested using available horizontal and vertical data. The success of the model is then assessed in discussion and concluding chapters.

## CHAPTER II

### LITERATURE REVIEW

#### Overview

There are four general modeling approaches that may be applied to contaminant transport: 1) analytical modeling; 2) numerical modeling; 3) physical modeling; and 4) analog modeling (Prickett, 1979). Of these four modeling approaches physical and analog modeling have decreased greatly in popularity in recent years. This decrease in popularity is due, in part, to the emergence of the digital computer as an analytical aid in groundwater modeling. Because of the small role of these two techniques in groundwater modeling they will not be discussed in this study.

Numerical models (Bachmat et al., 1980) are becoming increasingly popular with the recent advances in computer technology and reductions in computer cost. The benefits of numerical models are obvious. Their computational power make them well suited for the complex groundwater problems that often arise. However, numerical models are not without drawbacks.

Baski (1979) expressed his belief that computer groundwater (numerical) models can be sources of incorrect information. He stated that there are three means by which

this may occur: 1) incorrect models are frequently chosen by the modeler; 2) clients may become disillusioned with model results as a result of modeler oversell in the early stages of project planning and budgeting; and 3) often the numerical code of the model is unknown to the user, obscuring the model methodology and underlying assumptions. Another disadvantage of numerical models is that they rely on a great deal of data in order to develop a proper analysis (Hamilton et al., 1985). Often this quantity of reliable data is not available (Prakash, 1982). These numerical modeling drawbacks represent some of the reasons why the development of analytical models should be considered, either along with numerical models, or separately.

Hamilton et al. (1985) compared an analytical model, a finite element model, and a method of characteristics, finite difference model. As a part of their study a cost/benefit analysis was performed on these three models. Hamilton et al. (1985) concluded that the analytical solution was the most effective on this basis. They further stated that an analytical model is an obvious first step in mass transport models, and that in many situations the analytical model is enough. Only when the situation complexities and project goals truly warrant a more refined analysis should one be used. Wilson and Miller (1978) believed, as well, that many problems could be handled by

analytical techniques. Wilson and Miller (1978) suggested that prior analytical work would help in the choice of model boundaries and grid densities for numerical models. Gelhar and Collins (1971) stated that when the limited precision of data that describe most field situations is considered, simple analytical estimates of dispersive effects may be as meaningful as detailed numerical solutions. Thomson et al. (1984) noted that, in the case of numerical models, for large advection/dispersion ratios (Peclet numbers) computational costs rise as well as computer core requirements, while in the case of analytical models a large advection/dispersion ratio facilitates analysis.

There are two general categories of contaminants that are modeled: 1) nonreactive contaminants; and 2) reactive contaminants. The transport of a nonreactive dissolved constituent in a saturated, porous medium is a balance of advective transport, diffusive transport, and storage change (Freeze and Cherry, 1979). Advective transport represents the transport of a solute by the organized motion of the fluid while diffusive transport represents the transport of the solute by the random motion of the fluid. The transport of a reactive dissolved constituent in a saturated, porous medium is simply the nonreactive transport case with the addition of a reaction or group of reactions.

### Reactive Modeling

Due to the complexities of the groundwater environment and, in many cases, of the groundwater plume itself, reactive processes commonly occur during contaminant transport. The reactive processes may be divided up into two basic categories: 1) equilibrium controlled reactions; and 2) nonequilibrium (kinetic) controlled reactions (Rubin 1983). These two categories may be further divided into the subcategories of homogeneous and heterogeneous reactions. Finally, the heterogeneous reactions may be divided into the subcategories of surface and classical reactions. A total of six different classes of reactions may be distinguished in this manner (See figure 1) (Rubin, 1983).

The first group of reactions that will be considered are those that are governed by kinetics. Reactions that proceed at rates of a comparable magnitude (or lower) to those of the other processes occurring in the aquifer that change the solute concentration are considered to be governed by reaction kinetics. Reactions that are irreversible are also controlled by kinetics (Rubin, 1983). Perhaps the most well known of these are radioactive decay reactions, which are often quite slow, depending on the isotope involved. Modeling of radioactive substances is well documented because the kinetics of radioactive decay reactions are very simple. Unfortunately, the kinetics of most subsurface reactions are quite complex and are

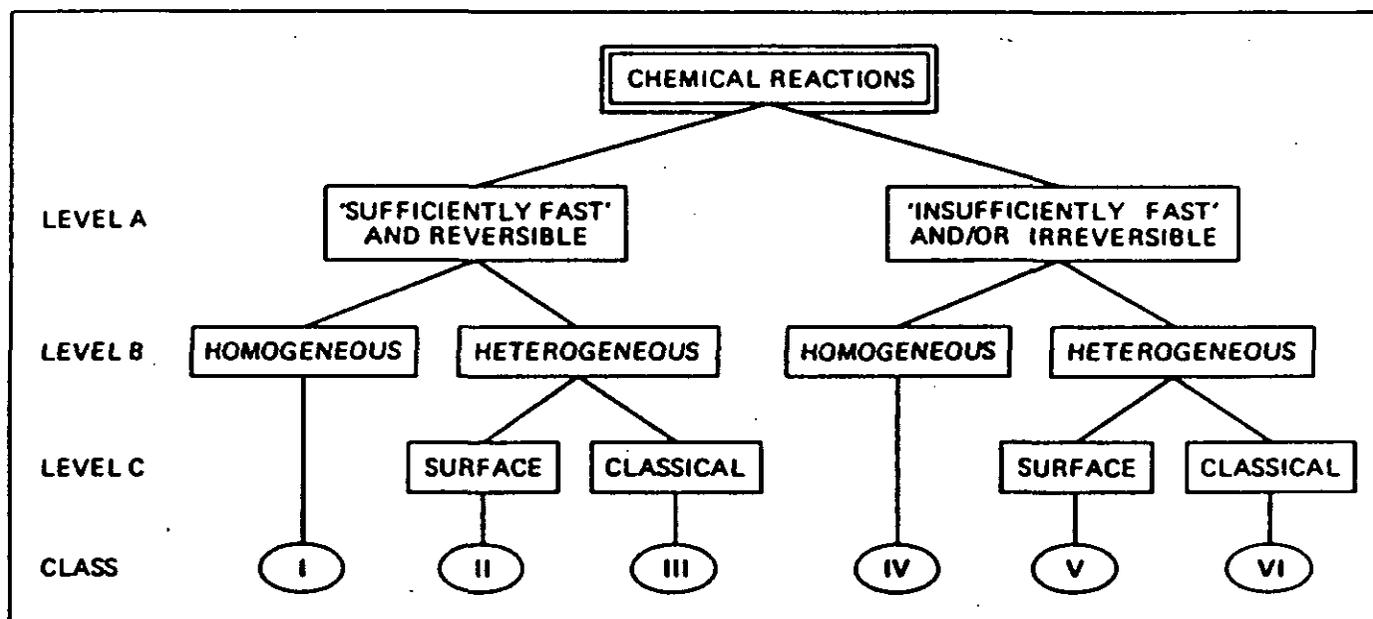


FIGURE 1: REACTION CLASSIFICATIONS

(RUBIN, 1983)

therefore difficult to quantify (Anderson, 1979). Rasmuson (1984) developed an analytical model of the migration of radionuclides in fissured rock. The reaction term in the transport equation is described by a first order decay relation. McLaren (1969) developed a transport model governed by the reaction rates occurring between ammonia ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), and nitrate ( $\text{NO}_3^-$ ) in an idealized soil column. The reaction rates were of a comparable magnitude to the flow rate through the soil column. Therefore, the reactions describing this process were governed by kinetics.

The second group of reactions that will be considered are those that are governed by equilibrium. In this case the reaction rates are fast relative to the rates of the other processes occurring in the aquifer that change the solute concentration. Therefore, the contaminants under investigation may be assumed to be at equilibrium at every point in the aquifer. These reactions must also be reversible for the equilibrium assumption to be valid (Rubin, 1983).

Jennings et al. (1982) observed that there are two basic techniques that may be used to solve equilibrium controlled transport problems. The first technique is to incorporate the equilibrium chemistry with the governing differential equations to produce a set of complex and perhaps nonlinear differential equations. This technique

works well if there are few reacting solute species. However, as the number of reacting solute species increases, the number and complexity of the simultaneous differential equations increases. The second technique is to solve a coupled set of algebraic chemical equilibrium equations and differential transport equations. This coupling technique is very powerful in that numerical solutions may be developed that can account for several types of reactions that may be occurring at one time. Grove and Wood (1979) used this approach to develop a numerical transport model that could handle ion exchange, dissolution, precipitation, and complexation reactions. Cederberg et al. (1985) developed a computer model, TRANQL, that could account for sorption, ion exchange, and complexation reactions. In order to analytically solve a transport problem using the second technique the differential equations must be transformed into algebraic equations. The resulting set of equations may be solved simultaneously (Rubin, 1983).

In the case where the equilibrium chemistry is inserted directly into the governing differential transport equation(s) two types of reactions have been studied: 1) heterogeneous reactions; and 2) homogeneous reactions. The majority of recent research on equilibrium controlled reactions in groundwater transport models has focused on heterogeneous reactions. In the papers presented by Rubin

and James (1973) and Valocchi et al. (1981), a one-dimensional, numerical transport model was developed for ion exchange reactions in the subsurface environment. Valocchi et al. (1981) developed a steady, one-dimensional flow model of the transport of municipal effluent injected into the subsurface environment. The ion exchange reactions were based on chromatography theory as presented by Helfferich and Klein (1970). Valocchi et al. (1981) showed that for a binary homovalent case (two species sorbing with valence states of magnitude one) the mobile components of the two species may be summed to produce a conservative value that may be more simply transported. The sorbed and aqueous species are related through an equilibrium constant.

