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Treatment and Transport Modeling of Landfill Leachate Contaminants in an Engineered Wetland System

A Ph.D. thesis submitted for
partial fulfillment of
the requirements for
Ph.D. degree in Civil Engineering

Submitted by

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Under the Supervision of

Dr. L. Fernandes

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Abstract

Most landfill leachates in Ontario do not meet the surface water discharge criteria for boron. Although an essential micronutrient, boron becomes toxic at concentrations slightly above the optimum range. The use of an engineered wetland system consisting of a peat filter and a surface water wetland for treatment of landfill leachate was investigated. Laboratory tests showed that boron is mainly present in inorganic form. Adsorption of boron by peat was a fast process and virtually complete within 2.5 hours. Drying of peat (at 105 °C, 90 °C, 75 °C, and air drying), pH, temperature, and solution composition had a significant effect on boron adsorption while shaking and solution-to-soil ratio did not have any significant effect on boron adsorption by peat. Also, the presence of other anions such as SO_4^-, Cl^- or combination of both in synthetic solutions made from boric acid had no significant effect on boron adsorption by peat. Maximum adsorption of boron on peat occurred at a pH around 9. Addition of lime, optimum ratio being 1 g lime to a 100 g peat, enhanced boron adsorption capacity of peat by 50-100%. Adsorption of boron decreased with temperature increase. Boron desorption showed hysteresis as only 24% to 45% of adsorbed boron was released into the solution when subjected to desorption test.

It was demonstrated that the current linear and non-linear regression procedures of batch adsorption data are not statistically correct. Two sources of errors associated with the current methods of parameter estimation. The first one is introduced by linear transformation of a non-linear equation such as Freundlich adsorption model, which violates the basic assumptions of least-square. The second error is related to the way that dependant and independent variables for regression analysis are defined. A new non-linear code, NLPEFM, was developed that does not produce any of these two errors.

A second-order design model for adsorption of boron by peat was developed, which incorporates the effect of pH and temperature. It offers some advantages over Freundlich adsorption model by describing boron adsorption at any pH and temperature while Freundlich adsorption model can only be used for a specific set of environmental conditions under which they were developed. Development of second-order design model also can be achieved with less laboratory effort.

Adsorption capacity of peat was directly related to organic matter content and showed a positive effect, i.e. boron adsorption increased with organic matter content increase. Amberlite resin was far superior to peat and other organic material in adsorbing and removing of boron from leachate. Peat also proved to be effective in removing metals such as iron, lead, and zinc from landfill leachate. Peat removed organic matter to some extent; 27-39% removal for BOD_5 in column tests during initial stages and 45% BOD_5 removal in the field; and 65% removal for TOC in the field.

A new transport code (in Fortran), SOLTRAN, was developed which has the capability of handling non-linear adsorption isotherms. It also incorporates the effect of pH and temperature into transport model. This model was successfully verified and calibrated with laboratory column test results. An engineered wetland system consisting of a peat filter followed by a free water surface wetland at Huneault Waste Management landfill, Ontario, was used as a case study. It was demonstrated that peat filter can effectively treat landfill leachate. However, the free water surface component of the system proved to be ineffective in reducing boron concentration. Although the treated leachate through the peat filter did not meet the discharge requirement for boron, as much as 92% of boron was removed by this system. SOLTRAN was used to predict the performance of the engineered wetland system.

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Notations and Symbols

α_d	Dispersivity (cm or m)
α	Significance Probability (%)
BOD_5	5-day Biochemical Oxygen Demand (mg/L)
C_e	Equilibrium Concentration (mg or mM/L)
C_i, C_o	Initial or Influent Concentration (mg or mM/L)
COD	Chemical Oxygen Demand (mg/L)
D	Hydrodynamic Dispersion Coefficient (cm^2/s)
ε	Error
J	Solute Flux
K, 1/n	Freundlich Model Parameter
k_d	Distribution Coefficient (mL/g)
K_{oc}	Octanol-Water partition coefficient (mL/g)
R	Retardation Factor (dimensionless)
R^2	Correlation Factor
ρ_b	Dry Bulk Density (g/cm^3)
q, S	Solid Phase Concentration of Adsorbed Solute (mg or mM/Kg)
TN	Total Nitrogen (mg/L)
TOC	Total Organic Carbon (mg/L)
TP	Total Phosphorous (mg/L)
TDS	Total Dissolved Solids (mg/L)
TSS	Total Suspended Solids (mg/L)
θ	Effective Porosity (dimensionless)
VS	Volatile Solids (%)
v	Average Linear Fluid Velocity (cm/s)
$v1$, $v2$	Degrees of Freedom for Statistical Analysis
A-D	Advection-Dispersion
ADE	Advection-Dispersion Equation
BTC	Break Through Curve
CDY	Conductivity
DM	Dry Matter
DO	Dissolved Oxygen
DW	Distilled Water
E( )	Expected value
EPA	Environmental Protection Agency
EWS	Engineered Wetland System
FWS	Free Water Surface wetland
GCMS	Gas Chromatography Mass Spectroscopy
HWM	Huneault Waste Management
ICP	Inductively Coupled Plasma
IC&I	Industrial, Commercial & Institutional
L-B	Boron Free Leachate (Leachate – Boron)
MC	Moisture Content
MRE	Mean of Residual Errors

MARE	Mean Absolute Residuals Error
MOEE	Ministry Of Environment and Energy
MW	Monitoring Well
MWWTP	Municipal Wastewater Treatment Plant
NLISOTHERM	Non-Linear parameter estimation for adsorption ISOTHERM
NLPEFM	Non-Linear Parameter Estimation for Freundlich Model
NMR	Nuclear Magnetic Resonance
PWQOs	Provincial Water Quality Objectives
SFS	Subsurface Flow System
SOLTRAN	SOLute TRANsport model
SS	Synthetic Solution
SSR	Sum Squares of Residuals
SW	Surface water
V, Vol.	Volume
VFS	Vertical Flow Subsurface wetland

INTRODUCTION

Chapter
1

Landfilling is the primary means of solid wastes disposal and will continue to be so for the foreseeable future. The 3 R's (Reduce, Reuse and Recycle) program has become one of the main environmental issues in recent years with the aim of diverting the waste from landfills as much as possible. For example, California mandated that 50% of the waste be diverted by 2000 (Vesilind *et al.*, 2002). Also, the national target for waste diversion in Canada by the year 2000 was 50% (Vitello, 2001). However, most municipalities have not been able to achieve this target and at present time the majority of the solid waste is still disposed of in landfills. In 1997, only 15% of the total waste stream in Ontario was recycled (Eyles and Boyce, 1997). According to Vitello (2001) only 25% of the collected solid waste in Toronto was recycled during the year 2000. Toronto city council recently voted to increase recycling from 25% to 60% by the year 2006. The situation is relatively the same in other parts of the world. In the U.K. about 80% of municipal solid waste was disposed of in landfills during 1998 (ETRA, 1999). This compares to 90% landfill disposal of all domestic and commercial wastes in 1985 (Robinson and Maris, 1985). While the price of landfilling tends to increase with the imposition of higher environmental standards, the gap between landfill costs and recycling methods is not closing quickly enough to meet the governments' objectives for a more sustainable waste management (ETRA, 1999). Consequently, there will remain significant quantities of unrecyclable waste that must be directed towards landfills. Additionally, landfills may remain the best practicable environmental option for certain wastes, and it will continue to play a significant role in waste management in the foreseeable future (DETR, 2000).

Landfills are potential threats to groundwater quality (Howard, 1997), the primary concern being the production and treatment of leachate (Eyles and Boyce, 1997; Farquhar, 1988). Major environmental problems have arisen from the production and migration of leachates from landfill sites and subsequent contamination of surrounding land and water (McBean *et al.*, 1995). To prevent the adverse impacts of landfill leachate on aquatic life and degradation of water quality, landfill leachate has to be collected and treated before final discharge into the environment. Conventional treatment systems are costly and require a long-term commitment. Moreover, the great variations in strength and flows of leachate as well as its toxic effect, due to presence of high concentrations of heavy metals and/or organic substances, make the use of these systems undesirable (Vesilind *et al.*, 2002; McLellan and Rock, 1988 and Tchbanoglous *et al.* 1993). Many landfill operators are now considering non-conventional systems such as engineered constructed wetlands, which are low energy, do not require chemicals, and can satisfactorily address the leachate management problems.

1.1. STATEMENT OF THE PROBLEM

In Ontario the discharge criteria into the surface water are listed under provincial water quality objectives (PWQOs). The PWQOs represent a desirable level of water quality that MOEE (Ministry of Environment and Energy) strives to maintain in the surface waters of the province. According to water management goals and policies of MOEE, PWQOs are set at levels that are protective of all forms of aquatic life during indefinite exposure to the water.

There are nearly 1200 active and inactive landfills in southern Ontario; all but a handful lack any engineered containment system and were in use prior to enactment of the Environmental Protection Act in 1971 (Eyles and Boyce, 1997). Though it is acknowledged that there is no typical leachate, there is evidence that many constituents occur within relatively consistent ranges at most landfills (McBean, 1995). According to Howard (1997), heavy metals, cyanide and boron are the most common pollutants among inorganic contaminants associated with groundwater contamination in industrialized areas. Landfill leachate is reported as the main source of boron contamination of groundwater (Howard and Livingston, 1997). In 1995, the allowable boron concentration listed as PWQO was decreased from 5 to 0.2 mg/l (MOEE, 1995).

The Huneault Waste Management (HWM) Landfill, located in Gloucester, Ontario, has been receiving industrial, commercial and institutional (IC&I) waste as well as construction/demolition waste since 1971. In 1991 and 1992, a leachate collection system was installed and the leachate has been collected and monitored since then. The leachate produced at the HWM landfill is significantly different from other landfills in Ontario since no municipal waste is accepted at this landfill. As a result, HWM leachate is relatively weak in terms of organic matter and nutrients when compared with other landfills in Ontario. At HWM landfill boron is one of the main parameters of concern and has been measured in high concentrations, up to 100 times higher than the acceptable limits for surface discharge.

At present time, there is limited information in the literature regarding removal of boron from landfill leachate. Some researchers have investigated boron adsorption on clay soils, but research on the adsorption of boron by organic soil is almost non-existent. Besides, most of these research works were conducted with synthetic solutions made of inorganic boron (boric acid) and there is no information available on the nature and speciation of boron and its adsorption in a complex environment such as landfill leachate. In addition, literature review on the adsorption of boron revealed that the effect of operational and environmental factors on boron adsorption has not been investigated thoroughly and often there are contradictory results reported in the literature. Moreover, the examination of the application of adsorption models such as the Freundlich equation showed that the equations and procedures that are commonly used are not correct. Therefore, there is a need for modification of equations and regression procedures that are used for parameter estimations of adsorption models.

An Engineered Wetland System (EWS) was proposed and constructed at HWM landfill site in order to treat the collected leachate prior to discharge into the adjacent surface water. The treatment system consisted of an engineered vertical flow subsurface (VFS) filter (using organic peat soil as the medium) followed by a free water surface (FWS) wetland. Both, natural and engineered (also called constructed) wetlands have been used to treat a variety of wastewaters, including agricultural and mine drainage, secondary wastewater effluent, stormwater and municipal waste leachate. However, the performance of engineered wetland systems for treating leachate from industrial, IC&I and construction/demolition wastes has not been studied. In order to determine long-term performance and life expectancy of this system there is also a need for mathematical modeling of the fate and transport of boron and metals within the treatment system. Modeling of boron transport through porous media such as peat has not been done yet.

1.2. RESEARCH OBJECTIVES

This research study aims to address the issues raised in the previous section. The specific objectives of this study are:

1. To investigate whether boron exists in the organic or inorganic form in landfill leachate;
2. To investigate the effect of different operational and environmental conditions on boron adsorption;
3. To critically review the current procedures for parameter estimation of Freundlich adsorption isotherm models and propose a new, more rigorous, and precise non-linear regression procedure to obtain parameters associated with the Freundlich isotherm and validate it;
4. To assess the adsorption/desorption mechanisms of boron and heavy metals by peat. Also to compare the adsorption capacity of peat for boron with a number of other different adsorbents. These include a commercial peat moss, peat obtained from another location (Alfered Bog), two sources of compost material, and an ion exchange resin;
5. To evaluate the attenuation capacity of an engineered wetland system for boron, heavy metals (iron, lead and zinc), ammonia, and organic matter (BOD_5 and TOC);
6. To develop a new adsorption isotherm model for adsorption of boron by peat, which can predict the adsorption capacity of peat soil under different pH and temperature conditions;
7. To develop a new mathematical model for the transport of boron through the VFS filter and to predict its performance over time, i.e. the life expectancy of the system. The outcome of the modeling should improve the understanding of landfill leachate treatment through the use of the VFS type of constructed wetlands and assist in developing practical design criteria for such systems.

1.3. RESEARCH METHODOLOGY

In order to achieve the objectives outlined in the previous section the following research plan was proposed. As schematically shown in Figure 1.1, the proposed plan includes laboratory studies, field monitoring and mathematical modeling of the engineered wetland treatment system. This research incorporated the HWM landfill as a case study and this landfill was monitored for a period of two years.