Analytical solutions to equilibrium-controlled homogeneous reactions applying the first technique cited by Jennings et al. (1982) have received little attention in recent past in comparison to the heterogeneous equilibrium-controlled reactions. Jennings et al. (1982) developed an equilibrium-controlled groundwater model applying the technique of inserting the algebraic chemical relations directly into the differential transport equation(s) for the transport of metals and ligands undergoing complexation and sorption reactions. Rubin (1983) compared the various mathematical formulations for the six different classes of reactions that were mentioned previously (see figure 1) that may occur in the subsurface environment. For the

homogeneous equilibrium-controlled reaction Rubin (1983) developed a transport equation for each conservative species or ion. In this way it was not necessary to include a reaction term. These transport equations could be altered through a simple linear transformation to produce a new set of algebraic equations that could be solved simultaneously with the existing algebraic chemical equilibrium equations. Rubin (1983) also noted that as an alternative to transforming the differential transport equations, the algebraic chemical equilibrium relations could be inserted into the differential transport equations, producing a set of differential equations that would need to be solved simultaneously.

#### Analytical Solution Methods

There are several analytical solution techniques that are used to determine the transport of a contaminant in groundwater. These techniques will be divided into three categories: 1) the linear reservoir method; 2) the differential method; and 3) the near field-far field method.

The lumped parameter technique, as described by Gelhar and Wilson (1974), attempts to describe the transport of chloride by modeling the groundwater system as a single linear reservoir. Mercado (1976) applied this approach to the transport of chloride and nitrate in Israel. The linear reservoir is analogous to a completely stirred tank reactor

(CSTR). In this reservoir the groundwater and contaminant are completely mixed and spatial variation of contaminant is unknown. However, in most cases, groundwater systems do not act like linear reservoirs, but exhibit plug flow behavior. Thus, in order to more closely approximate plug flow behavior the groundwater system may be divided up into several completely mixed cells. This is referred to as the distributed parameter approach (Anderson, 1979), and was modeled by Lederer (1983). The greater the number of cells, the closer the flow model will describe plug flow behavior (Montgomery Consulting Eng., Inc., 1985). The weakness of this modeling technique is that this approach only gives an estimate of plug flow and spatial variation is known only to a limited extent. Another weakness of this technique is that diffusive transport can not be accounted for using this method. The strength of this technique is that it is more applicable to cases where there is a limited amount of data, and groundwater systems often fall into this category. Also, the degree of confidence in the data available may not justify using a more complex method such as the differential technique.

The differential technique utilizes a mass balance about a differential element rather than about a linear reservoir. In this way a complete description of the spatial and temporal variation of the contaminant may be determined. Diffusive transport may be handled by this

method. In general, the analysis is more difficult for problems formulated in this manner since partial differential equations are formed, rather than ordinary differential equations, which are formed in the case of a linear reservoir.

Several individuals have applied the differential method in order to develop transport models. Bear (1979) developed several differential analytical solutions for conservative, first order decay, and sorbing contaminants. Valocchi (1986) described the transport of a sorbing contaminant in a well field and Prakash (1982) modeled a sorbing contaminant undergoing radioactive decay. Gelhar and Collins (1971) developed an analytical model utilizing the differential technique that describes uniform, radial, and spherical conservative contaminant flow while Wilson and Miller (1978) modeled the conservative contaminant hexavalent chromium originating from plating wastes in Long Island, New York. Rasmuson (1984) modeled the migration of radionuclides in fissured rock using the differential method.

The near field-far field approach is a combination of the linear reservoir technique and the differential technique. This approach is analogous to that used by surface water quality modelers (Fischer et al., 1979) in modeling solute transport. It is well suited for contaminant transport problems that involve a point source

of contamination, such as a landfill. In the case of a landfill, the near field control volume is directly below the landfill. This region is modeled as a linear reservoir since it is difficult to determine spatial variations in this area. The output contaminant leaves the near field and enters the well-behaved far field region at the source plane. The far field region is modeled using the differential solution method. The near field-far field technique has the potential to utilize the benefits of the linear reservoir technique and the differential technique. This solution technique was used by Ostendorf et al. (1984) and Ostendorf (1986) to model contaminant flow emanating from landfills and infiltration beds, respectively. Ostendorf et al. (1984) modeled chloride (conservative contaminant) and bicarbonate (undergoes first order decay) while Ostendorf (1986) modeled chloride (conservative contaminant), boron (undergoes linear adsorption), and synthetic detergents and total nitrogen (undergo first order decay).

## CHAPTER III

### CONSERVATIVE CONTAMINANT TRANSPORT

#### Overview

As an introduction to the modeling of the more complex coupled, nonconservative transport model the transport of a single conservative species, specifically chloride, will be developed. A near field-far field approach analogous to that used by surface water quality modelers will be used to model the contaminant transport (Fischer et al., 1979). The near field zone represents a linear reservoir in which contaminant and groundwater mix. The spatial variation of concentration is unknown in this region. The input source of the near field region is a constant source of contaminant, in this case a landfill. The near field control volume is directly below the landfill. The output contaminant leaves the near field and enters the well-behaved far field region at the source plane. The far field region, which consists of fully mixed one-dimensional flow, will be the focus of the analytical modeling, given known source conditions. A sketch of the near field-far field method as it applies to a landfill is presented in figure 2.



### Near Field

As suggested by figure 2, the landfill is an areally distributed contaminant source of width B and length  $\zeta$  in the direction of groundwater flow. The landfill pollution input is routed into the underlying near field, which is taken as an initially pure linear reservoir with output concentration  $c_s$ . In keeping with the simple modeling approach, P is the user population while S is a constant contaminant loading factor reflecting the per capita generation rate of pollution.

The integrated conservation of contaminant mass for the linear reservoir is a balance of storage, output, and input terms

$$(\zeta nh_s) \frac{dc_s}{dt_s} + q_s c_s = SP/B \quad (3.1)$$

The use of  $t_s$  for time reflects the function of the near field model as a far field source term, where s indicates source conditions. n represents aquifer porosity, h represents aquifer thickness, and q represents the discharge of water per unit of aquifer width. Equation (3.1) holds for a reactive or conservative pollutant since near field time scales are much shorter than far field time scales. Contaminants showing appreciable, relatively rapid decay in the near field will vanish in the far field and will not be of interest as a consequence. The simplicity of the near

field mass equation allows for the inclusion of linearly varying population growth segments, i.e.

$$P = P_i + G_i (t_s - t_{si}) \quad (t_{si} < t_s < t_{si+1}) \quad (3.2)$$

with population  $P_i$  at time  $t_{si}$  and growth rate  $G_i$  valid for the  $i$ th segment of time.

Equations (3.1) and (3.2) may be combined to yield

$$dc_s/dt_s + c_s/t_c = c_i (1 + t_s/t_i)/t_c \quad (3.3a)$$

$$t_c = \tau/v_s \quad (3.3b)$$

$$c_i = S(P_i - G_i t_{si}) / (Bq_s) \quad (3.3c)$$

$$t_i = P_i/G_i - t_{si} \quad (3.3d)$$

The landfill response time  $t_c$  characterizes the time required for concentrations to change noticeably in the near field. The user population parameters  $c_i$  and  $t_i$  will change for each growth segment. Equation (3.3) is to be solved subject to pure initial and matching conditions  $c_{si}$  between growth segments

$$c_s = 0 \quad (t_s = 0) \quad (3.4a)$$

$$c_s = c_{si} \quad (t_s = t_{si}) \quad (3.4b)$$

This nonhomogeneous, linear, first order ordinary differential equation with constant coefficients has the solution (Boyce and DiPrima, 1977)

$$c_s = c_1 \{ (1 - t_c/t_1) [1 - \exp(-t_s/t_c)] + t_s/t_1 \} \quad (0 \leq t_s \leq t_{s1}) \quad (3.5a)$$

$$c_s = c_i \{ 1 + (t_s - t_c)/t_i + c_{li} \exp[(t_{si} - t_s)/t_c] \} \quad (t_{si} \leq t_s \leq t_{si+1}) \quad (3.5b)$$

$$c_s = c_{sd} \exp[(t_{sd} - t_s)/t_c] \quad (t_{sd} \leq t_s) \quad (3.5c)$$

$$c_{li} = c_{si}/c_i - 1 - (t_{si} - t_c)/t_i \quad (3.5d)$$

with source concentration  $c_{sd}$  at the time of shutdown  $t_{sd}$  of the facility.

The model simplifies considerably for a constant user population ( $P_1$ ) with zero growth rate

$$c_s = SP_1 [1 - \exp(-t_s/t_c)] / (Bq_s) \quad (0 \leq t_s \leq t_{sd}) \quad (3.6)$$

The post shutdown behavior is still given by equation (3.5c). The source plane concentration may be used as an initial concentration in the far field analysis.

### Far Field

The far field region consists of a shallow, unconfined aquifer underlain by a gently sloping aquiclude, subject to a constant, immiscible recharge. The hydraulics are steady and one dimensional. In order to be able to model the transport of a contaminant in an aquifer the groundwater hydraulics must first be a known function. The steady conservation of water mass equation in one dimension, subject to constant recharge  $\epsilon$ , is expressed as

$$q = q_s + \epsilon x \quad (3.7)$$

where  $x$  is the distance downgradient of the source plane. The discharge per unit width  $q$  and the average linear velocity  $v$  in the aquifer are related through the equation

$$v = q / (nh) \quad (3.8)$$

where  $n$  and  $h$  are as defined previously. The aquifer thickness can be expressed as

$$h = h_s + x \tan \beta - \eta \quad (3.9)$$

Equation (3.9) describes an aquifer with a plane, sloping, underlying aquiclude of small angle  $\beta$  with respect to the horizontal as sketched in figure 2.  $\eta$  is the change

in water table elevation with respect to the source plane value. Equations (3.7), (3.8), and (3.9) may be combined to form the relationship for the average linear velocity given below (Ostendorf et al., 1984):

$$v = v_s [1 + \gamma (x/h_s)] \quad (3.10a)$$

$$\gamma = \epsilon h_s / q_s + q_s v / (k g h_s) - \tan \beta \quad (3.10b)$$

The three terms in equation (3.10b) represent recharge, headloss, and bottom slope effects, respectively. The effects are modest, so that  $\gamma(x/h_s)$  is small.  $\nu$ ,  $k$ , and  $g$  represent kinematic viscosity, permeability, and gravitational acceleration, respectively.

Contaminant transport through the far field may now be studied since the steady hydraulic transport of the aquifer is a known function of downgradient distance. With the assumption that the recharge will form a fresh water lens above the plume, the conservation of contaminant mass equation is simply a balance of advection and storage change in the absence of longitudinal dispersion (Ostendorf et al., 1984)

$$v \partial c / \partial x + \partial c / \partial t = 0 \quad (3.11)$$

The reaction term is zero in this equation since chloride is a conservative species, while longitudinal dispersion is relatively unimportant for continuous, areally distributed pollution sources like landfills. In this equation  $c$  represents the concentration of the chloride ion in the aquifer. Note the presence of the average linear velocity, which was determined through an analysis of the aquifer hydraulics, in the conservation of contaminant mass equation.

A method of characteristics solution technique will be used to produce two more easily solvable differential equations from equation (3.11) (Eagleson, 1970). The method of characteristics is based on the chain rule (equation (3.12)

$$dc/dt = \partial c / \partial t + (\partial c / \partial x) (dx/dt) \quad (3.12)$$

$dc/dt$  represents temporal change in a frame of reference moving at speed  $dx/dt$ . The two equations that are developed by comparing equations (3.11) and (3.12) are as follows:

$$dc/dt = 0 \quad (3.13a)$$

$$dx/dt = v \quad (3.13b)$$

where  $v$  is given in equation (3.10a).

Equation (3.13a) may be integrated to show that  $c$  is a constant value along the length of the aquifer equal to the source plane value

$$c=c_s \quad (3.14)$$

Equation (3.13b) may be integrated from source values  $x_s=0$  and  $t_s$  to any subsequent  $x$  and  $t$  values in the far field to produce the algebraic relationship

$$t-t_s = x[1-\gamma x/(2h_s)]/v_s \quad (3.15)$$

Equations (3.14) and (3.15) are necessary and sufficient to describe the temporal and spatial variations in chloride concentration along the length of the aquifer in the far field.

## CHAPTER IV

### CARBONATE SYSTEM SPECIES TRANSPORT

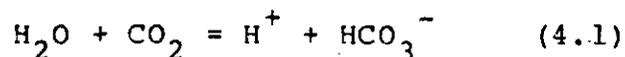
#### Overview

The second case that will be studied is the transport of a single binary system. The system that will be investigated is the carbonate system. In this model inorganic carbon leaching from a landfill enters the near field region and is transported into the far field region where a high gaseous carbon dioxide concentration slowly diffuses out of the aquifer (Kimmel and Braids, 1980). Traditionally, inorganic carbon enters the system through infiltration of water in contact with the atmosphere, through decay of organic matter, and through respiration of plant roots. However, in the case that will be looked at in this study, the majority of the inorganic carbon will be attributed to the decomposition of incinerator ash from landfills. The inherent assumption in this analysis, and the driving force for the reactions that occur in this system, is that the concentration of aqueous carbon dioxide in the aquifer is greater than the aqueous carbon dioxide value that would be found under equilibrium conditions. This condition is easily met at landfills that accommodate ash disposal.

The species that may exist in solution in the aquifer

are carbon dioxide (aqueous  $\text{CO}_2$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ), carbonate ( $\text{CO}_3^{--}$ ), hydroxide ( $\text{OH}^-$ ), and hydrogen ion ( $\text{H}^+$ ). However, carbonic acid, which is formed through the reaction of aqueous carbon dioxide and water, is approximately 0.1 percent of the  $\text{CO}_2(\text{aq})$  concentration, and is therefore insignificant in the analysis. In other words, very little carbonic acid is formed in this reaction.  $\text{CO}_3^{--}$  and  $\text{OH}^-$  concentrations will also be negligible in this analysis since these species are found in insignificant quantities under the pH conditions that will be of concern in this study (neutral to slightly acidic) (Stumm and Morgan, 1981). A constant pH assumption will be used in this analysis so that the number of unknown species will be reduced to two. The constant pH assumption is reasonable if the aquifer is well buffered.

At this point, only two species are left to consider in this system: aqueous carbon dioxide and bicarbonate. These two species are related through the reaction shown below:



The rate at which this reaction reaches equilibrium is extremely rapid as compared to the carbon dioxide diffusion rate. The diffusion rate is on the order of one year while the rate at which the above reaction reaches equilibrium is approximately 20 seconds (Stumm and Morgan, 1981).

Therefore, the carbonate system species may be considered to be at equilibrium at any instant in time in the far field region of the aquifer. The equilibrium equation for the reaction involving the two unknown species is as follows:

$$k_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (4.2a)$$

$$k_1 = 10^{-6.31} \text{ moles/liter} \quad (4.2b)$$

The equilibrium constant  $k_1$  is weakly dependent on temperature and ionic strength. The value shown in equation (4.2b) is for a temperature of  $14^\circ\text{C}$  and a specific conductance of 1500 micromhos/centimeter (see appendix). This equilibrium constant value is reasonably representative of leachate plumes and will be adopted in this study.

The same assumptions that were necessary for the conservative contaminant model will be necessary for the carbon species transport model. The model will be developed for an initially pure, underlying, shallow, unconfined aquifer with a plane, sloping bottom under steady, one-dimensional hydraulic conditions. The aquifer must be relatively shallow so that concentration gradients in the vertical direction resulting from differential density effects may be considered insignificant (Wilson and Miller, 1978). Dispersion will be neglected in the direction of advective transport. The assumption that dispersion is

insignificant in this analysis may be justified by assuming that the source of pollution is continuous rather than instantaneous. This is based on the fact that the driving force of dispersion is the concentration gradient and that large concentration gradients occur for instantaneous sources of contamination, such as an accidental spill, but not for continuous sources of contaminant, such as a landfill (Gelhar and Wilson, 1974).

In order to keep the carbonate system transport model from becoming excessively complex several additional restrictions must be placed on the aquifer. The amount of dissolvable bedrock in the area that can effect the carbonate system (such as calcite or dolomite) will be assumed to be negligible. This assumption is necessary because the kinetics of these precipitation /dissolution reactions are very difficult to quantify (Stumm and Morgan, 1981). The temperature must remain constant throughout the analysis since the equilibrium constant ( $K_1$ ) varies with changes in temperature. Also, the ionic strength of the groundwater must be approximately constant since equilibrium constants vary with ionic strength (Butler, 1982). The biological activity in the aquifer will be assumed to be negligible since biological activity may effect carbon concentration. As a result of the restrictions placed on the aquifer the landfill is the only source of carbon while the atmosphere is the only carbon sink.

In order to model the transport of the carbonate system, again, the aquifer hydraulics must first be known. The aquifer hydraulics are identical to those of the chloride transport example and are described by equations (3.10a) and (3.10b).

#### Carbonate Speciation

The transport of the carbonate system, with constant pH, is based on the transport of the carbon species. The modeling is divided into two parts: 1) depth varying vertical transport, and 2) depth averaged horizontal transport. For these transport cases the variable  $c_1$  will represent the aqueous carbon dioxide concentration, the variable  $c_2$  will represent the bicarbonate concentration, and the variable  $c$  will represent the sum of  $c_1$  and  $c_2$ .

$$c_1 = [\text{CO}_2(\text{aq})] \quad (4.4a)$$

$$c_2 = [\text{HCO}_3^-] \quad (4.4b)$$

$$c = c_1 + c_2 \quad (4.4c)$$

This total carbon species concentration,  $c$ , will be the focus of the transport model. Once the total carbon species concentration is a spatially and temporally known function through the two modeling steps, the individual carbon

species may be determined through the equilibrium relationship (equation (4.2a)). The total carbon concentration  $c$  is related to the aqueous carbon dioxide concentration through the following equation:

$$c = c_1 (K_1/[H^+] + 1) \quad (4.5)$$

The loss of carbon to the atmosphere due to degassing is dependent on the gaseous carbon dioxide concentration gradient between the water table and the ground surface in the unsaturated zone. This inorganic carbon mass flux,  $F$ , may be roughly estimated by the following gaseous diffusion relationship (Hillel, 1982)

$$F = -D_a \rho / b \quad (z=0) \quad (4.6a)$$

$$\rho = p / (RT) \quad (4.6b)$$

with temperature  $T$ , unsaturated zone thickness  $b$ , and gas constant  $R$ . The gaseous diffusivity  $D_a$  will be about  $10^{-5}$   $m^2/s$  in magnitude (Hillel, 1982), while the gaseous carbon dioxide density,  $\rho$ , and partial pressure,  $p$ , will be related by the ideal gas law at the water table. Henry's law equates  $p$  to the aqueous carbon dioxide concentration at the water table by the following relationship:

$$cl = K_H p \quad (4.7a)$$

therefore,

$$cl = (K_H RT) \rho \quad (4.7b)$$

Note that the Henry's law constant is a weak function of temperature, and, for the purposes of this study, will be taken as independent of ionic strength. At a temperature of  $T = 287^\circ\text{K}$ , an ideal gas constant of  $R = 0.00821 \text{ atm-l/mole-}^\circ\text{K}$ , and a Henry's law constant of  $10^{-1.32} \text{ moles/l-atm}$  at  $T = 287^\circ\text{K}$  equations (4.6) and (4.7) suggest that  $cl$  and  $\rho$  will be roughly equal in size. Therefore, the flux of inorganic carbon through the unsaturated zone at the water table will be approximately given by

$$F = -D_a cl/b \quad (z=0) \quad (4.8)$$

#### Depth Varying Vertical Transport

The depth varying vertical transport model is the first of two modeling steps that will be used to determine the temporal and spatial variation in carbon dioxide and bicarbonate concentrations along the length of the aquifer in the far field region. In this step the transport of the total carbon species concentration  $c$  in the vertical direction  $z$  will be modeled.