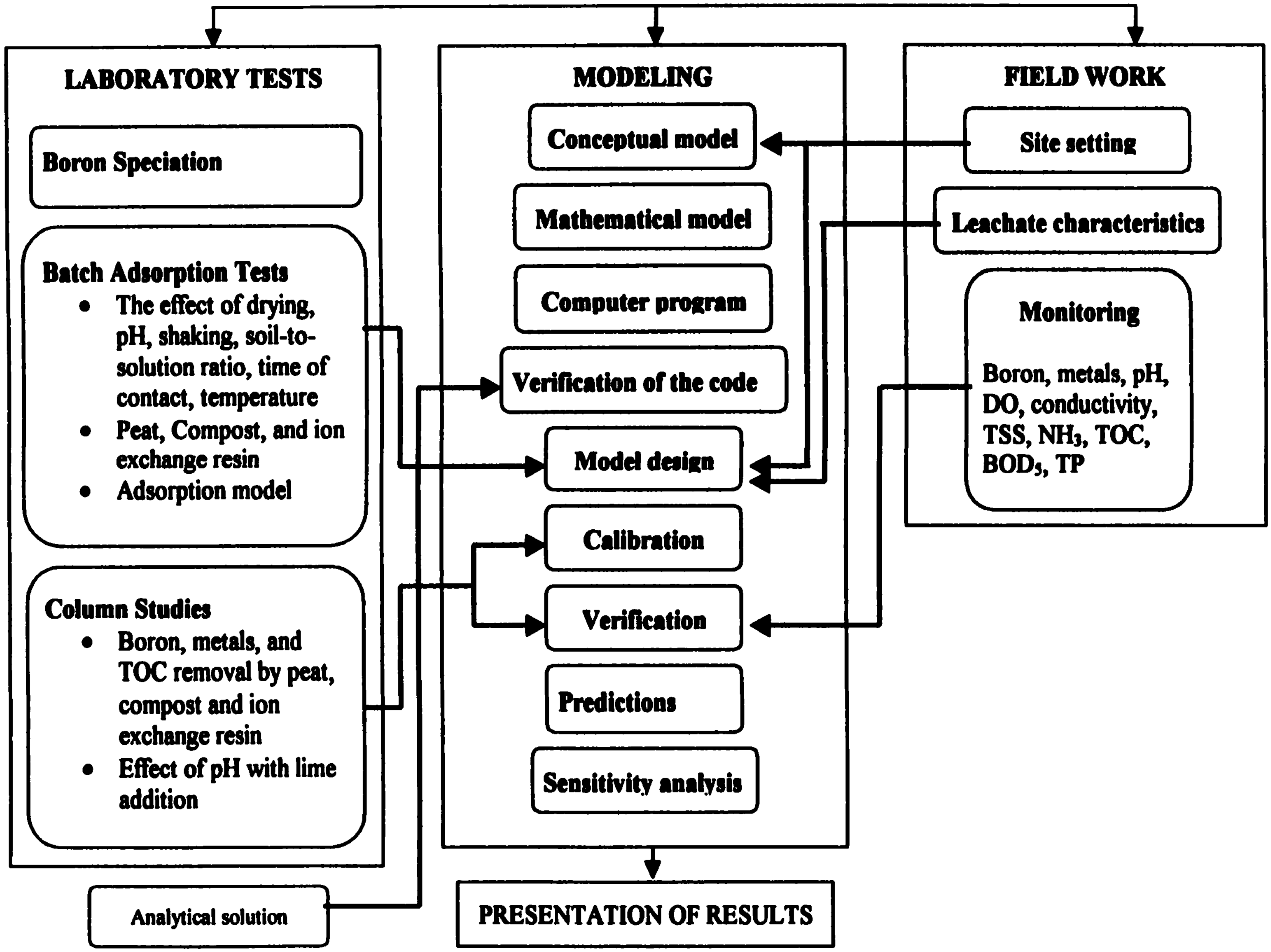
In the laboratory, different sets of batch adsorption and column test were conducted. Several adsorption tests were carried out in order to evaluate the effect of different parameters on the adsorption of boron on peat including pH, temperature, competing ions, solution composition, shaking, soil-to-solution ratio, time, and drying of peat. The parameters required for the calibration of the model were obtained from laboratory batch adsorption and column test studies. The laboratory experiments also included a physical model (column tests) to simulate the VFS wetland (peat filter). The results obtained from this simulation exercise were used to calibrate and verify the results obtained from the mathematical modeling. Once the model was calibrated and verified, it was used to predict the future performance of the system and to determine its life expectancy.

1.4. ORGANIZATION OF THE THESIS

This thesis is divided into eight chapters. The first chapter gives an introduction and objectives of the research. Literature review is presented in Chapter Two. Chapter Three discusses the properties of the materials as well as the experimental and analytical procedures that were used during the course of this research. Chapter Four deals with the results from batch adsorption tests and its modeling. Development of the basic equations and numerical procedures for modeling of contaminant transport is the subject of Chapter Five. Results from column studies including the transport and distribution of contaminants through columns are presented in Chapter Six. The data and information collected in the field are presented in Chapter Seven. Concluding remarks as well as recommendations are included in the last chapter, which is followed by the list of references and appendices.

FIGURE 1-1: Treatment of Landfill Leachate in an Engineered Wetland

Organization of the Research Study



LITERATURE REVIEW

Chapter 2

A thorough literature review on all aspects of this research work was carried out and it is presented in the following sections. Since this research is about the treatment of landfill leachate, relevant information on landfill leachate was reviewed and these are covered in the first section. As mentioned in the previous chapter, an engineered wetland system was chosen for the treatment of landfill leachate at HWM site. Consequently, information about wetland systems found in literature was reviewed and these are presented in Section Two. Since peat was used as the medium in the VFS component of the treatment system, its effectiveness for the removal of contaminants is described in the third section. Boron is the main parameter of concern and Section Four deals with information on boron contamination sources, toxicity effects, standards, and available treatment methods. Adsorption is the main process for removal of boron in the EWS. Section Five covers the adsorption process, its applications, and modeling. One of the objectives of this thesis is to develop a mathematical model for the transport of contaminants through the VFS filter component of the treatment system. The basic equations of contaminant transport and relevant information found in the literature are discussed in Section Six. A summary of all the information is presented in the final section of this chapter.

2.1. LANDFILL LEACHATE

The current practice of land disposal, called engineered or containment landfill, consists of the following main components: a landfill final cover, an impermeable or low permeable barrier at the base of the waste pile, a gas collection system, and a leachate collection system. Landfill leachate is generated as a result of the percolation of rainfall, snow melt, and/or groundwater through waste material, which contains a variety of pollutants and if not properly managed could potentially contaminate surface and subsurface waters. Over the past ten years the concept of engineered bioreactor landfills has been developed. In this type of landfill the infiltration of precipitation into the waste is minimized in order to decrease the volume of leachate. The moisture content of the waste is increased and the waste is shredded and nutrients can be added to the waste to enhance the rate of biological degradation of organic matter and methane production (Warith, 2000). As a result, the waste stabilization is accelerated and the time period for leachate treatment, i.e. time period for leachate collection and treatment during and after landfill operation, is reduced.

As mentioned in the previous chapter, conventional treatment systems are not economically a suitable alternative for leachate treatment. Landfill leachate may be recirculated within the waste pile to enhance the stabilization of the organic contents (Townsend *et al.*, 1996). Leachate recirculation is also reported to reduce the toxicity of raw leachate (Cameron and Koch, 1980). Leckie *et al.* (1979) reported that raising the moisture content of wastes accelerated stabilization process and the rate of settlement of landfilled material. Robinson and Maris (1985) recommended a combination of leachate recirculation and aerobic treatment as the most effective option for leachate treatment. According to Vesilind et al. (2002) the most economical alternative for leachate treatment is often to transport the leachate off-site to a wastewater treatment plant.

If leachate recirculation is chosen as part of leachate management, it would result in a higher volume of leachate within the landfill. As a result, part of the leachate tends to be recirculated and the excess leachate is managed through some form of treatment for eventual off-site disposal. Conventional treatment systems are costly and require a long-term commitment. Moreover, the great variations in strength and flows of leachate as well as its toxic effect due to presence of high concentrations of heavy metals, ammonia, and various organic substances make the use of these systems undesirable (Tchbanoglous *et al.* 1993; McLellan and Rock, 1988; Cameron and Koch, 1980). Many municipalities in Ontario discharge raw landfill leachate into a wastewater sewer. However, in some cases such as the city of Ottawa's Trial Road Landfill the concentrations of contaminants approach or exceed the discharge limit of the local Sewer By-Law. Therefore, it is necessary to pre-treat the landfill leachate in order to reduce the level of contaminants to meet the local Sewer By-Law limits.

Many landfill managers are now considering non-conventional systems such as constructed wetlands, which are not energy and chemical intensive and can address the above referred leachate management problems. The application of both natural and constructed wetlands for water quality improvements have received great interest and acceptance in recent years. This has resulted in the construction of more than 1500 wetland systems worldwide during the past 15 years (Berezowsky, 1997).

Leachate composition varies significantly among landfills, depending on waste composition, waste age, climate, hydrogeological conditions and landfilling technology (McBean *et al.*, 1995). For example, leachates from landfills receiving municipal wastes have higher organic contents than landfills receiving industrial wastes. On the other hand, the concentrations of some inorganic contaminants, such as heavy metals, in leachates generated at landfills receiving industrial wastes are higher than those receiving municipal wastes (McBean *et al.*, 1995). The age of landfill is also an important factor, since young leachates contain readily biodegradable organic matter, which are easier to treat by biological processes. Following the depletion of readily biodegradable organic matter and the accumulation of reluctant compounds, the treatment efficiency decreases over time (McBean *et al.*, 1995).

The leachate characteristics of the Huneault Waste Management (HWM) landfill and other Ontario landfills are presented in Table 2-1. Two landfills located in the regional municipality of Ottawa-Carleton (Trail Road and Canadian Waste Management) are also included in Table 2-1. Comparison of average values of parameters for HWM and Ontario landfills show that landfill leachate generated at HWM landfill is a weak leachate with most parameters significantly lower than those in other Ontario landfills except boron and copper. This can be attributed to the type of wastes that is disposed of at this site.

2.2. WETLAND SYSTEMS

Wetlands occupy about 14% of Canada (WRC, 1992). "Wetlands are defined as those areas that are saturated by surface or groundwater at a frequency and duration sufficient to support the prevalence of vegetation typically adopted for life in saturated soil conditions" (EPA, 1987). As a treatment method, the use of constructed rather than natural wetlands is generally preferred since all natural wetlands are considered as part of natural water resources and have to comply with the water quality requirements of regulatory agencies (EPA, 1987). Other advantages of constructed wetlands include greater degree of control of the medium used, vegetation types, flow characteristics, flexibility in sizing and the potential to treat more wastewater (Berezowsky, 1997).

Table 2-1: Characteristics of Leachates produced at different Landfills in Ontario[*]

	Huneault WM			Ontario Landfills			CWM[**]	Trail Rd	Glenridge	Guelph	Burlington
	Min	Max	Ave	Min	Max	Ave	Ave	Ave	Ave	Ave	Ave
pH							5.8	6.7	7.3	7.4	7.1
Conductivity (mmhos/cm)	669	4750	3792	475	26100	6088		9833	6175	8621	6521
TDS	1920	2572	2234	196	9030	4327				4500	6214
Alkalinity	185	2000	1507	7	11640	2626		5459	2555	3633	2390
BOD5	1.6	173	39.9	1	66000	4976		14176	28	18153	1971
COD	69	600	289	1	47300	7855	35000	16050		21514	4525
TN	2.1	39.4	28.9	0	2488	256		2488	237	606	167
TP								1.65		0.45	1.23
Ammonia	0.1	31	18.5	0.03	1302	171		318.8	206	300	152
Boron	0.4	16.9	10.2	0.12	63.2	10.5	3.23	2.52	3.1	43.3	3.02
Calcium							2140		188	203	290
Copper	0.002	4.5	0.4	0.001	8.8	0.11	0.03	0.11	0.002		0.09
Iron	0.003	8.09	2.8	0.03	3853	131	11.5	395	39.5	28.3	79.8
Magnesium	17	252	136	4.8	7600	232	374	439	281	311.6	219
Manganese	0.1	8.6	1.8	0.01	14.1	2.7	14		0.29	0.31	4.9
Nickel	0.02	0.2	0.04	0.01	0.3	0.07	0.53		0.08	0.09	0.09
Potassium	11.8	99.2	71.3	0.1	2000	207	719	276	273.5	352	145
Sulphate							480	49	67	0.9	92
Lead	0	0.1	0.03	0	0.8	0.05	0.1	0.04	0.03	0	0.12
Zinc	0.01	0.13	0.03	0	82.6	1.47	4.13		0.07	0.09	3.9

* All parameters in mg/L unless indicated otherwise
** Based on leachate collected from Canadian Waste Management Landfill, Ottawa, 1999
Reference: Jones (1993), Castonguay (1997) and Howard and Livingston (1997)

The operating costs of wetland systems are very low, compared to conventional treatment systems, since they do not require expensive energy and/or chemical inputs. Wherever sufficient, reasonably priced land is available, engineered wetland treatment can be a cost-effective treatment alternative, which is receiving increased attention in Canada (Pries, 1994). The land requirement for constructed wetland systems is in the range of 0.4 to 2.6 ha per thousand cubic meters per day (EPA, 1999b).