The conservation of mass equation for the total carbon may be expressed as

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial z^2} = 0 \quad (4.9)$$

and is a balance of storage change, advective flux in the x-direction, and dispersive flux in the z-direction, respectively. Note the presence of the linear velocity,  $v$ , which was determined through a hydraulic analysis, in the conservation of contaminant mass equation. Dispersive flux in the x-direction is considered negligible since a landfill is a continuous source of pollution (Prakash, 1982). The only transport mechanism in the z-direction is the dispersive flux, by definition. The coefficient of hydrodynamic dispersion,  $D$ , can be expressed in terms of two components (equation (4.10a))

$$D = \alpha v + D^* \quad (4.10a)$$

$$D = \alpha v_s \quad (4.10b)$$

where the first term represents vertical dispersion through random velocity affects which result from small scale heterogeneities, and the second term represents diffusion through random molecular motion (Freeze and Cherry, 1979).  $\alpha$  is defined as a characteristic property of the porous

medium known as the dynamic vertical dispersivity or simply vertical dispersivity (Freeze and Cherry, 1979). Equation (4.10b) suggests that a constant dispersion coefficient will be adopted for this study, on the premise of rapid flow ( $\alpha v \gg D^*$ ) and a constant first order velocity ( $v$  is approximately equal to  $v_s$ ). Note that there is no reaction term in equation (4.9). The reaction term may be set equal to zero in this equation because total carbon is being transported. The only reactions that are taking place are between the two components that make up the total carbon concentration. Therefore, the total carbon concentration does not change with respect to the reaction between the two carbon species. A method of characteristics solution technique will be used for this model as it was used for the conservative contaminant model. Upon comparing equation (4.9) with the method of characteristics relation developed in chapter 3 (equation (3.12)), two more easily solvable equations may be formed, the first of which is simply the frame trajectory, which was also developed in chapter 3 (equation (3.13b)). The second equation that is formed is the governing equation for the depth varying vertical transport model in the moving reference frame

$$\partial c / \partial t - D \partial^2 c / \partial z^2 = 0 \quad (4.11)$$

The governing equation is in the form of the well known diffusion equation.

Two boundary conditions and one initial condition are necessary to properly define the problem. These conditions are listed below:

$$\partial c / \partial z = 0 \quad (z=h, t \geq t_s) \quad (4.12a)$$

$$D \partial c / \partial z = D_a c / (Kb) \quad (z=0, t \geq t_s) \quad (4.12b)$$

$$c = c_s \quad (t = t_s) \quad (4.12c)$$

The first boundary condition states that there is no flux through the bottom of the aquifer. The second boundary condition states that the flux through the saturated zone is equal to the flux through the unsaturated zone at the top of the aquifer. This boundary condition may be simplified for the usual case of a strongly diffusive unsaturated zone which efficiently carries off contamination at a relatively low concentration

$$D_a \gg D \quad (4.13a)$$

therefore,

$$c = 0 \quad (z=0) \quad (4.13b)$$

The initial condition (equation (4.12c)) states that the concentration is a constant value equal to the source concentration.

A separation of variables solution technique may be utilized to solve this transport problem as summarized in the appendix. This technique is based on the assumption that the spatial and temporal variation of the total carbon concentration may be expressed as two independent functions. One independent function is solely a function of depth while the other independent function is only a function of time. This method yields a Fourier series solution of the form

$$c = 4c_s/\pi \sum_{j \text{ odd}} \{ \exp[-a_{1j}(t-t_s)]/j \} \{ \sin[j\pi z/(2h)] \} \quad (4.14a)$$

$$a_{1j} = [j\pi/(2h)]^2 D \quad (4.14b)$$

Equation (4.14a) may be expressed in terms of the bicarbonate concentration,  $c_2$ , as

$$c_2 = 4c_{2s}/\pi \sum_{j \text{ odd}} \{ \exp[-a_{1j}(t-t_s)]/j \} \{ \sin[j\pi z/(2h)] \} \quad (4.15)$$

### Depth Averaged Horizontal Transport

The depth averaged horizontal transport model is the second of two modeling steps that will be used to determine the temporal and spatial variation in carbon dioxide and bicarbonate concentrations along the length of the aquifer in the far field region. In this step the transport of the total carbon species concentration in the downgradient x-direction will be modeled. This model will be developed by depth averaging the vertical transport solution (equation (4.14a)) and then applying the frame speed relationship, which was developed through a method of characteristics analysis.

The definition of depth averaging is presented by the following equation:

$$c' = 1/h \int_0^h c \, dz \quad (4.16)$$

The depth averaged form of equation (4.14a) is

$$c' = 8c_s/\pi^2 \sum_{j \text{ odd}} \exp[-a_{1j}(t-t_s)]/j^2 \quad (4.17)$$

Equation (4.17) may be expressed in terms of the bicarbonate concentration,  $c'_2$ , as

$$c'_2 = 8c_{2s}/\pi^2 \sum_{j \text{ odd}} \exp[-a_{1j}(t-t_s)]/j^2 \quad (4.18)$$

The bicarbonate concentration,  $c_2'$  may be related to the distance downgradient from the landfill through the frame speed relationship developed for conservative contaminant transport (equation (3.15)).

The depth averaged total carbon, as well as its bicarbonate and carbon dioxide species, exhibits exponential decay to leading order. This behavior is in accord with the ad hoc postulates of first order decay (Ostendorf et al., 1984 and Prakash, 1982) adopted by one-dimensional modelers. An examination of the horizontal transport equation yields an analytical estimate of the "decay constant",  $\lambda$ , to leading order, as

$$\lambda = \pi^2 \alpha v_s / (4h^2) \quad (4.19)$$

The flux of total carbon out of the contaminant plume may be estimated as well. By definition

$$F = -D \partial c / \partial z \quad (z=0) \quad (4.20a)$$

therefore,

$$F = -2Dc_s/h \sum_{j \text{ odd}} \exp[-a_{1j}(t-t_s)] \quad (4.20b)$$

The loss may be determined from the following integral:

$$L = \int_{t_s}^t F dt \quad (4.21)$$

The loss is evaluated as

$$L = 2Dc_s/h \sum_{j \text{ odd}} 1/a_{1j} \{ \exp[-a_{1j}(t-t_s)] - 1 \} \quad (4.22)$$

## CHAPTER V

### CASE STUDY: BABYLON LANDFILL

#### Background

The site under investigation in this study is a contaminated aquifer located downstream of a municipal landfill serving and located in the town of Babylon, Long Island. This landfill is bordered to the east and west by light industry and to the north and south by cemeteries. The location of this landfill is presented in figure 3. The contaminant plume was the subject of a study performed by the United States Geological Survey (Kimmel and Braids, 1980). This study, which was initiated in 1971, was performed in order to determine the effect of the Babylon landfill on groundwater quality.

The Babylon landfill, which began operation in 1947, was servicing a population of approximately 287,000 at the time of the study (Kimmel and Braids, 1980). Due to the anomalous surge of growth in the early 1960's three growth segments will be used for the Babylon area (Ostendorf et al., 1984). The data describing these periods of growth were taken from census figures for Suffolk County (U.S. Department of Commerce, 1977) and are presented in table 1. Measured chloride and carbonate values at the source plane were used in order to back calculate the constant

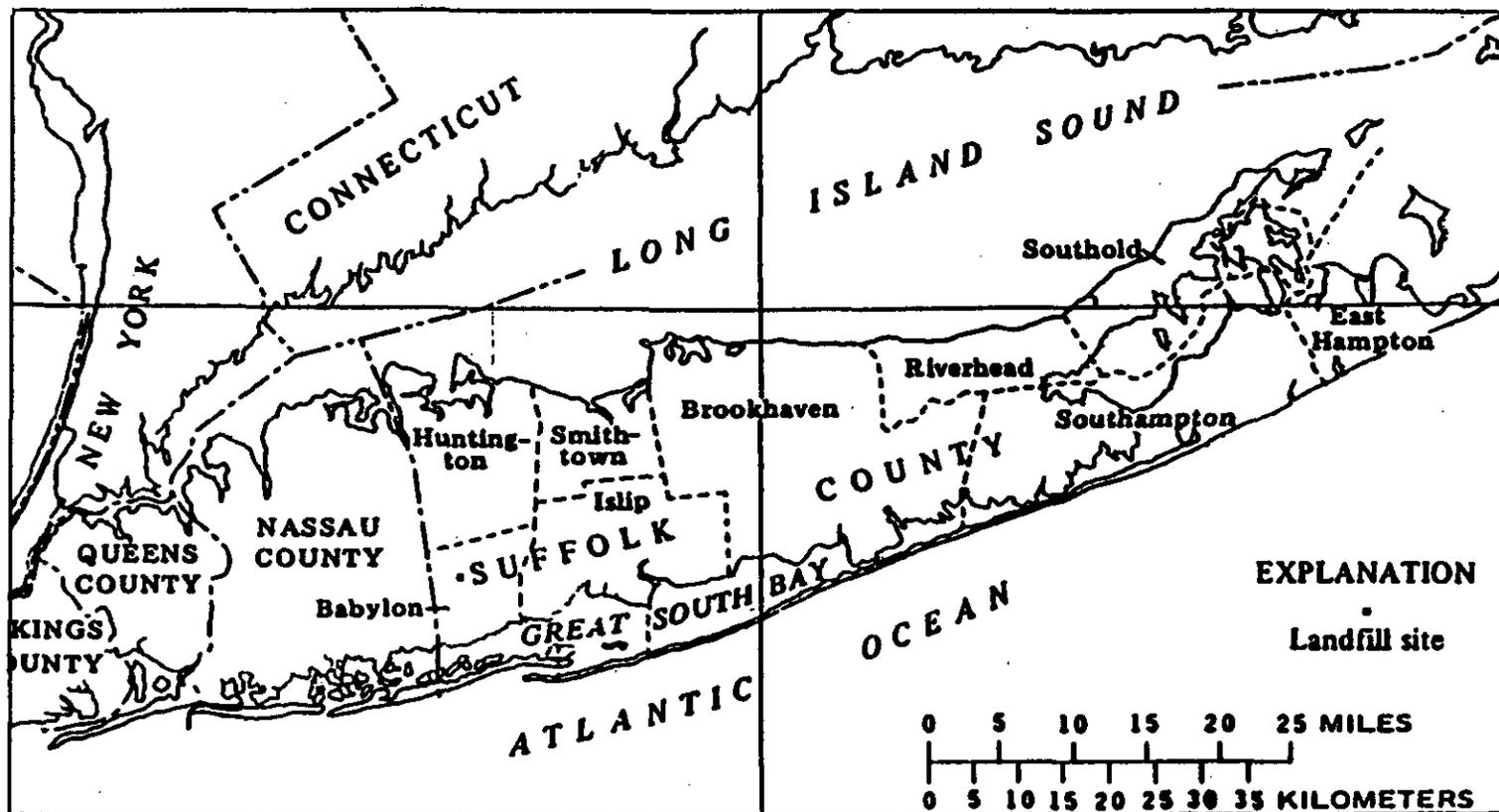


FIGURE 3: LOCATION MAP OF BABYLON LANDFILL

(KIMMEL AND BRAIDS, 1980)

TABLE 1: POPULATION SEGMENT PARAMETERS, BABYLON LANDFILL

	i		
	1	2	3
$t_{si}, s \times 10^8$	0	4.10	5.68
$G_i, \text{cap/s} \times 10^{-4}$	1.06	7.11	3.05
$P_i, \text{cap} \times 10^4$	5.44	9.79	21.00
$t_i, s \times 10^8$	5.13	-2.72	1.21
$c_i, \text{kg/m}^3 \times 10^6$	5.25S	-18.70S	3.53S
$c_{si}, \text{kg/m}^3 \times 10^6$	0	6.93S	11.60S

contaminant loading factor,  $S$ . The contaminant loading factor could then be used to calculate  $c_s$  values from the near field model. The landfill site may be described by a rectangle 505 meters wide ( $b$ ) by 689 meters long ( $z$ ) (Kimmel and Braids, 1975). The refuse deposited at this landfill is a combination of incinerated waste, scavenger (cesspool) waste, urban refuse, and a small amount of industrial refuse.

The contaminant plume, which has developed as a result of landfill leachate reaching groundwater, flows in the upper glacial aquifer, which is the saturated portion of an outwash plain. This outwash plain is associated with the terminus of a Wisconsin-age glacier. The unsaturated portion of the outwash plain is, on average, 4.6 meters thick. The upper glacial aquifer is approximately 22 meters thick at the landfill ( $h_s$ ) and approximately 24 meters thick near the end of the plume. The aquifer consists of coarse quartz sand, a small amount of heavy minerals, and some gravel. The deposit, which has a porosity,  $n$ , of approximately 27 percent and a permeability,  $k$ , of  $6.34 \times 10^{-11}$  meters<sup>2</sup> (Collins et al., 1972), is unusually uniform for outwash. The upper glacial aquifer is underlain by the Gardiners Clay. This clay formation extends upstream of the landfill and downstream of the plume. The Gardiners Clay is approximately 4 meters thick and acts as a barrier

to groundwater flow due to its low hydraulic conductivity (Kimmel and Braids, 1980).

The water table is less than nine meters below the ground at this site and there is usually no space between the water table and the bottom of the fill. As a result, there is no zone of aeration of the pure leachate prior to it reaching groundwater. The elevation of the water table varied considerably during the USGS study, however, this variation is negligible compared to the thickness of the aquifer. Therefore, the hydraulic gradient,  $dn/dx$ , may be taken as a constant value of 0.00161 at the source plane. The bottom slope of the aquifer is given as  $\tan \beta = 0.0027$  and the kinematic viscosity,  $\nu$ , is estimated at  $1.1 \times 10^{-6}$  meters<sup>2</sup>/second. In view of Darcy's Law, the average linear groundwater velocity at the source plane,  $v_s$ , was approximately  $3.37 \times 10^{-6}$  meters/second at the time of the study. With a groundwater recharge,  $\epsilon$ , of  $3.25 \times 10^{-9}$  meters/second the velocity modification factor,  $\gamma$ , which reflects recharge, headloss, and bottom slope effects becomes 0.00248 (Ostendorf et al., 1984).

The contaminant plume was 579 meters wide at the landfill and 213 meters wide at its terminus at the time of the United States Geological Survey Study. The plume extended 3049 meters downgradient from the landfill and extended the entire depth of the aquifer. A specific conductance of 400 micromhos/centimeter or greater was

interpreted as contaminated groundwater for the purposes of defining the plume. A site plan of the landfill and plume is presented in figure 4 (Kimmel and Braids, 1980).

Due to high concentrations of incinerated waste at the Babylon landfill high concentrations of inorganic carbon (carbon dioxide and bicarbonate) were present in the contaminant plume. The high carbon dioxide concentration diffuses out of the aquifer as the plume travels downgradient from the landfill. The models developed in the previous chapters will be used to model the chloride and bicarbonate species at this site. Figures 5 and 6 describe the horizontal variation in chloride and bicarbonate concentrations in the aquifer, respectively.

Nine chloride concentration values and ten bicarbonate concentration values that were recorded in 1974 at several locations downgradient from the landfill facility will be used to test the depth averaged horizontal transport models. Five bicarbonate concentration values were recorded in 1973 at well 12, which is approximately 1660 meters downgradient from the landfill, at depths varying from 5.8 to 23.8 meters. These data points will be used to test the depth varying vertical transport model.

#### Model Test: Horizontal Transport

The conservative horizontal transport model (equations (3.14) and (3.15)) is tested against measured chloride

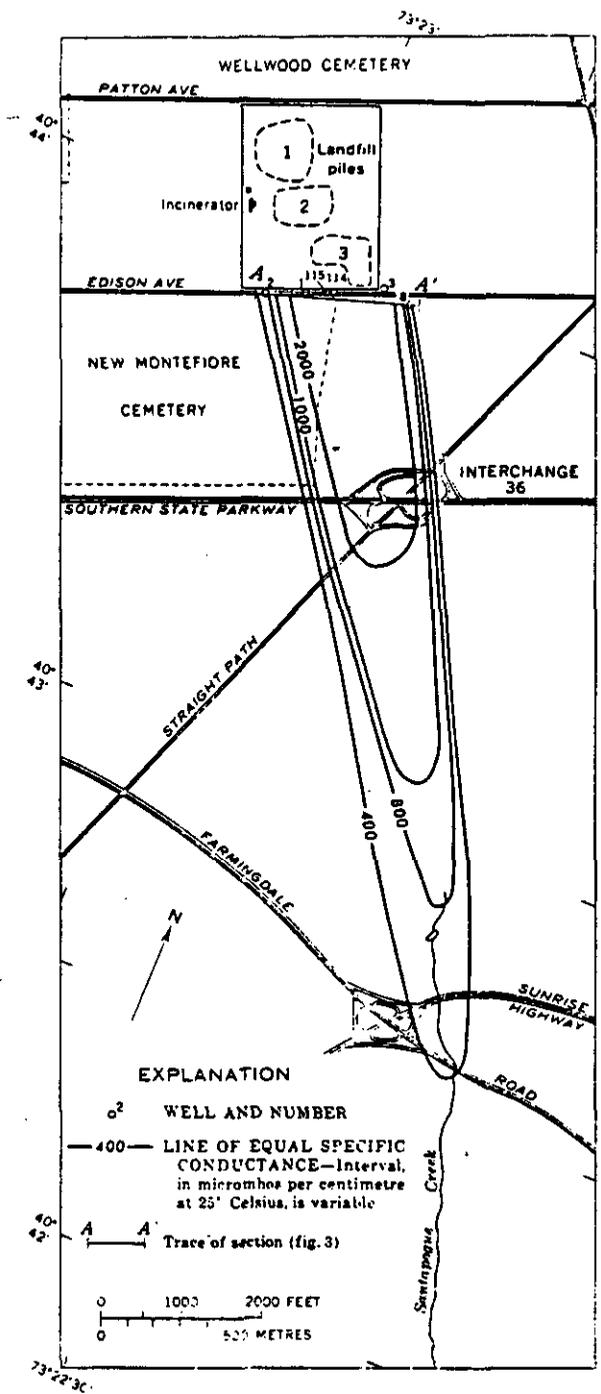


FIGURE 4: SITE PLAN OF THE BABYLON LANDFILL AND PLUME  
(KIMMEL AND BRAIDS, 1975)