Wetland systems have been used to treat a variety of wastewaters including agricultural and mine drainage, secondary effluent, stormwater, municipal, industrial and pulp and paper wastewater (Pries, 1994, EPA 1993). However, the treatment of municipal wastewater, stormwater and acid mine drainage are by far the most common applications of wetland systems for water quality improvement (Berezowsky, 1997; Pries, 1994). The use of constructed wetland systems for treatment of acid mine runoff in more than 100 sites in Ohio, Virginia, Maryland and Pennsylvania was reported by EPA (1987). By 1994 there were at least 67 wastewater and stormwater wetland systems in Canada in operation or under development (Pries, 1994).

Constructed wetlands are categorized into two main groups (EPA, 1999b): free water surface (FWS) and subsurface flow system (SFS). The scheme of various types of constructed wetlands are shown in Figure 2.1. The FWS wetlands typically consist of basins lined with a subsurface barrier to prevent seepage. These are filled with soil or other suitable medium to support vegetation and water at a relatively shallow depth; 30 to 45 cm is typical (Brown and Reed, 1994). FWS constructed wetlands typically cost between US$10,000 and US$50,000 per hectare (Pries, 1994). SFS wetlands are similar to FWS systems in many respects; however, water flows horizontally or vertically through the porous media. In SFS, media depth ranges from 30 to 75 cm and the materials used are sand, peat, gravel or rock. SFS are more costly but are usually smaller in size (Brown and Reed, 1994). In addition, the use of SFS systems is advantageous in cooler climates since much of the treatment occurs below ground surface. The vertical flow subsurface (VFS) system allows manipulation of the flow in the vertical direction (Pries, 1994). In this system, water flows vertically through the porous media and is collected at the base of the filter. This system is similar to trickling

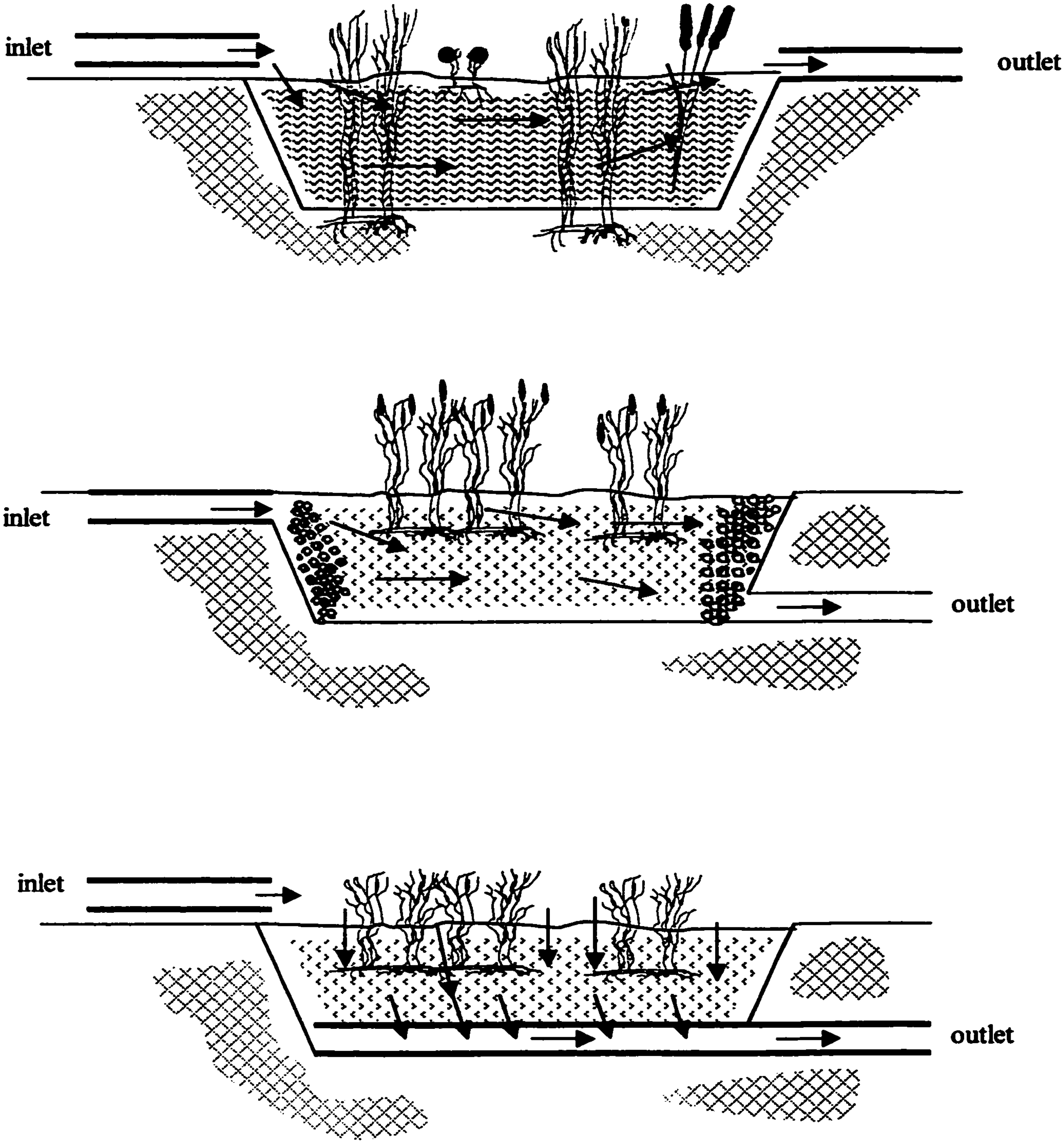


Figure 2-1: Free Water Surface (top), Horizontal Subsurface Flow (middle) and Vertical Subsurface Flow (bottom) wetlands

filters and permits a decrease in the size of the wetland. The major drawbacks include the risk of plugging as well as the higher cost of construction due to the cost of media (EPA, 1999b; Brown and Reed, 1994).

A 1991 survey documented the presence of over 150 constructed wetland systems in U.S., with almost equal number of FWS and SFS operating systems, but SFS were projected to outnumber FWS system in the future (Brown and Reed, 1994). According to an EPA database of wetland treatment systems of North America (EPA, 1999b), in 1999 there were as many as 245 wetland systems used for wastewater treatment in U.S. and Canada. 205 of these systems were constructed wetlands, 38 natural wetlands, and the rest were not classified.

The performance of constructed wetlands is measured by the removal efficiencies of pollutants. Wetland systems can significantly reduce organic matter, measured in terms of 5-day biochemical oxygen demand (BOD_5), total suspended solids (TSS), nutrients (nitrogen and phosphorous), and pathogens as well as heavy metals (EPA, 1993). Wetlands support a large and diverse population of bacteria and other organisms that are of particular importance in the removal of BOD_5. Quiescent conditions and filtering effect of porous media are the main factors for SS removal. Nitrification/denitrification is the major path for nitrogen removal (EPA, 1993 and EPA, 1987). Brix (1987) reported on the performance of eight constructed wetland systems used for wastewater treatment in Denmark, with removal efficiencies of 51-95%, 10-88% and 11-94% for BOD_5, TN and TP, respectively. For subsurface systems, BOD_5 and TSS removal efficiencies in the range of 85 to 90% were reported (WPCF, 1990). Also, the results of a survey on the removal efficiency of 97 sites, mainly in U.S., showed an average removal of 73%, 69%, 64%, and 55% for BOD_5, TSS, TN, and TP, respectively (Knight *et al.*, 1993). Gresberg *et al.* (1983) reported 60-86% nitrogen removal in a constructed wetland. Heavy metals are basically removed through precipitation, adsorption and complexation mechanisms. Removal efficiencies for metals in the range of 70-90% were reported by Pries (1994). Gresberg *et al.* (1985) reported removal efficiencies of 99, 97 and 99% for Cu, Zn and Cd, respectively. Wetlands were also reported to be effective in removing iron from coal drainage and metals from mine drainage (Eger, 1994).

2.3. PEAT AS A POLLUTANT ATTENUATING MEDIUM

The use of peat for pollution control has received increasing attention over the past couple of decades. Peat is a natural, inexpensive and widely available substance and posses several characteristics that make it effective for adsorption and ion exchange (McKay, 1996). About 90% of Canada's 127 million hectares of wetlands are classified as peatlands, where peaty soils are predominant (Pries, 1994). Peat is primarily composed of remains of plants, which are at various stages of decomposition (Mitsch and Gosselink, 1993). Depending upon the parent plant matter and age, the structure of peat ranges from a fibrous type with recognizable plant remains to an amorphous structure with no recognizable plant matter (Landva *et al.*, 1983). Peat contains lignin, cellulose, and humic acids as its major constituents. These constituents bear polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides, which can participate in chemical reactions (Viraraghavan and Ayyaswami, 1987; Dissanayake and Weerasooriya, 1981).

Soil organic matter is divided into nonhumified (such as lignin) and humified material. Humic acids are primarily responsible for the ability of peat to adsorb metals by forming complexes with metal ions (McKay, 1996; Dissanayake and Weerasooriya, 1981). Peat is reported to have a large specific area (>200 m^2/g) and is highly porous (95%), which makes it a good adsorbent material (McLellan and Rock, 1988). Peat is also reported to exhibit excellent ion exchange properties similar to natural zeolites (Sharma and Forster, 1993; McKay, 1996). The combination of the above mentioned properties, i.e. being a good adsorbent, capability of forming complexes with metals and having a capacity for ion exchange, makes peat an excellent metal trapping medium.

Dry bulk density of organic soils is much lower than mineral soils. Mitsch and Gosselink (1993) reported that dry bulk density of a well decomposed organic soil is generally 0.2 to 0.3 g/cm^3 although peatland soils with bulk densities as low as 0.04 g/cm^3 have been observed. The same authors stated that peat soils generally have at least 80% pore space. Buttler *et al.* (1994) analyzed 90 samples of peat materials collected from nine sampling stations in Quebec. pH, dry bulk density, and total porosity were in the range of 3.2-5.3, 0.03-0.1 g/cm^3, and 90.2-96% respectively. Rana and Viraraghavan (1987) conducted column studies with varying dry bulk density of peat. The columns that were compacted to a dry bulk density of greater than 0.15 g/cm3 clogged when subjected to septic tank effluent. This compares to a dry bulk density of 0.08-0.1 g/cm^3 of sphagnum peat measured in the field. Cameron (1978) observed a reduction in gravity flow rate of landfill leachate after the initial runs in peat columns with a dry bulk density of 0.08 g/cm^3. McLellan and Rock (1988) suggested a dry bulk density of <0.12 g/cm^3 based on results obtained from the treatment of landfill leachate using columns packed with sphagnum peat at various bulk densities. The build up of solids and biological activities were stated as possible reasons for clogging of columns. According to Cameron (1978) free water represents 70% of total water content of the peat.

Peat has proven to be effective in removing Hg, Cd, Cu, Pb, and Zn from water (McKay, 1996), hexavalent Cr from wastewater (Sharma and Froster, 1993), Cd, Cr, Cu and Pb from landfill leachate (McLellan and Rock, 1988), and Cu from industrial wastewater (Dissanayake and Weerasooriya, 1981). Rana and Viraraghavan (1987) reported on the use of peat columns for treatment of septic tank effluent, and found removal efficiencies of 85-99%, 40-80%, 0-90%, 0-25%, and >95% for SS, BOD$_5$, TN, TP and fecal coliforms respectively. Cameron (1978) investigated the use sphagnum peat columns for treating landfill leachate. Peat was effective in reducing toxicity, TS, TN, COD, Fe, Mn, Pb and K of a landfill leachate. However, the peat requirement was substantial, 159 Kg (dry) per 1000 L of leachate. Hammer and Kadlec (1980) investigated a full-scale peatland system for removal of nutrients. Peat was very effective in removing TP as its initial concentration of 2.5 to 3.0 mg/L from discharge pipe dropped to less than 0.1 mg/L within 100 m from the discharge pipe. Other uses for peat include the adsorption of gases, such as ammonia and hydrogen sulphide, as well as the removal of oil, phenol, and textile dye (Viraraghavan and Ayyaswami, 1987; McLellan and Rock (1986).

One of the physical properties of peat is moisture content. As a consequence of its high porosity, peat has a high moisture content (MC) value. A temperature of 105°C is usually used to determine the moisture content of peat. However, according to MacFarlane (1969), there is evidence that such a high temperature may change the characteristics of peat.

This researcher suggested 85°C as a suitable temperature for MC determination if peat is going to be used for any subsequent test. Among the functional groups, the most important sites for adsorption of water on organic matter are provided by carboxylic groups. Upon drying and exposure of polar sites, an internal paring of OH and C=O may occur, as shown in Figure 2-2. Internal pairing of functional groups produces stable sites, preventing peat and other organic matter to rehydrate upon wetting. This may be part of the reason for the irreversible behaviour of organic matter upon wetting and drying (Tan, 1998).

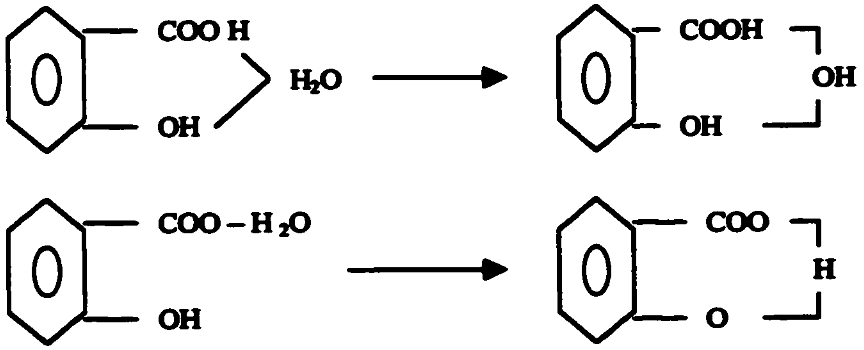


Figure 2-2: Internal pairing upon drying of organic matter (Tan, 1998)

Hammer and Kadlec (1980) studied the adsorption of ortho-phosphate on peat. They observed an approximate decline of 25% in adsorption following double autoclaving peat samples at 160°F (71°C). They concluded that the autoclaving process resulted in breaking down of peat structure and the release of some phosphorous. They based their conclusion on the fact that the measurements at the very beginning of the experiment were highly variable and often showed higher concentration than present in the stock solution. However, their conclusion was not supported by any statistical analysis. Internal pairing phenomena could likely be the reason for the decline observed in the adsorption of ortho-phosphate. The process of peat saturation was reported to be very slow as the water content of peat measured in the field increased for some days under steady state condition (Lischeid, 2000).

2.4. BORON

Boron is one of the most troublesome trace elements in soil management. While low concentrations of boron are essential for plant growth, it becomes phytotoxic at concentrations only slightly higher than the optimal range (Gupta *et al.*, 1985). Its production in the USA in 1992 was about one million metric tons of ore worth $340 million. This represented 39% of world production (Smith and Medrano, 1996). The principal world source of boron chemicals is a massive deposit of sodium borate in California, USA. Argentina and Turkey are the only other geological locations where rich deposits of Na or Ca borates occur. Boric acid and its salts account for 99% of production tonnage and sale value (Thomson and Welch, 1985).

Boron is quite unique in the sense that no other element in nature has such versatile uses as boron. It has been used in mummification, the glass industry, rocket fuel, and in cancer therapy just to name a few in order to grab the readers' attention (Garret, 1998 and EPA, 1991). Boron is a major industrial material which is widely used in the production of glass and textile fiberglass, disinfectants, cosmetics, cleaning and bleaching agents, wood preserving material and fire retardant material for wood products, plastics, ceramics, food preservatives, synthetic rocket fuels, abrasives, absorption units in nuclear reactors, medicine, insecticides, cancer therapy and agricultural fertilizers (Garret, 1998; Murray, 1996; Hubbard and Sullivan, 1996; Canadian Water Quality Guidelines, 1995; Hawthorne, 1995; EPA, 1991; Thomson and Welch, 1985). According to a report by Garrett (1998), the major markets for boron consumption in U.S. are insulation fiberglass (30.5%), textile (15.5%), borosilicates glass (9.5%), cleaning and bleach (8%), fire retardant (6%) and agriculture (4%). One innovative method of using boron as a source of energy under development is boron fuel cell. The case for boron as fuel begins with a safety advantage. Although very combustible, it also is very hard to ignite. The most important advantage of boron fuel cell is that it does not produce any exhaust gases at all (Eagle.ca, 2001).

2.4.1. Boron Chemistry

Boron, a non-metal element with the only known valence states of 0 and +3, does not occur as a free element in the environment, but it is usually found combined with oxygen to form borates and borosilicates. Boron is a widespread constituent of the earth's upper crust with an average concentration of 15 ppm. Boron is one of the lightest and most mobile elements, it is much more soluble, 4.7% at 20 °C, than other trace elements of concern such as As, Cd, Ni and Cu and generally behaves as a conservative element (EPA, 1991; Tanji, 1990). For this reason, it is sometimes treated as a tracer (Bundschuh, 1992). However, as it will be mentioned in the next sections, boron does get adsorbed on clay and organic particles as well as some mineral oxides. One has to be cautious in using boron as a conservative element and it is recommended that its behavior be checked against some other conservative elements such as Cl^-. This approach was used by LeBlanc (1984) for modeling of a plume of sewage-contaminated groundwater in a sand and gravel aquifer. He checked the concentrations of boron against that of chloride and obtained a linear relationship between the two, and then he utilized the boron plume to model groundwater movement within the aquifer.

Because of its high water solubility, the majority of the earth's boron occurs in the oceans with an average concentration of about 4.7 ppm (Garrett, 1999 and Murray, 1996). Boron plays an important role in controlling the pH of the seawater (Thomson and Welch, 1985). In surface waters boron is usually present in relatively low concentrations. A survey of 1542 surface water samples reported a mean boron concentration of 0.1 mg/L (EPA, 1991). However, concentrations in the range of 0.5 to 1000 mg/L has been measured in salt lakes and hydrothermal waters (Bassett, 1976). Boron is the only element that is normally present in soils as a non-ionized molecule over the pH range suitable for plant growth (Gupta, 1993). In soils boron is present in three forms: 1) inside silicate minerals, 2) adsorbed on clay minerals and aluminum and iron hydroxide, and 3) in organic matter (Borax, 1982). In natural waters, boron exists either as borate ion or as undissociated boric acid. Results from nuclear magnetic resonance (NMR) and Raman spectroscopy have shown that boric acid has a tridiagonal planar structure, while borate ion forms a tetrahedral structure in aqueous solution (Goldberg, 1993). The pK_a value of the dissociation reaction is

$$B(OH)_3 + H_2O \Rightarrow B(OH)_4^- + H^+ \quad pK_a = 9.24 \quad \text{(Bassett, 1980)} \qquad (2\text{-}1)$$

At concentrated aqueous solutions (>0.025 M or > 270 ppm) polyboric acids form, main species being $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$. These polyborate ions are unstable and rapidly transform to the monoborate form upon dilution (Keren and Bingham, 1985). In natural waters, boron concentrations are much below 0.025 M. The only boron species are borate ion or undissociated boric acid. Keren and Bingham (1985) used the computer program GEOCHEM to simulate irrigation water containing high concentration of boron (0.3 mM or 3.25 mg/L) and other common elements in irrigation water (45 mM of Na, 2.5 mM of Ca, 2.5 mM of Mg, 50 mM of Cl and 2.5 mM of CO_3^{2-}) to calculate the distribution of boron species at different pH values. The results for 3 pH values are presented in the Table 2-2. As it can be seen, even in a saline soil solution, the borate ion and boric acid are the main species and the concentrations of the boron cation complexes are low. The results also show that at neutral pH value 99% of total boron is present as undissociated boric acid. Studying boron isotope composition and concentration in marine carbonate, Hemming and Hanson (1992) concluded that tetrahedral $B(OH)_4^-$ is the dominant species adsorbed on flocculating clay or other reactive surfaces.

Table 2-2: Distribution of free boron species and metal-boron ion pairs in a simulated irrigation water (in %)

pH	$B(OH)_3$	$B(OH)_4^-$	$NaB(OH)_4^0$	$CaB(OH)_4^+$	$MgB(OH)_4^+$
7.0	99.0	0.9	<0.1	<0.1	<0.1
8.4	79.9	17.9	0.8	0.7	0.7
9.2	39.2	55.3	2.4	0.9	2.2

Organo-boron compounds and boron hydrides do not occur in nature. But, true organic boron compound, which contain B-C bonds, do exist. These include compounds such as triphenyl boron and tetraphenyl borate. However, these represent such a tiny fraction of the industrial boron compounds in use that they are not considered to be significant sources of boron in soil and in landfills. (Schubert, 2000). If present in natural environment, these organic boron compounds would break down into inorganic borates and boric acids through processes such as volatilization, thermal decomposition, oxidation and hydrolysis (EPA, 1991). Nevertheless, most of the research studies on adsorption of boron have dealt with inorganic form of boron (synthetic solution made of boric acid) and there has never been any systematic research to verify if organic boron compounds in wastewaters such as leachate do in fact exist. Boron does not appear to be chemically or biologically degraded in soils and natural waters (EPA, 1991, Tanji, 1990). Boron occurs at concentrations ranging from 10 to 300 ppm in soils, with the lowest and highest concentrations being reported for igneous rocks and marine shales, respectively (EPA, 1991).

2.4.2. Boron Deficiency and Toxicity

The biological importance of boron, both as an essential element and as a toxic element was recognized as early as 1930s (Walker, 1975). Boron is one of the more important of the essential micronutrients for terrestrial plants (Borax, 1982). It is important in cell division and a necessary constituent in the cell walls of plants. Boron deficiency disrupts cell division and cell elongation (Lukaszewski and Blevins, 1996). It also plays an important role in the synthesis of proteins (Gupta *et al.*, 1985). Boron facilitates the movement of surges, significantly increases the oxygen uptake by root tissue, enhances photosynthesis and the rate of CO_2 absorption from the air (Garret, 1998). One of the earliest effects of boron shortage is the alteration of the activity and integrity of the cytoplasm of the root cells, which is then followed by the rapid cessation of plant growth (Lukaszewski and Blevins, 1996). The control of the level of phenols in cells is another important role which boron plays to prevent the damaging effects of phenol accumulation. Phenol buildup is responsible for many of the effects of tissue breakdown (Borax, 1982).

There is an optimum boron concentration range for plant growth, which can be schematically shown such as the one depicted in Figure 2-3. In case of boron, the optimum range, the gap between deficiency and toxicity, is relatively narrow. The first symptoms of boron deficiency will be in growing points. The youngest leaves are misshapen, thick, brittle and small (Gupta, 1993). Toxicity, in contrast, is first detected in older leaves as chlorosis (yellowing) and necrosis (browning) on leaf tips progressing along the leaf margin and into the blade. Necrosis of the leaf tissue results in a loss of photosynthesis capacity (EPA, 1991;

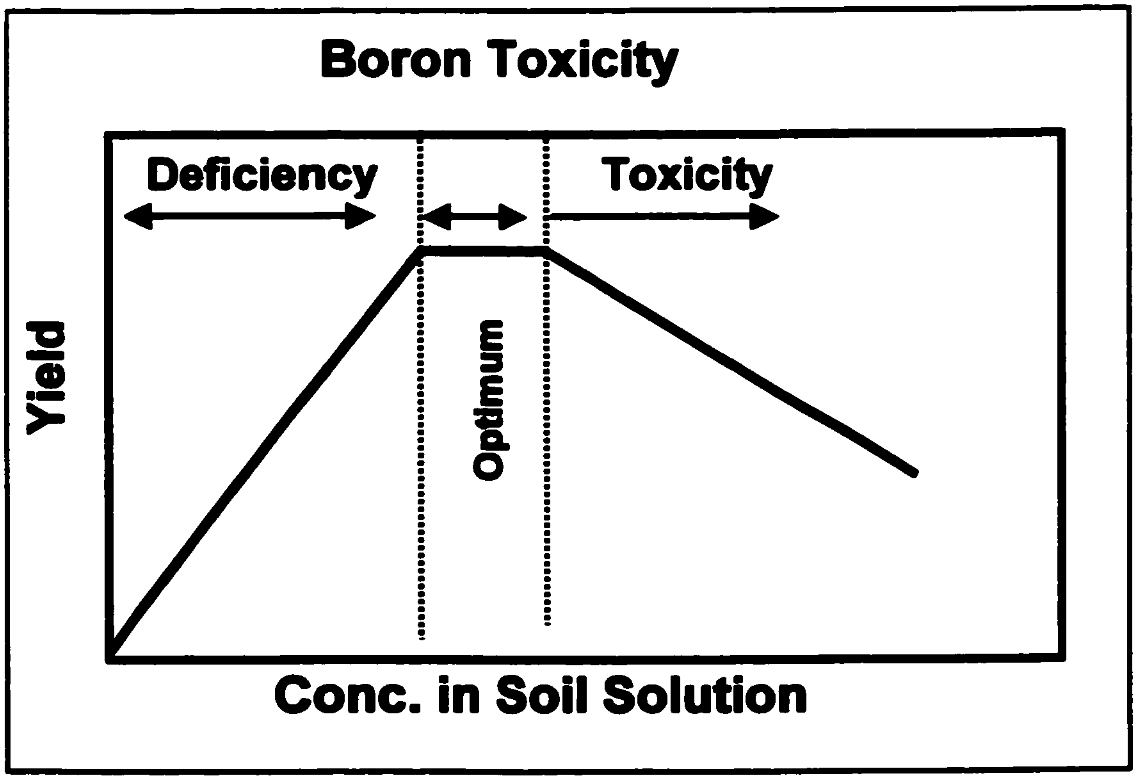


Figure 2-3: Deficiency and Toxicity effects of Boron

Tanji, 1990; Gupta, 1993). Although boron is accumulated in plants, according to Jame *et al.* (1982) plant uptake of boron is usually small compared with the amounts applied in the irrigation water. Using available data, they calculated that alfalfa plant yielding 11 000 Kg/ha would remove less than 2 Kg B/ha. The symptoms of boron toxicity and deficiency are often so striking in character that they are of great value in the interpretation of boron conditions existing on irrigated lands (Eaton, 1944).