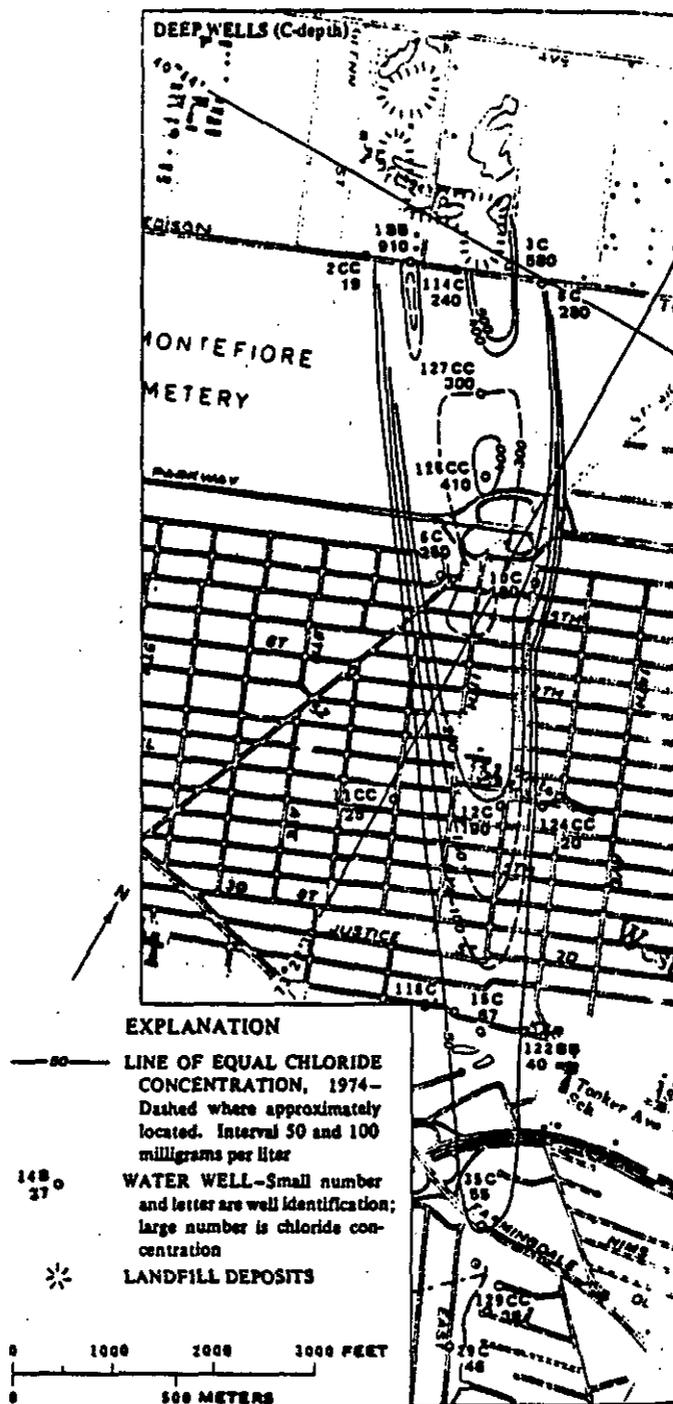


FIGURE 5: CHLORIDE VARIATION IN THE PLUME  
(KIMMEL AND BRAIDS, 1980)



FIGURE 6: BICARBONATE VARIATION IN THE PLUME  
(KIMMEL AND BRAIDS, 1987)

values. A measure of how well the model fits the given data points is given by the error associated with a comparison between the measured and calculated concentration values, by the mean error of the data, and by the standard deviation of the errors. The error  $\delta$  is defined as

$$\delta = (c - c_m) / c_m \quad (5.1)$$

with mean  $\delta'$  and standard deviation  $\sigma$  (Benjamin and Cornell, 1978)

$$\delta' = 1/j \sum \delta \quad (5.2a)$$

$$\sigma = (1/j \sum \delta^2 - \delta'^2)^{1/2} \quad (5.2b)$$

The chloride values are arrived at through two steps. The first step is to calculate the source concentrations and source times through a near field analysis (equation (3.5)). The results of the near field analysis are summarized in table 2. The second step is to use the near field results and apply them to far field transport in order to test the model. Table 3 summarizes the far field chloride test

TABLE 2: NEAR FIELD RESULTS--CHLORIDE TRANSPORT

WELL	X (METERS)	SOURCE TIME (SX10 <sup>8</sup> )	SOURCE CONC. (KG/M <sup>3</sup> )	GROWTH PERIOD
127	360	7.47	0.256	3
6	900	5.98	0.180	3
10	920	5.93	0.176	3
12	1570	4.26	0.100	2
124	1580	4.24	0.100	2
118	2180	2.83	0.073	1
122	2230	2.71	0.071	1
35	2810	1.47	0.044	1

TABLE 3: FAR FIELD RESULTS--CHLORIDE TRANSPORT

WELL	X METERS	MEASURED CONC. (KG/M <sup>3</sup> )	CALC. CONC. (KG/M <sup>3</sup> )	ERROR (%)
127	360	0.245	0.256	5
6	900	0.190	0.180	-6
10	920	0.170	0.176	4
12	1570	0.175	0.100	-43
124	1580	0.058	0.100	72
118	2180	0.055	0.073	34
122	2230	0.048	0.071	49
35	2810	0.057	0.044	-23
29	3190	0.044	0.023	-47

MEAN ERROR=5%

STANDARD DEVIATION=38%

results. The mean error of  $\delta'_{Cl} = 5\%$  and standard deviation of  $\sigma_{Cl} = 38\%$  indicate a good fit of the conservative, far field transport model to the measured chloride values (Ostendorf et al., 1984). No systematic error is present in the model, as shown by the random variation in the errors. A graph of chloride concentration vs. downgradient distance is presented in figure 7.

The calculated bicarbonate values are arrived at through the same steps presented for chloride transport modeling. Table 4 summarizes the near field results. The horizontal transport model is tested by calibrating the vertical dispersivity  $\alpha$  so that the depth averaged model predictions (equations (4.18) and (3.15)) will best fit the ten measured bicarbonate values. This is accomplished by choosing a dispersivity value so that the mean error equals zero. A measure of how well the model fits the given data points is given by the error associated with a comparison between the measured and calculated bicarbonate values for the calibrated coefficient and by the standard deviation of the errors. Table 5 summarizes the calibrated bicarbonate test results in the far field. A dispersivity of  $\alpha = 0.02$  m zeros the mean model error with a standard deviation of  $\sigma_{HCO_3} = 37\%$ . This value indicates good model accuracy, and is

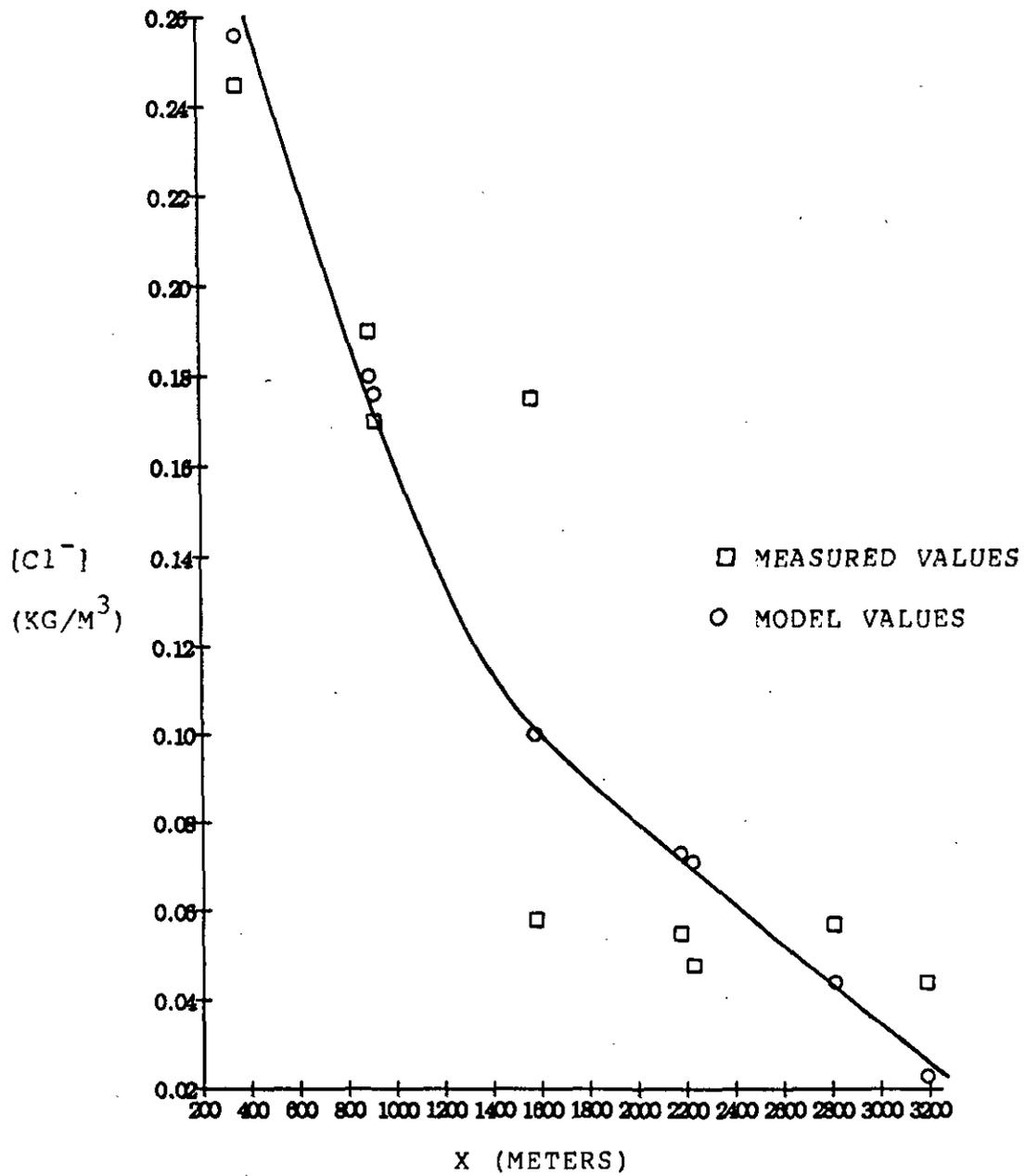


FIGURE 7: CHLORIDE CONC. VS. DOWNGRADIENT DISTANCE  
(OSTENDORF ET AL., 1984)

TABLE 4: NEAR FIELD RESULTS-BICARBONATE TRANSPORT

WELL	X (METERS)	SOURCE TIME (SX10 <sup>8</sup> )	SOURCE CONC. (KG/M <sup>3</sup> )	GROWTH PERIOD
127	360	7.47	0.487	3
128	630	6.72	0.416	3
6	900	5.98	0.341	3
10	920	5.93	0.336	3
124	1580	4.20	0.190	2
118	2180	2.83	0.140	1
122	2230	2.19	0.115	1
35	2810	1.47	0.083	1
29	3190	0.71	0.044	1
--	3320	0.47	0.030	1