Boron toxicity results in the reduction of crop yield and/or impairment of crop quality or even in more severe cases termination of plant growth or dying. Sensitive crops could show reduced yield when the boron concentration in soil solution exceeds 0.3 mg/L (Tanji, 1990). The literature on boron toxicity and its effects on plants are abundant. One study, which is very often cited, is the research conducted by Eaton (1944) on plant tolerance to boron. He investigated the effect of nutrient solutions containing trace (0.03-0.04 ppm) to 25 ppm of boron on 50 species of plants. The tolerance was estimated by dividing the average of the plant weights by the weight in trace or 1 mg B/L level; the quotient was multiplied by 100 and recorded as relative tolerance. The values of the relative tolerance varied from below 10 for highly sensitive plants such as grape, peach and strawberry to above 200 for the most tolerant plants such as cotton and asparagus. The relative tolerance of the plants showed a linear relationship with boron content of the irrigation water.

Eaton (1944) also concluded that the range between optimum and toxic concentrations is so small that for some plants there is some overlapping of the beneficial and injurious effects of boron. Goldberg (1993) also stated that the gap between beneficial and toxic levels of boron was so small that both deficiency and toxicity of boron could be encountered in a single growing season. Eaton explained this observation by stating that so much boron could accumulate in the older leaves that yellowing or burning results, while at the same time the boron supply to actively growing tissues is insufficient for their most rapid growth. In the author's opinion, although this work is very popular and often referred to, the lack of replicates in Eaton's work is a drawback. Garret (1998) collected the information on optimum and toxic concentrations of boron for different plants from the literature. The data presented by him also shows overlapping in some cases. It is worth noting that for some of the semi tolerant and tolerant species, such as sugar beats, oat and turnip, the optimum boron concentrations are in the range of 5 to 10 mg/L. When compared to toxic levels for sensitive species, such as cherry, peach and grape (<1.0 mg/L), it shows that there is also overlap between beneficial and injurious effects of boron for different plant species.

Typically, the growth of plants and agricultural crops is suppressed when a threshold value of salinity or concentration of some elements is exceeded. The threshold value is the maximum concentration that does not restrict the yield. Maas (1984) classified the tolerance of a wide variety of crops based on the threshold concentration. This classification is presented in Table 2-3.

The response of plants and agricultural crops to boron and salinity in general can be expressed with the use of two parameters, in the form of an equation, called yield response function (Tanji, 1990).

$$Y = 100 - m(B - A) \qquad (2\text{-}2)$$

Table 2-3. Tolerance of agricultural crops to boron

Tolerance	Concentration of boron in soil solution (mg/L)	Representative agricultural crops
Very sensitive	<0.5	Blackberry
Sensitive	0.5-1.0	Peach, cherry, grape, wheat, sunflower, strawberry, cowpea
Moderately sensitive	1.0-2.0	Red pepper, carrot, radish, potato, cucumber
Moderately tolerant	2.0-4.0	Lettuce, cabbage, celery, oat, corn, tobacco, mustard
Tolerant	4.0-6.0	Sorghum, tomato, alfalfa, purple vetch, parley, red beet
Very tolerant	6.0-15.0	Asparagus

Where B is the boron concentration in mg/L, A is the threshold value in mg/L, and *m* is the slope factor, relating yield decrease with further increases in boron concentration in excess of threshold value. Y is expressed as percent decrease in yield per unit increase in B.

Bingham *et al.* (1985) applied the above response function to data obtained from boron toxicity data for grain yield of wheat, barely and sorghum. The threshold concentrations for the grain yields of wheat, barely and sorghum were measured to be 0.3, 3.4 and 7.4 mg B /L, respectively. The slope for wheat, barely and sorghum were calculated to be 3.3%, 4.4% and 4.7%, respectively.

Boron toxicity on tomato by Francois (1984) showed that each unit increase in boron concentration above the threshold level of 5.7 mg B/L resulted in 3-3.4% reduction in tomato yield. The quality of the marketable fruit was also significantly affected as boron concentration increase resulted in reduced fruit size. All plants receiving 4 mg B/L or higher had developed marginal burns by the end of third week. Reduction in fruit yield and premature softening of kiwifruit was also reported as a result of boron toxicity by Tsadilas *et al.* (1997).

Francois and Clark (1979) investigated the boron tolerance of 25 ornamental plants of which about 15 were sensitive. These sensitive plants were moderately damaged by 2.5 mg B/L and were severely damaged or killed (showing a growth reduction of 50 to 100%) at boron concentration by 7.5 mg B/L in irrigation water. Tip burn, cupping of leaves, reduced leaf size and premature leaf drop were some of the symptoms of boron toxicity observed by these investigators. Choi *et al.* (1996) investigated the effect of boron toxicity on ornamental specie. All plants grown with 1 mM (10.8 ppm) boron showed leaf burns and yellowing. They recommended a limit of 0.25 mM (2.7 ppm) for the species under study.

It is known that boron is of nutritional importance, if not necessary, to humans and other higher animals. It is a necessary element for absorption and maintaining calcium and magnesium metabolism and bone health (Murray, 1996; Murray, 1995). Populations that live in an area where the soil or the drinking water contain high levels of boron are free of arthritis. And some hot mineral spas in New Zealand where the water boron content is very high acquired the reputation of healing arthritis (NHLRC, 2000). Humans and animals readily absorb boron orally. In humans boron is not metabolized, not accumulated and is excreted with a half-life of less than 24 hours (Hubbard and Sullivan, 1996; Waggott, 1969). However, there are some reports concerning the bioaccumulation potential of boron in aquatic fauna. It is reported that the salmon exposed to boron levels that were 10 mg/L above background concentration exhibited elevated boron concentration in the bone and kidney tissues (EPA, 1991).

Boron is not carcinogenic (Health Canada, 1996), but can affect the reproductive organs in male species at toxic levels. High doses of boron have also been shown to cause developmental effects (Hubbard and Sullivan, 1996; Murray, 1996; EPA, 1991). Boron trifluoride is reported to cause mortality in mice and weight loss in dogs and cats (EPA, 1991). Symptoms of exposure to high boron concentration may include nausea, vomiting, gastric discomfort, depression, and vascular collapse. The excessive loss of scalp hair in female humans is also reported (Cluver and Hubbard, 1996). However, the daily doses for human population is much below these levels. There are no U.S. EPA regulatory or guidance values available for human exposure to the boron compounds in the form of boric acid, sodium borate, borax, boron trifluoride and boron trichloride (EPA, 1991). Murray (1996) calculated a reference dose of 0.3 mg B/d/kg body weight as an acceptable daily intake for humans. For a person who weighs 60 Kg the acceptable intakes would be 18 mg B/day. The average U.S. adult male dietary intake is reported to be 0.9 to 1.5 mg B/day. If 1.5 mg B/day is subtracted from 18 mg B/L and assuming that a person drinks 2 liters of water per day, a safe drinking water level of 8.3 mg B/L would be obtained. The boron concentration in drinking water is much below this level and would not pose any health risk to the public.

2.4.3. Contamination Sources and Methods of Removal

The main discharge routes of boron to the environment are wastes and wastewaters, boron mining and processes, geothermal power plant, and landfill leachates (Grilc and Petkovsek, 1997; Howard and Livingston, 1997; EPA, 1991; Basset, 1976). According to Howard (1997), heavy metals, cyanide and boron are the most common pollutants among inorganic contaminants associated with groundwater contamination in industrialized areas. Landfill leachates in Ontario are reported as the main source of boron contamination of groundwater and have minimum, maximum and average concentration values of 0.12, 63.2 and 10.5 mg/l, respectively (refer to Table 2-1). At present time, there is limited information in the literature regarding removal of boron from landfill leachate since this has become a new environmental issue after lowering of boron limits for discharge criteria (MOEE, 1995).

The boron-oxygen bond in boron compounds is very stable. Boron is not affected by evaporation, volatilization or oxidation/reduction processes (Goldberg, 1997). Sorption on soil surface is the only mechanism, which removes boron from surface or groundwater (Bassett *et al.*, 1995). Under acid conditions and high concentrations of Ca, a fraction of boron could co-precipitate. Evans (1987) calculated that at a pH of 7, a solution containing more than 0.01 M $CaCl_2$ and 0.001 M boron (> 10.8 mg/L) could become supersaturated and boron will co-precipitate with calcium. There is no easy method for removing boron from aqueous solutions (Bassett, 1980 and1976; Waggott, 1969). Conventional treatment methods remove little, if any, boron from sewage. The removal of boron through the use of adsorption processes and anion exchange resins or extraction techniques would seem to be the most promising treatment method. Recently, a multi stage reverse osmosis process was also suggested for boron removal by Magara *et al.* (1998). However, more research and studies are required to fully investigate the performance of this system. HWM (2000) reported on a reverse osmosis treatment process for non-hazardous landfill leachate. The treatment process consisted of two reverse osmosis stages with 54% and 40% (94% total). However, the cost of a reverse osmosis system was reported to be prohibitive.

The strong tendency of boron to form bonds with oxygen and oxygen-carbon allows the selective extraction of boron by mannitol and some alcohols. Some specific organic compounds were also synthesized to achieve maximum boron extraction from solutions. A large boric acid recovery plant was built in 1963 at Searles Lake (Garret, 1998). The unique chemical properties that allow boron to be extracted apply to ion exchange resins. Rohm and Haas Company produces a resin named Amberlite IRA-743, which is an anion exchange resin specifically used to remove borate and boric acid under a variety of conditions (Rohm and Hass, 1989). It has a capacity of 5.7 mg B/mL. The capacity is flow-rate dependent and the resin is regenerated with a dilute H_2SO_4 solution followed by dilute NaOH solution. In a laboratory test on simulate irrigation water, Amberlite reduced the initial boron concentration of 10 ppm to below 1 ppm. Additional information on this ion exchange resin is presented in Appendix A. Based on verbal communication with a representative of the company, this resin is being used in ion exchange columns in a few plants, however no further information was disclosed. Suzuki *et al.* (1999) also reported on the preparation and use of an anion exchange resin loaded with chromotropic acid, which strongly retained boric acid/borate in the acidic region (pH 1.8-4.5).

2.4.4. Discharge Criteria and Standards

Considering the information presented on the effect of boron on plants, and humans, it is not surprising that the maximum allowable concentration for drinking water standards is higher than the discharge criteria for surface waters. Boron concentration for drinking water guidelines in Canada and Council of European Communities are set at 5 and 1 mg/L respectively (Howard and Livingston, 1997). In Ontario, the allowable boron concentration for discharges into surface water is listed under provincial water quality objectives. The discharge limit into surface water has been decreased from 5 to 0.2 mg/L recently (MOEE, 1995). This means that although a source of water could be acceptable for drinking, it could be unacceptable for watering of plants. The criteria for irrigation water in Ontario is 0.75 mg/L for waters used continuously on all soils, and 2.0 mg/L for waters used up to 20 years on fine textured soils of pH 6.0 to 8.5 (Ontario Ministry of the Environment, 1984). This is higher than the tolerance concentration for very sensitive plants such as blackberry. The Ministry of Environment does not establish a limit for boron discharge into sewers. As a general guideline when a limit is not specified in the municipal sewer by-law, the Ministry of Environment may permit discharges of up to 100 times the drinking water criteria. The region of Ottawa-Carleton has established an interim level of 25 mg B/L at sewage treatment facilities (HWM, 2000). After entering the sewage system the leachate is basically diluted, which results in lower concentrations of dissolved species including boron.

Comparison of average boron concentration in Ontario landfills with PWQOs criteria indicates that boron concentration in landfill leachates in Ontario is on average 50 times greater than the discharge criteria. This implies that sooner or later most of the landfills in Ontario including the Trail Road and Canadian Waste in Ottawa-Carleton region have to address the issue of boron.

The author finds that the criteria set as PWQOs for boron in Ontario is too stringent. Usually the methodology for deriving environmental criteria involves establishing some threshold levels for each element or compound by conducting short-term (acute) and long-term (chronic) toxicity tests on representative species or through gathering such information from literature, and then applying a safety factor. For example this procedure was followed by Erickson and Stephan (1988) for calculation of water quality criteria for aquatic organisms and also by Roux *et al.* (1996) for establishing criteria for South African freshwater ecosystems. For the case of boron, for example, Roux *et al.* (1996) considered a safety factor of 1000 due to lack of extensive data. When the element is not essential for the growth of plants and animals, large safety factors are justified. However, when dealing with essential elements such as boron safety factors must be chosen carefully because as mentioned earlier the gap between beneficial and injurious levels is very small and there could be some overlapping. Reducing boron levels to very low values such as 0.2 mg/L set in PWQO will most probably cause boron deficiency in more tolerant species. An alternative could be, if feasible, to setup case specific guidelines and criteria based on plant species and/or background concentration.

2.5. ADSORPTION PROCESS

Adsorption/desorption are the main processes that will affect the boron uptake by plants since plants respond to the activity of boron in soil solution (Keren and Bingham, 1985; Gupta *et al.*, 1985). Many researchers have investigated the adsorption of boron on different types of soils, but the majority of the work has been carried out using pure soil constituents such as Fe and Al oxides or clay soils. Factors affecting boron adsorption on soils include pH, soil texture, moisture, temperature, organic matter, wetting and drying, soil solution composition and clay mineralogy (Goldberg, 1997; Yermiyahu *et al.*, 1995; Hou, 1995; Goldberg *et al.*, 1996, 1993a and 1993b; Meyer, 1992; EPA, 1991; Goldberg and Glaubig, 1986a; Goldberg and Glaubig, 1986b; Gupta, 1985; Mattigod *et al.*, 1985; Elrashidi and O'Conner, 1982 and Keren *et al.*, 1981).

2.5.1 Boron Adsorption Surfaces

Boron adsorbing surfaces in soils are: aluminum, iron and magnesium hydroxide, clay minerals, and organic matter (Goldberg, 1997; Bingham *et al.*, 1971; EPA, 1991). It is suggested that boron adsorption occurs on broken edges of clay minerals (Gupta, 1993). Metwally *et al.* (1974) conducted some adsorption tests on Al and Fe hydroxide. By monitoring pH of the solution, they calculated the amount of boron sorbed and OH^- released into the solution. The amount of boron sorbed was positively correlated with OH^- release and it was concluded that anion exchange was one of the main mechanisms of boron sorption. Keren and Bingham (1985) conducted boron adsorption tests with illite, kaolinite, and montmorillonite clays. By comparing the amounts of boron adsorption, surface area and surface area of the edges of clay soils under investigation, they concluded that boron is adsorbed on the clay edges rather than planar surfaces. At a concentration of 1.0 mM B/L, these clay soils adsorbed between 1 to 10 mM/Kg of boron.

Although most soils contain small amounts of organic matter (<5%), it can significantly contribute to boron adsorption. However there is not much information on the adsorption of boron by organic soils such as peat. The available information is mostly qualitative. Gu and Lowe (1990) stated that on a weight basis, soil organic matter adsorbs more boron than other sorbents. Elrashidi and O'Conner (1982) observed significantly positive correlation between native soil boron and organic carbon content of 10 soils from New Mexico. Yermiyahu *et al.* (1995) used mature compost to simulate organic matter. The soil was mixed with varying amounts of mature compost. At a given pH, they observed higher boron adsorption by soils containing higher amounts of compost. Hou (1995) assessed the adsorption capacity of clay and humic acid fractions of soil and concluded that the extent of adsorption on humic fraction was up to two orders of magnitude larger than clay fraction suggesting that soil organic matter was the major pool of extractable boron. Evans and Sparks (1983) also stated that organic matter holds much of the total boron in soils. In contrast to the above studies, Marzadori *et al.* (1991) stated that boron adsorption was increased after they removed the organic matter portion of the soil. However, it should be noted that they used chemical agents and high temperature for destruction of organic matter, which could have changed the adsorption characteristics of the soil.

The work by Huettl (1976) was the only quantative study found in the literature that deals with the adsorption of boron by organic soils. He studied the adsorption of boron on an agricultural muck soil, which contained about 29% ash content. For the majority of the adsorption test he dried the soil and treated it with a mixture of HF-HCl acid. This is a drawback since this procedure might possibly have changed the characteristics of the soil. There was only one set of data with respect to untreated soil. Nevertheless, the results showed that more than 90% of adsorption was achieved within 30 minutes and boron adsorption increased as pH increased from 3.4 to 8.0. He suggested that boron sorption on organic matter was a ligand exchange mechanism occurring either as a single OH^- exchange or diol or cis-diol complexes, see Figure 2-4 (Goldberg, 1997; Gupta, 1993; Harter, 1991; Huettl, 1976).

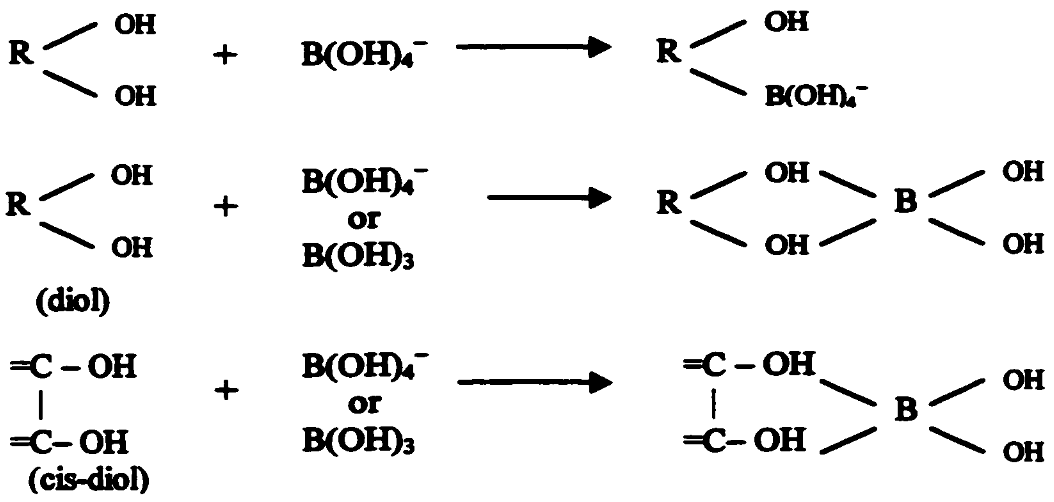


Figure 2-4: Ligand Exchange Mechanisms of Boron Adsorption (Goldberg, 1997; Gupta, 1993; Harter, 1991 and Huettl, 1976)

The adsorption of boron by humic material has been investigated by few researchers. Humic substances are partitioned into three groups. The fraction soluble in alkali, insoluble in acid is called humic acids (HA), the fraction soluble in both alkali and acid is called fulvic acid, and the fraction insoluble in alkali is called humin. Baohua and Lowe (1990) reported that boron adsorption by HA was pH dependant showing a peak at pH of 9. Meyer and Bloom (1997) used Freundlich and Langmuir models to fit the data they obtained from boron adsorption on humic acids extracted from a peat soil. The Freundlich model revealed a better fit. The maximum adsorption was 100 mM B/Kg at an equilibrium concentration of 2.5 mM B/L that occurred at a pH between 8.15 to 8.7. They also observed that most of adsorption took place in less than 4 hrs. A maximum adsorption of 78 mM/Kg (dry weight) at an equilibrium concentration of 1.6 mM B/L and a pH range of 8.0 to 8.5 was reported in a similar study by Gu and Lowe (1990).

2.5.2. Effect of pH

There is consent among the results obtained by the studies referred to in the previous sections that pH is the most important factor affecting adsorption, and that increasing pH enhances boron adsorption. Subsequently, boron becomes less available to plants with increasing pH. As mentioned earlier, at acidic pH levels boron is mainly present as molecular boric acid. Since it does not carry a charge and soils affinity for this specie is low the amount of adsorption is small.

As pH increases, $B(OH)_4^-$ concentration increases which results in higher amounts of adsorption. At pH levels above the range of 9-10, high concentrations of OH^- ions results in a decrease in adsorption due to competition effect (EPA, 1991 and Gupta, 1985). It is stated that the addition of lime reduces the availability of soil boron (Goldberg, 1993). Midgley and Dunklee (1940) also reported that liming of acidic organic soils doubled the amount of boron fixed against hot water extraction. The optimum pH is generally reported to be in the range of 7-10 (EPA, 1991); pH 9-10 was found to be optimum for adsorption on humic acids extracted from peat soils (Meyer, 1992), pH of 9 for three clay minerals (Bassett, 1976); and pH 9 for clay soil and humic acid (Hou, 1995). Using Fourier transform infrared spectroscopy, Su and Suarez (1997, 1995) concluded that both $B(OH)_3$ and $B(OH)_4^-$ get adsorbed on aluminum hydroxide, iron hydroxide and kaolinite and the type of adsorption is a ligand exchange with reactive surface hydroxyl groups. The use of sulfuric acid as an amendment to reclaim soils high in boron is reported by Keren and Bingham (1985). Addition of acid lowers the pH, which enhances boron desorption.

2.5.3. Effect of Temperature

Information on the effect of temperature on boron adsorption is scant and contradictory. Adsorption on illite clay increased with increasing temperature (Couch and Grim, 1968). However, this result was obtained under very high temperatures, 60 to 215 °C, which significantly differs from temperature range seen in nature. In contrast to this finding, Bassett (1976) reported that boron adsorption on illite, kaolinite, and chlorite decreased as temperature was raised from 25°C to 75°C. Guimarin (1995) investigated the effect of temperature on adsorption of boron on a silt loam soil. Sorption of boron decreased with increasing temperature from 2°C to 30°C. In another study by Singh (1971), adsorption of boron on sandy loam, loamy sand and three clay soils increased when temperature increased from 22°C to 45°C. Goldberg *et al.* (1993b) investigated the effect of temperature on boron adsorption by goethite, gibbsite, kaolinite, montmorillonite and calcite. The results of this study also showed that boron adsorption on clays was exothermic as boron adsorption decreases with increasing temperature for all materials, except for montmorillonite at high pH. In contrast, Bingham *et al.* (1971) found an increase in boron adsorption on amorphous soils from Mexico and Hawaii as temperature was increased from 10 °C to 40 °C. Su and Suarez (1995) gave an explanation on the opposite reaction of boron adsorption in response to temperature changes. On one hand the dissociation of boric acid is favored by an increase in temperature and on the other hand it renders the surface more negative at a given pH, thus decreasing the adsorption of anions. Therefore, the combination of these two factors would determine the net effect of temperature changes on adsorption of boron.

2.5.4. Solution Composition and Ionic Strength

The composition of solution and ionic strength can have an affect on adsorption by changing the surface potential and the characteristics of boron sorbing sites, and relative amounts of the dissolved boron species (Huettl, 1976). Couch and Grim (1968) observed an increase in boron adsorption on illite when they increased the ionic strength of the solution by adding $CaCl_2$. Similar results were attained by Fleet (1965) with increased salinity of artificial seawater. The above findings can be explained by electrical double layer theory. According to this theory the thickness of the charged layers on soil surface decreases with increasing ionic strength of the solution. This results in an increase in adsorption. Goldberg *et al.* (1993a) observed a pH dependent role for ionic strength. Ionic strength was varied by two orders of magnitude, from 0.01 to 1.0 M NaCl. At low pH increasing ionic strength resulted in a decrease in boron adsorption while at high pH values a reverse effect was observed. The same trend was also reported by Barrow (1989). According to Guimarin (1995) salinity had little effect on sorption of boron on a silt loam soil. Bassett (1976) reported that boron adsorption on clays increased with increasing ionic strength. Hou (1995) also stated that boron adsorption on clay fraction of soil was dependent on ionic strength. In another study by Melamed (1993) the increased mobility in boron was associated with the presence of phosphate, but there appeared to be interactions between phosphate and pH on the movement of boron. Results of research by Goldberg *et al.* (1996) and Goldberg and Glaubig (1986a) showed that boron adsorption by clay soil was not affected by high concentrations of silicon, nitrate, sulphate, molybdate, and phosphate. They suggested that majority of boron adsorbing sites are specific to boron. They did not provide any explanation of possible mechanisms. Bingham and Page (1971) also reported that boron adsorption sites are very specific and the presence of other anions such as sulphate and phosphate, as competitive ions, does not have any effect on boron adsorption. Investigating the adsorption of metals on peat, Cameron (1978) found that removal capacity for metals depended on the chemical characteristics of the leachate.

2.5.5. Effect of Time

Boron adsorption is a relatively fast process, which reaches equilibrium within a few hours. In a study, boron adsorption equilibrium was established in less than 30 min for Kaolinite and in less than 2 hrs for bentonite (Goldberg, 1993). Adsorption tests showed that adsorption of boron on a mixture of soil with varying amounts of mature compost was practically complete after 3 hrs (Yermiyahu *et al.*, 1995). More treatment time, however, resulted in additional boron fixation on illite. Increasing the treatment time from 30 to 120 days led to additional uptake of boron (Couch and Grim, 1968). A two-step mechanism was proposed consisting a rapid adsorption of $B(OH)_4^-$ followed by much slower diffusion of boron into the tetrahedral part of the structure. Following the initial uptake of boron, the subsequent uptake proceeded very slowly with no sign of reaching equilibrium. Bassett (1976) also mentioned a study that reported a rapid uptake of boron initially, then a gradual uptake continuing for over 135 days.

2.5.6. Operational Factors

In addition to geochemical parameters such as pH and temperature there are other parameters which deal with the way the adsorption test is conducted (operational factors). These include drying of adsorbent, soil-to-solution ratio, and shaking of samples. Soil-to-solution ratio and shaking (mixing) are listed as possible factors causing discrepancy between sorption distribution coefficients obtained from batch adsorption and column tests (Maraqa, 2000). Unfortunately the effect of these parameters usually are ignored and not reported in the literature. There is a need to determine if these factors have any significant effect on adsorption of boron from leachate.