TABLE 5: FAR FIELD RESULTS-HORIZONTAL BICARBONATE TRANSPORT  
 - $\alpha$  CALIBRATION-

WELL	X (METERS)	MEASURED CONC. (KG/M <sup>3</sup> )	CALC. CONC. (KG/M <sup>3</sup> )	ERROR (%)
127	360	0.540	0.420	-22
128	630	0.277	0.340	23
6	900	0.665	0.270	-59
10	920	0.154	0.270	75
124	1580	0.158	0.140	-11
118	2180	0.086	0.097	13
122	2230	*0.138	0.080	-42
35	2810	0.050	0.050	0
29	3190	0.020	0.030	50
--	3320	0.023	0.020	-13

\* CALCULATED FROM 1973 DATA

$$\alpha = 0.02 \text{ m}$$

STANDARD DEVIATION OF THE ERRORS=37%

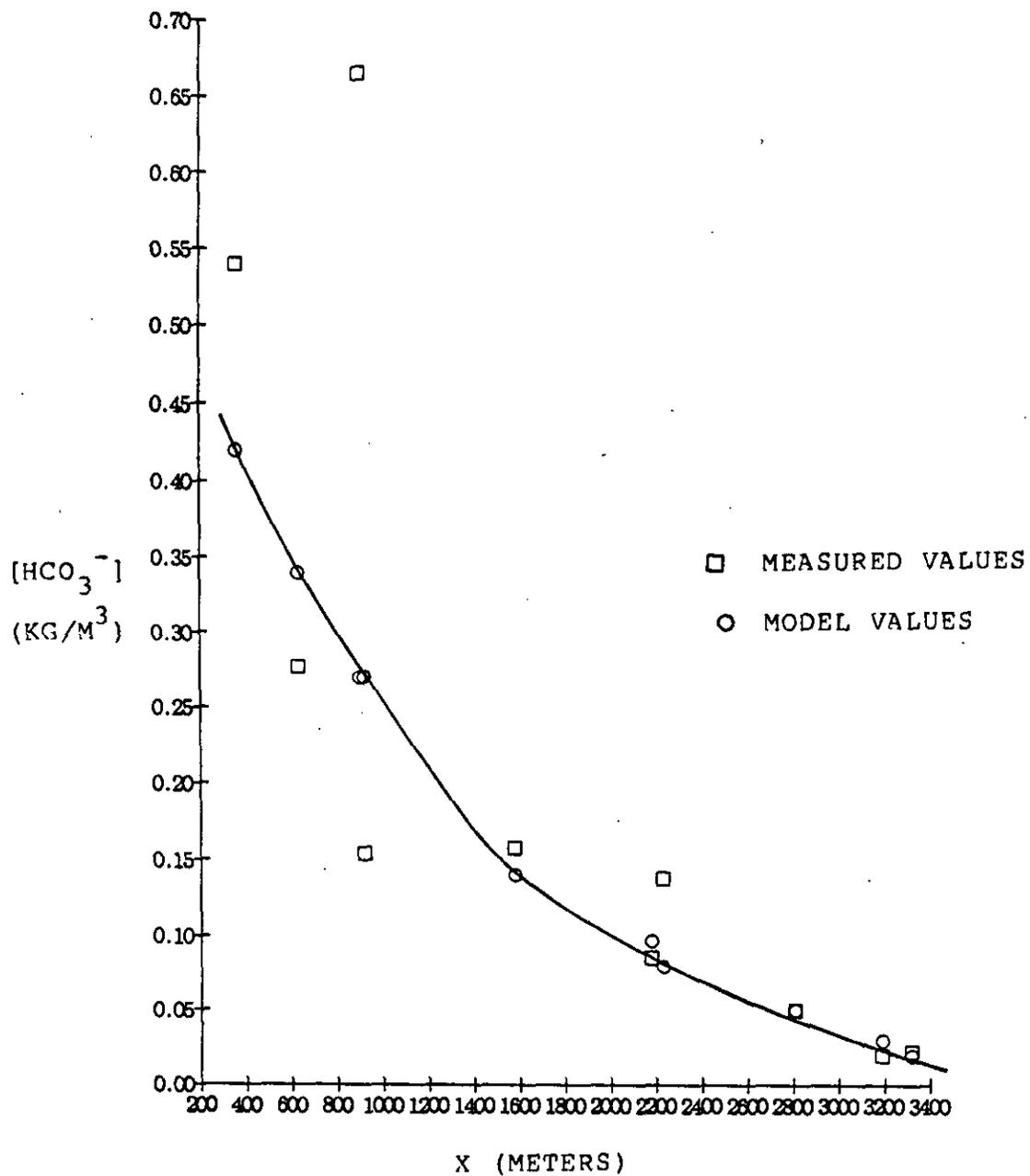


FIGURE 8: BICARBONATE CONC. VS. DOWNGRADIENT DISTANCE

particularly encouraging in view of the possible sampling errors in wells 6, 10, and 122. A graph of concentration vs. downgradient distance is presented in figure 8.

#### Model Test: Vertical Transport

The depth varying vertical bicarbonate transport model is tested by comparing model values that are calculated using the calibrated dispersivity against the measured bicarbonate values. A measure of how well the model fits the given data points is given by the error associated with a comparison between the measured and calculated concentration values, by the mean error of the data, and by the standard deviation of the errors. Table 6 summarizes the vertical bicarbonate test results. The mean error of  $\delta' = -14\%$  and standard deviation of  $\sigma = 33\%$  indicate a good fit of the vertical transport model to the measured vertical profile. No systematic error is present in the model, as shown by the random variation in errors. A graph of bicarbonate concentration vs. depth is presented in figure 9.

TABLE 6: FAR FIELD RESULTS-VERTICAL BICARBONATE TRANSPORT

 $(\alpha=0.02)$ 

DEPTH, Z (METERS)	MEASURED CONC. (KG/M <sup>3</sup> )	CALC. CONC. (KG/M <sup>3</sup> )	ERROR (%)
5.8	0.067	0.093	34
12.2	0.170	0.152	-13
14.6	0.230	0.161	-31
18.9	0.420	0.169	-60
23.8	0.170	0.171	1

MEAN ERROR=-14%

STANDARD DEVIATION OF THE ERRORS=33%

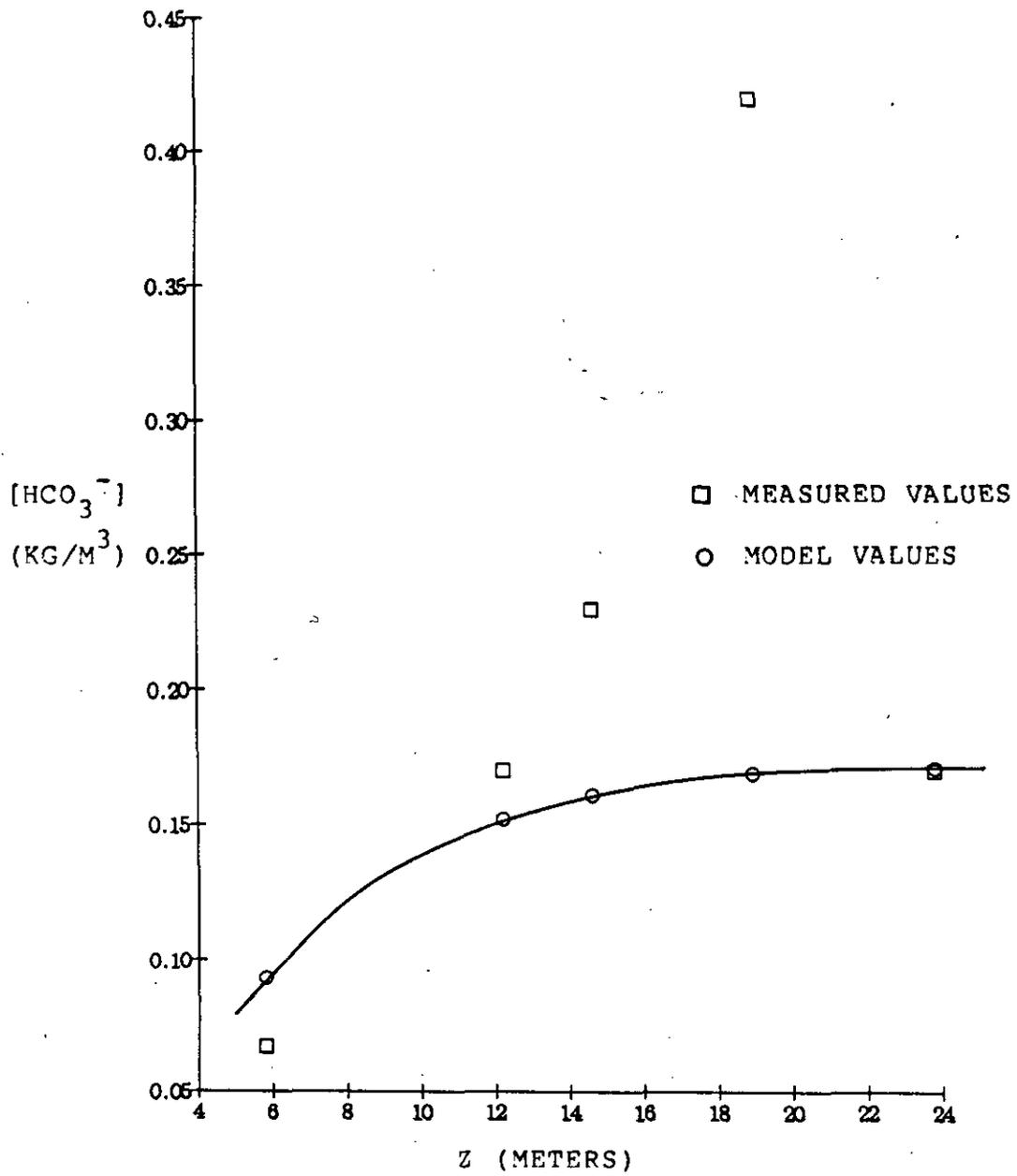


FIGURE 9: BICARBONATE CONC. VS. DEPTH

## CHAPTER VI

### DISCUSSION

#### Horizontal transport

The depth averaged total carbon concentration, as well as its bicarbonate and carbon dioxide species, exhibits an exponential decay to leading order, by virtue of equation (4.16). This behavior is in accord with the ad hoc postulates of first order decay (Ostendorf et al., 1984 and Prakash, 1982) adopted by one-dimensional modelers. The horizontal transport model, which was rigorously developed in this study, gives credence to earlier work that has used a first order decay reaction to model bicarbonate transport and credibility to future work in which a first order decay approximation will be used.