Increasing soil-to-solution ratio resulted in a decrease in boron adsorption by kaolinite and montmorillonite (Goldberg, 1997; Keren and Bingham, 1985; Keren and Gast, 1981). Lower soil-to-solution ratios provide more contact between soil and solution and thus help equilibrium to establish in a shorter period of time. It is suggested to conduct the tests as close as possible to the conditions that exist in the field. However, due to difficulties associated with phase separation it is not practical to conduct a batch adsorption test with a soil-to-solution ratio similar to that of a column test or in the field. Oscarson and Hume (1998) believe that soil-to-solution effect is largely due to particle-particle interactions, or the blocking of some adsorption sites. If such an effect were present, it would be expected that adsorption increases with decreasing soil-to-solution ratio. As a result, the retardation factors obtained from batch adsorption would be lower than those obtained from column studies.

Wetting and drying of soil samples resulted in increased boron fixation for kaolinite and montmorillonite (Goldberg, 1997; Keren and Gast, 1981). A problem arising from wetting and drying is a decrease in volumetric water content and porosity of the peat. Saturation of peat is a very slow process. Consequently, a dry period could result in lower values for water content and porosity in the field, sometimes referred to as air-filled porosity (Lischeid, 2000).

For batch adsorption tests to reach equilibrium in a short period of time adsorption samples are usually agitated with a shaker. This also ensures that proper (enough) contact between adsorbent and adsorbate is provided. However, some researchers are against shaking the samples. Their argument is that shaking might break down soil particles and thus create more adsorption sites. Nevertheless, this is something that has to be checked for each specific case.

2.5.7. Desorption of Boron

Conflicting information on the reversibility of boron adsorption exists in the literature. While in some cases desorption isotherms closely corresponds to adsorption isotherms, in many cases desorption reactions exhibit hysteresis (Goldberg, 1997; Goldberg, 1993; Gupta, 1985). A research study on 25 different soils showed that the degree of hysteresis of boron desorption increased with increase in organic carbon (Datta and Bhadoria, 1999). The results from a study on adsorption of boron on peat soils indicated that the hysteresis effects are pH dependent as desorption of boron on humic acid showed hysteresis at pH 7.6 but not at pH 8.15 and 8.7 (Meyer, 1992). McLellan and Rock (1988) investigated the treatment of landfill leachate using peat. They observed desorption of up to 50% of metals tested (Cd, Cu, and Pb) when deionized water was applied to spent peat columns.

Since boron is adsorbed onto and released from the surface of the soil particles, soil solutions are buffered against rapid changes in boron concentration in irrigation water. For example, if high boron soils are reclaimed by leaching the soil with low boron water, boron is released, resulting in elevated soil solution boron concentration. This process is called boron regeneration (Peryea *et al.*, 1985). The regeneration of boron is reported to impede the removal of toxic levels of soluble boron from soils with leaching (Rhoades *et al.*, 1970). Leaching experiments showed that a large fraction of boron in soils can be removed by percolating water (Keren and Bingham, 1985). Several methods have been proposed for determination of available B in soils; among them hot water extraction is used most often and is claimed to give reliable results (Tsadlis, *et al.*, 1997; Gestring and Soltanpour, 1987).

2.5.8. Adsorption Models

Several models have been used to describe boron adsorption/desorption isotherms; among them Freundlich and Langmuir models are the most commonly used ones. These two models were first introduced about 90 years ago. There are numerous examples of the application of these two models for the adsorption of boron as well as metals in the literature. For example, Evans (1987) applied both of these models to 20 agricultural soils in Ontario out of which 19 conformed to both models. The adsorption maxima of the Langmuir model ranged from 0.63 to 7.9 mM/Kg of soil. Throughout the rest of this thesis more emphasis will be placed on the use of Freundlich model, since this model has been shown to give better fit to experimental data and for the same reason is used more often to describe adsorption by soils. In a mathematical form it is written as

$$q = KC_e^{1/n} \tag{2-3}$$

where C_e is the solution equilibrium concentration, q is the solid concentration, and K and 1/n are constants. One drawback of this model is that it does not predict any maximum adsorption. q would be expected to increase so long as C_e increases. For this reason it is recommended to use this equation at lower concentrations (Jenne, 1998). The success of both Freundlich and Langmuir models may have partly been due to appealing simplicity and the ease with which their adjustable parameters can be estimated (Kinniburgh, 1986). Traditionally a linearized form of the equation is utilized in order to estimate isotherm parameters. There are two problems associated with this approach. The first problem arises from the transformation of the Freundlich equation to a linear form. In the case of Freundlich model, the transformation is:

$$Logq = LogK + \frac{1}{n} LogC_e \tag{2-4}$$

However, closer examination of data often reveals systematic deviation from fitted isotherms. It is important to understand that a transformation of the data involves a transformation of the disturbance or error term, which affects original assumptions about regression analysis (Bates and Watts, 1988). In the case of Eq. 2-4 the log transformation implies that the absolute error increases with C_e and that the relative error ε/C_e is constant. Even for cases where a linear transformation is possible there are usually more than one way to transform the original equation, each of which result in a different set of adjustable parameters. For example Kinniburgh (1986) presented 3 different ways of linearizing the Langmuir isotherm, which resulted in different parameter estimates for the same set of data. In order to avoid the difficulties of changes in error distribution and biased parameters estimation due to linear transformation, Kinniburgh (1986) suggested direct fitting of data using non-linear regression or weighted least square methods be employed. Very few research studies have applied the non-linear regression method in order to calculate the constants. Most often the traditional linearized form of the Freundlich equation has been used and presented in many publications and textbooks such as the ones by Faust and Aly (1987) and Watts (1997) without realizing that some of the basic assumptions of least square method are violated and the values obtained might not be the best and unbiased parameter estimates. Two of just a few studies where the non-linear approach was used were the studies by Goldberg *et al.* (1993b) and Meyer (1992). Goldberg *et al.* (1993b) used a least square program (ISOTHERM) developed by Kinniburgh (1986) to fit the Freundlich model to a set of experimental data.

The second problem is related to the unique features of adsorption and the way the adsorption tests are carried out. The problem stems from the way dependent and independent variables are defined in carrying out the regression analysis, which is not considered in the procedure used by Kinniburgh and others. In Chapter 4 this matter will be further discussed where a new non-linear procedure and a new computer code for executing this procedure will be presented.

Keren and his co-workers proposed an equation for adsorption of boron that included the effect of pH (Keren and Bingham, 1985; Keren *et al.*, 1981; Keren and Gast, 1981; Keren and Mezuman, 1980). It is based on the assumption that boric acid, borate ion, and hydroxyl ion all compete for the same adsorption sites. It has three equilibrium constants and a maximum adsorption parameter which are found through fitting of the equation to experimental data. No physical significance could be attributed to the absolute values of the equilibrium constants (Goldberg, 1993). This is nothing more than fitting an empirical equation to data.

There exists a group of models called surface complexation or chemical models that are conceptually more advanced and take into account characteristics of solid surfaces and background solution including pH (Goldberg and Sposito, 1984). These include constant capacitance, diffuse double layer, and triple layer model. A significant difficulty in using these models is that there is not enough published data on values of the related parameters and they require an intense and costly data collection effort. Additionally, they include several adjustable parameters and practically their application becomes a data-fitting exercise. The adsorption reactions must be identified as well (Jenne, 1998). For example, Meyer (1992) applied constant capacitance model to data obtained from adsorption of boron by extracted humic acids. Humic acids are very complex with no well-defined characteristic. Different functional groups such as salicates, catechol, and glucose were tested to see which one could describe the adsorption of boron. This is more of a data-fitting exercise. Goodness of fit to experimental data cannot be used as evidence for the actual presence of any of the surface species postulated in the models (Goldberg, 1997). Veith and Sposito (1977) went another step further by stating that conformity to adsorption equations such as Langmuir or Freundlich does not in itself constitute a proof of adsorption reaction. Considering the above information, it can be concluded that such models are more suitable for simple systems with well-defined characteristics.

2.6. MATHEMATICAL AND EXPERIMENTAL MODELING OF CONTAMINANT TRANSPORT

Understanding the fate and transport of contaminants in the subsurface environment is becoming increasingly more important as groundwater contamination has become one of the most important environmental issues. It is essential that the important geochemical processes affecting contaminant transport be identified and accurately incorporated in the model. The basic processes governing the transport of solutes in the groundwater are advection, diffusion, dispersion and reaction. As groundwater moves through the porous media it carries with it dissolved solutes and the solute transport is due to bulk movement of groundwater. This process is called advection. Dissolved chemicals also move due to concentration gradient, and this is called diffusion. Solutes tend to spread out as the groundwater moves, a process called dispersion. This mixing causes dilution of a mass of chemical. Since diffusion is a Fickian process, and dispersion is assumed to be Fickian, they are combined together and represented as a single term, the coefficient of hydrodynamic dispersion. And finally, there are physical and chemical processes such as adsorption that influence the movement of solutes, which is called retardation. The general equation of mass balance (continuity) for solutes is:

$$-\nabla \bullet J = \frac{\partial \theta C}{\partial t} \pm G \qquad (2\text{-}5)$$

where J is the mass flux (mass of solute/area/time), C is the solute concentration (mass of solute/volume), θ is water content (or effective porosity), and G is the sink/source term. Total solute flux can be mathematically represented as:

$$J = \theta v C - D\nabla(\theta C) \qquad (2\text{-}6)$$

where v is average linear velocity (length/time) and D is the coefficient of hydrodynamic dispersion (area/time). Adsorption can be incorporated by assuming a sink term according to the following equation.

$$G = \rho_b \frac{\partial S}{\partial t} = \rho_b \frac{dS}{dC}\frac{\partial C}{\partial t} \qquad (2\text{-}7)$$

where S is the concentration of the solute in the sorbed phase (mass of solute/mass of dry soil), and ρ_b is the dry bulk density (mass/volume). Combining Equations 2-5 and 2-6 and replacing the G term with Equation 2-7 one obtains the final equation of solute transport through porous media as:

$$\frac{\partial C}{\partial t} = \frac{1}{R}\nabla(D\nabla C) - \frac{v}{R}\nabla C \qquad (2\text{-}8)$$

where $$R = \left(1 + \frac{\rho_b}{\theta}k_d\right),\quad k_d = \frac{dS}{dC}$$

R is the retardation factor and k_d is the slope of the sorption isotherm; it is often equated with the partition coefficient (also called distribution coefficient) defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution under equilibrium conditions. In fact, the two quantities are only equal when the sorption isotherm is linear. Otherwise k_d depends on C and eq. 2-8 becomes non-linear. The later definition is thermodynamically based while the former is based on the solute transport equation. For ideal transport of contaminants it is assumed that the porous medium is homogeneous and the reactions are instantaneous. This equation, known as advection-dispersion equation is by far the most widely used equation for describing the transport of dissolved matter in porous media (EPA, 1999a).

k_d is one of the most important parameters used in estimating the migration potential of contaminants in subsurface. For site-specific calculations, partition coefficient values measured at site-specific conditions are absolutely essential. The use of values found in the literature can result in significant errors in predicting the impacts of contaminants migration or site-remediation (EPA, 1999a). Values of k_d vary as a function of aqueous and solid chemistry. The k_d value is usually obtained from laboratory experiments which include batch adsorption test, column test, or can be estimated from K_{OC} (Octanol-Water partition coefficient). One should be aware though that some discrepancies between the k_d values obtained by batch adsorption and column tests have been reported (Maraqa, 2000). Some causes for this discrepancy include: factors related to differences between the two system such as level of mixing, soil-to-solution ratio, and particle spacing; those related to sorption nonidealities; and those related to experimental artifacts such as loss of sorbent in column tests.

Although there are mechanistic models (surface complexation models) to accommodate the dependency of k_d values on contaminant concentration, competing ions, surface charge and solution species distribution, the linear k_d model is currently the most common method for quantifying chemical interactions of dissolved contaminants with soils (EPA, 1999a). Installing these mechanistic models into existing computer codes is very difficult to accomplish. Additionally, these models require a more intense and costly data collection effort than is likely available. And finally, the surface of natural soils is very irregular and difficult to characterize. For the reasons mentioned the mechanistic models are rarely, if ever, applied to complex natural soil (EPA, 1999a).

Inherent in the linear k_d isotherm adsorption model is the assumption that the slope is independent of the concentration in the aqueous phase. However, it is common knowledge that contaminants adsorption on soils can deviate from the linear relationship. Nonlinear isotherms are used to describe the case where sorption deviates from linearity. The original usage of k_d is a special case of thermodynamic equilibrium constant for the ion exchange reaction

$$AS + B \Leftrightarrow BS + A, \qquad K = \frac{\{BS\}\{A\}}{\{AS\}\{B\}} \tag{2-9}$$

where S refers to the exchange site, and A and B are the exchanging ions. When one of the exchanging ions is present at trace concentrations, the amount of the other ion (which is being replaced) in the solution and exchange site remains constant. These two terms can be replaced by a constant and the equation can be simplified to $k_d = \{BS\}/\{B\}$or $=\{S\}/\{C\}$ according to the previous notation.