The reactive, first order decay behavior of the bicarbonate concentration is indicated by a depression of the concentration vs. downgradient distance curve (figure 6), as compared to figure 7, which was developed for the conservative contaminant chloride.

#### Vertical Transport

It should be observed from figure 8 and table 6 that if the measured value at 23.8 meters depth is neglected the vertical transport model will exhibit a strong systematic

error. A concentration profile that follows the first four measured points would yield a more statistically valid representation of bicarbonate transport, in the absence of the low measured bicarbonate value at 23.8 meters. However, the fact that the model developed in this study did yield a quite reasonable value of standard deviation of  $\sigma=33\%$ , which describes the spread of the data, can not be ignored. Since there were only five measured data points constituting the vertical profile throwing out any of these values would not be justified. Thus, there is a strong need to test the vertical transport model with more data in order to determine whether this model is truly describing the transport processes that are occurring in the aquifer.

#### Validity of Modeling Assumptions

Several assumptions were necessary in this study in order to sufficiently simplify conditions for the development of the transport equations. The validity of the assumptions will determine how well the transport models can describe the movement of contaminants in the aquifer. Therefore, these modeling assumptions will be looked at in greater detail in order to determine their validity.

The first group of assumptions that will be investigated are those that restrict the hydraulics of the aquifer. The groundwater flow must be steady and one-dimensional. Since the Babylon aquifer is unusually uniform

the steady flow assumption is quite reasonable. The fact that the aquifer is underlain by low permeability clay and is very uniform supports the assumption that the flow is one-dimensional.

The second group of assumptions that will be investigated are those that relate to contaminant transport. The aquifer was assumed to be shallow so that the plume would be fully mixed and differential density effects would not produce two-dimensional transport. The upper glacial aquifer is approximately 23 meters thick, on average, and is therefore relatively shallow. The aquifer was assumed to be initially pure prior to contamination by the Babylon landfill. This appears to be a good assumption since there are few other sources of contamination in the area, especially those that might contribute significantly to a high concentration of inorganic carbon. The assumption that longitudinal dispersion may be neglected is a good assumption for continuous sources of contamination, such as a landfill.

Several assumptions were necessary so that the carbonate system reactions taking place in the aquifer could be reasonably modeled. The temperature and ionic strength were assumed to stay constant throughout the transport process. However, the temperature actually varied from approximately 11°C to 17°C. Therefore, an average value of 14°C was used for modeling purposes. The ionic strength,

however, stayed in the range of 1000 to 2000 micromhos/cm throughout most of the plume. It should be noted that the models were developed in such a fashion that the equilibrium constant cancelled out of the equation for the transport of bicarbonate. Therefore, temperature and ionic strength changes did not effect the results of this model. However, if it became necessary to determine one species from another, the equilibrium constant would play a role in the solution and ionic strength and temperature effects would again be important. The assumptions that geological and biological effects are negligible with respect to changes in inorganic carbon concentration are difficult to evaluate. The site geology indicates that there is probably little contribution to inorganic carbon from geological sources. The biological contribution, however, is difficult to quantify with available data. There is some anaerobic activity in the aquifer, but the extent of this activity is unknown.

Perhaps the most important of the assumptions in this model is that the pH is a constant value. The USGS report on the Babylon plume indicates that the pH changes from about 7 at the landfill to an ambient pH value of about 5 along the perimeter of the plume. This pH range appears to signify dilution of plume water with ambient water at the edges of the plume as well as sufficient buffering of the plume along the aquifer to prevent significant pH changes.

If pH changes were occurring in the aquifer, one would suspect that the pH value would be considerably lower than ambient conditions at the landfill and would slowly increase toward ambient conditions near the toe of the plume as the carbon dioxide diffuses out of the aquifer.

## CHAPTER VII

### CONCLUSIONS

#### Modeling Summary

In this study an analytical groundwater transport model of the reactive contaminants bicarbonate and carbon dioxide was developed. The driving force for the reactions occurring in this reaction was the gaseous diffusion of carbon dioxide out of the aquifer. The diffusion process occurred at a comparable rate to the advective flux of the aquifer, and thus was included in the governing transport equation. The reactions, however, were very fast in comparison to the gaseous diffusion or advective flux of the aquifer. Therefore, the bicarbonate and carbon dioxide values were taken to be at equilibrium at any instant in time in the aquifer. In order to simplify the model total inorganic carbon was transported so that the reaction term could be set equal to zero. The total carbon value is related to the two carbon species by an equilibrium relationship. A critical assumption in this analysis is that the pH must be a constant value in order for the reactions to be sufficiently simple to be incorporated into the transport model.

Because of the two dimensional nature of this contaminant transport problem (advective flux in the

horizontal x-direction and diffusive flux in the vertical z-direction) transport models were developed to describe carbon concentration variations in the x or z direction at any time. The horizontal transport model, which was developed from the vertical transport model, yields a solution which may be described by a series of exponential decay terms. This solution, which was developed rigorously, presents a basis for the use of a first order decay term to approximate bicarbonate reactions in a groundwater transport model.

#### Future Work

The assumptions used in the development of the models in this study should be investigated more thoroughly, especially the constant pH assumption, the assumption that geological contributions are insignificant, the assumption that biological activity is insignificant, and the assumption that differential density effects are not producing a concentration profile in the aquifer. The models should be checked with more data in order to determine whether the models developed in this study truly describe the transport processes that are occurring in the aquifer.

## APPENDIX

### k1 Temperature and Ionic Strength Corrections

Temperature correction:

The equilibrium constant  $k_1 = 10^{-6.43}$  moles/liter at a temperature of  $14^\circ\text{C}$  (Freeze and Cherry, 1979).

Ionic strength correction:

Using the Extended Debye-Hückel Equation, which is valid for ionic strengths less than 0.1, activity coefficients may be determined for bicarbonate and the hydrogen ion (Drever, 1982). These activity coefficient values are divided into the equilibrium constant adjusted for temperature to correct for ionic strength. For a specific conductance  $sc$  of 1500 micromhos/cm the ionic strength  $I$  equals 0.024. This is determined through the approximation

$$I = 1.6 \times 10^{-5} (sc) \quad (\text{A.1})$$

The Extended Debye-Hückel Equation is

$$\log a = -Aw^2(I)^{1/2} / [1 + Ur(I)^{1/2}] \quad (\text{A.2})$$

where  $a$  is the activity coefficient,  $w$  is the ion charge,  $A$  and  $U$  are constants dependent on temperature and pressure, and  $r$  is a constant reflecting the hydrated radius of the ion. The activity coefficients are determined as

$$a_{\text{HCO}_3} = 0.8634 \quad (\text{A.3a})$$

$$a_{\text{H}^+} = 0.8846 \quad (\text{A.3})$$

Therefore,

$$k_1 = 10^{-6.31} \text{ moles/liter} \quad (\text{A.4})$$

for a temperature of  $14^\circ\text{C}$  and an ionic strength of 1500 micromhos/cm.

#### Separation of Variables Solution

$$c = f(t)g(z) \quad (\text{A.5})$$

where  $f$  and  $g$  are two independent functions. Equation (A.5) may be applied to equation (4.11) to produce the two independent equations

$$df/dt + a_{1j}f = 0 \quad (\text{A.6a})$$

$$d^2g/dz^2 - a_{1j}g/D = 0 \quad (\text{A.6b})$$

The product of the solutions of these two equations is represented by exponential and trigonometric terms (Boyce and DiPrima, 1977)

$$c = \sum_{j=1}^{\infty} \exp[-a_{1j}(t-t_s)] [a_{2j} \cos(zm) + a_{3j} \sin(zm)] \quad (\text{A.7a})$$

$$m = (a_{1j}/D)^{1/2} \quad (\text{A.7b})$$

In view of equation (4.13b)

$$a_{2j} = 0 \quad (\text{A.8})$$

In view of equation (4.12a)

$$a_{1j} = [j\pi/(2h)]^2 D \quad j \text{ odd} \quad (\text{A.9a})$$

$$a_{3j} = 0 \quad j \text{ even} \quad (\text{A.9b})$$

The initial condition is a Fourier sine series representation of  $c_s$  over the interval 0 to  $2h$  (Boyce and DiPrima, 1977)

$$c_s = \sum_{j=1}^{\infty} a_{3j} \sin[j\pi z/(2h)] \quad (\text{A.10a})$$

$$a_{3j} = 1/h \int_0^{2h} c_s \sin[j\pi z/(2h)] dz \quad (\text{A.10b})$$

Evaluating this integral

$$a_{3j} = 4c_s/(j\pi) \quad j \text{ odd} \quad (\text{A.11a})$$

$$a_{3j} = 0 \quad j \text{ even} \quad (\text{A.11b})$$

Thus, the separation of variables solution is

$$c = 4c_s/\pi \sum_{j \text{ odd}} \{ \exp[-a_{1j}(t-t_s)]/j \} \{ \sin[j\pi z/(2h)] \} \quad (\text{A.12})$$

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