An important limitation of the measurement of k_d values is that the total concentration of the adsorbate is measured, thereby treating the adsorbate as a single species. Also, experiments cannot distinguish between adsorbed and precipitated species. The greatest limitation of using linear k_d value to calculate retardation term is that it describes solute partitioning for only one set of environmental conditions. Such homogeneity does not exist in nature and k_d values could vary by orders of magnitude if aqueous phase chemistry changes. To address this problem k_d can be defined as a function of empirically derived relationship with aqueous and solid phase parameters. In this approach, called parametric approach, the k_d values vary according to the chemistry of the system at each node. Statistical methods such as factorial design and regression analysis are employed to find such a relationship for k_d. If parametric approach is incorporated in the transport equations then the advection- dispersion equation becomes non-linear and the code must keep track of the current value of the independent variables at each point to continually update the k_d value. Because of the added complexity in solving the transport equation with the parametric k_d this approach has been used very seldom. Due to spatial variability a single k_d is not sufficient for an entire study site. The easiest variable k_d method is look up table, where separate k_d values are assigned to a matrix of discrete categories defined by chemically important parameters.

Due to issues mentioned above, *i.e.*, non-homogeneous nature of transport, non-linearity in k_d, and non-equilibrium reactions, the observed behavior of contaminant transport deviates from ideal conditions. Brusseau (1994) gave several examples of field experiments where the observed data showed non-ideal behavior. Spatially variable hydraulic conductivity, non-linear sorption, spatially variable sorption, rate-limited sorption or combination of theses factors was suggested as possible causes for non-ideal transport of contaminants. Recently some researchers have started to look at the non-linear nature of contaminant transport. Bruseau (1995) presented a mathematical model that described the transport of solute undergoing non-linear, rate-limited and first-order transformation. He used a two-domain approach where it is assumed that sorption is instantaneous for a fraction of the sorbent and is rate-limited for the remainder. He also used the Freundlich model to represent the nonlinear adsorption. Results showed that linear sorption could not provide an accurate simulation when $1/n$ (Freundlich constant) is less than 0.9. It should be noted that as in the case of adsorption models, these approaches are used to describe the data and any conformity between predicted and measured values is not a proof or evidence to the actual mechanism process. Another approach taken by some researchers is stochastic analysis approach where a random variation in physical and chemical parameters are considered. This approach showed that depressive properties for reactive solute were dominated by the flow-field variability, even when large variability was considered for k_d (Bosma and Zee, 1996, Robin *et al.*, 1991).

For simple geometry and boundary conditions there are analytical solutions for the advection-dispersion equation, such as the one developed by Ogata (1970). For more complicated situations the equation has to be solved using numerical techniques such as finite difference method. It is not intended to discuss these numerical approaches here since there are numerous books and articles that explain the details of application of these methods such as Fetter (1993).

2.7. SUMMARY

Boron is regarded as both an essential and a toxic element in the environment. The gap between optimum and toxic levels is very narrow. Landfill leachate is one of the main boron contamination sources. In Ontario, landfill leachates contain an average value of 10.5 mg B/L, that is over 50 times greater than discharge criteria. Conventional treatment methods are not effective for boron removal and adsorption processes and anion exchange resins would seem to be the most promising treatment methods for boron removal.

Constructed wetland system seems to be a promising alternative for treatment of landfill leachate. Constructed wetlands are categorised into two main groups: free water surface and subsurface flow system. Wetland systems have been shown to be effective in removing BOD_5, TSS, TN, TP as well as metals. Peat is reported to have a large specific area and is highly porous (95%), which makes it a good adsorbent material to be used in sub-surface flow systems.

Results from geochemical modeling shows that at dilute solutions (<0.025 M) inorganic boron exists either as $B(OH)_3$ or $B(OH)_4^-$. Although it is claimed by many researchers that boron mostly exists in inorganic form in the natural environment, there has never been any systematic research effort to verify if organic boron compounds exist in wastewaters such as landfill leachate.

Adsorption/desorption are the main processes, which will affect the boron uptake by plants since plants respond to the activity of boron in soil solution. pH, soil texture, moisture, temperature, organic matter, wetting and drying, soil solution composition and clay mineralogy are the factors that could affect boron adsorption on soils. There is not much information on adsorption of boron by organic soils such as peat. The presence of clay minerals, aluminum and iron hydroxides as well as organic matter enhances the adsorption of boron in soils. It is suggested that boron sorption on organic matter is a ligand exchange mechanism.

The effect of pH is very well established and there are numerous studies indicating boron adsorption increases with pH increase. For other parameters such as ionic strength and competitive ions as well as temperature there are conflicting results reported in the literature. The reason could be that a combination of these factors control boron adsorption and their cumulative effect could be different depending on the characteristics of the soil and aqueous solution under study. Unfortunately the effect of operational factors such as wetting and drying, soil-to-solution ratio, and shaking of samples are often neglected and not reported in research studies. There is need to investigate their effect, if any, on adsorption of boron from leachate.

Several models have been developed to describe boron adsorption/desorption isotherms; among them Freundlich and Langmuir models are the most commonly used ones. In order to avoid the difficulties of changes in error distribution and biased parameters estimation due to linear transformation it is suggested to use non-linear regression.

k_d is one of the most important parameters used in estimating the migration potential of contaminants in subsurface. However, there are some limitations for using linear k_d value to calculate retardation term. The adsorption is usually not a linear process resulting in a concentration dependent value and it also describes solute partitioning for only one set of environmental conditions. Heterogeneity as well as non-linear adsorption, rate-limited adsorption and first-order transformation have been suggested as possible causes of non-linear behavior of contaminant transport.

MATERIALS AND METHODS

To accomplish the objectives outlined in the first chapter of this thesis, four sets of laboratory experiments plus a two-year field monitoring program of Huneault Waste Management landfill site were carried out. The first set of laboratory experiments included boron speciation tests; the second set was the investigation of the effect of operational factors on boron adsorption; the third set consisted of batch adsorption tests; and the fourth set included column tests. Materials and procedures used in this research work are reported and explained in the following sections.

3.1. CHARACTERISTICS OF MATERIALS USED

The peat used as the main adsorbing medium in this study was obtained from a peat deposit site at Casselman near Ottawa, Ontario. The peat was very moist (MC=81%), had a dark brown colour, a fibrous structure, and was very spongy and fluffy. Its characteristics are shown in Table 3-1. Besides Casselman peat, peat from Alfred Bog near Ottawa, Ontario, a commercial peat moss, and two sources of composts were evaluated as a potential replacement material for Casselman peat. The terms *peat*, *Alfred peat*, and *peat moss* will be used to refer to Casselman peat, Alfred Bog peat, and commercial peat moss, respectively, through the rest of this thesis. The two sources of compost being investigated were HWM Site compost (CompostH) and Trail Road landfill site compost (CompostT). Both composts were produced mainly from yard and garden wastes collected within the municipality of Ottawa-Carleton. CompostH contained about 25% coarse material (3/8" sieve, 9.5 mm) and CompostT had 10% coarse material; both fractions were disregarded in order to have a more uniform and homogeneous material for batch adsorption tests. The characteristics of three types of peat as well as two composts are presented in Table 3-1. In addition to organic sources, an anion exchange resin, Amberlite-743, was used for boron removal. Amberlite IRA-743, a product of Rohm and Haas Company, is an anion exchange resin specifically used to remove borate and boric acid under a variety of conditions without removing other ions and organic matter (Rohm and Hass, 1989). Detailed information on this resin is provided in Appendix A.

Table 3-1. Characteristics of peat and compost materials

	MC (%)	VS (% DM)	pH
Peat	81 (25)	84.4 (24)	6.4 (5)
Alfred peat	72 (9)	70.1 (5)	6.5 (5)
Peat moss	14.8 (5)	97.2 (4)	5.0 (5)
CompostH	33.4 (10)	18.3 (10)	8.3 (5)
CompostT	29.6 (10)	29.4 (10)	8.0 (5)

DM = on Dry Matter basis
( ) shows the number of tests

Leachate generated at the Huneault Landfill has been monitored on a continuous basis since 1990. The characteristics of the leachate collected at HWM were presented in Table 2-1 along with the values for other landfills in Ontario. HWM landfill is unique in the sense that the collected leachate is distinctly different from most other landfill leachates in Ontario. With the exception of boron most parameters have lower concentrations than the average values presented for Ontario as well as other landfills. This is attributed to the type of waste landfilled at this facility. Concentrations of some selected contaminants were on average 18.5 mg/L of ammonia, 40 mg/L of BOD_5, 28.9 mg/L of nitrogen, 10.2 mg/L of boron, 2.8 mg/L of iron, 0.03 mg/L of lead, and 0.03 mg/L of zinc. In addition to HWM leachate, one set of experiments was conducted with leachate obtained from Trail Rd landfill, Ottawa, Ontario. For experiments carried out with synthetic solution (SS) only containing boron, boric acid was dissolved in distilled water to prepare the synthetic solution.

3.2. ANALYTICAL PROCEDURES AND INSTRUMENTS

Ammonia. Ammonia was measured by an Ammonia-selective Orion electrode according to the procedure in Standard Methods (APHA, 1992).

Anions. Anions, chloride (Cl^-), sulphate (SO_4^{-2}), and phosphate (PO_4^{-2}), were measured using a DIONEX High Performance Liquid Chromatographer (HPLC).

Boron and metal analysis. All samples were filtered using Glass-fiber filters (0.45 μm) and acidified using nitric acids to a pH of 2. The filtrate was then analyzed by Inductively Coupled Plasma (ICP) using a Termo Jarrell ICP machine. To determine whether boron is in organic form or not the extract organic solvents were tested by a gas chromatography mass spectroscopy (GCMS) instrument.

Conductivity & TDS. Conductivity (CND) was measured by a Radiometer Copenhagen conductivity meter for laboratory experiments. In the field a HACH TDS/CND meter was used to measure TDS and CND.

Temperature and DO. Temperature and dissolved oxygen (DO) in the field was measured using a YSI-55 DO meter.

pH. pH was measured by a Fisher accumet electrode (model 210) for laboratory experiments. In the filed a HACH-1 pH meter was used. For adsorption tests, pH of the filtrate was measured to prevent any interference of soil particles and minerals.

TOC. Total Organic Carbon (TOC) was measured by a Folio Instruments DC-190 TOC analyzer.

Total Phosphorous. Total Phosphorous was measured by a Spectronic 70 spectrometer according to the procedure suggested by Standard Methods (APHA, 1992).

MC, VS, BOD_5, COD. Moisture content (MC), Volatile Solids (VS), 5-day Biological Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) were measured according to Standard Methods (APHA, 1992).

3.3. BORON SPECIATION

As indicated in the previous chapter there was a need to verify if any organic boron compounds in leachate exist. Potential analytical methods that can be used to determine organic boron were gathered from the literature. These include organic extraction methods, combination of organic extraction methods and gas chromatography mass spectroscopy (GCMS), and the use of a boron specific ion exchange resin (Amberlite-743).

Dichloromethane and chloroform were used as organic solvents to separate organic fraction of the leachate. Ten milliliters of the organic solvent was added to 50 mL of leachate or synthetic solution containing only boron and the mixture was agitated for one minute. About 5 minutes were allowed for the two solutions to separate. The bottom solution (solvent) was separated and the above procedure was repeated for either 3 or 5 times and the remaining solution was analyzed for boron using ICP. The idea was that if there existed any organic boron compound in the leachate, organic solvent would remove it from the leachate and organic boron should not appear in the remaining solution. The same procedure was carried out with a synthetic solution (SS) containing inorganic boron (made of boric acid) to check if inorganic boron forms any type of bond or reaction with organic solvents. These two solvents remove a fraction of organic matter not all of it, nevertheless, they were proven to be ineffective for the purpose of separating organic and inorganic source of boron.

For the second method both extracts from SS and leachate, obtained from the previous step, were further analyzed by a Gas Chromatography-Mass Spectroscopy (GCMS) analyzer. Any potential association between inorganic boron and organic solvents would be very weak and it would break during the volatilization step before detection. Thus, organic boron compounds will pass through the system and be detected while the week bonds of inorganic boron and organic solvent will be broken off during the volatilization step before the detector. Thus, it is possible to differentiate between inorganic and organic boron.

For the last method Amberlite -743 anion exchange resin was used to separate any boric acid and borate ions from the leachate and SS. Amberlite-743 is an anion exchange resin, which is claimed to specifically remove borate and boric acid under a variety of conditions without adsorbing other anions or organic compounds. Five grams of Amberlite resin was added to each litre of leachate and agitated for one day using an orbital shaker. Then Amberlite resin was separated by filtering the solution. The remaining solution was analyzed for boron. The rational is that if any significant amount of boron in the remaining solution is detected, it should be in the organic form, which could not be removed by Amberlite resin.

Also, to check if Amberlite resin removes other anions and organic compounds other than boron, leachate samples were analyzed before and after adding Amberlite resin to the solution for Cl^-, SO_4^{-2}, and COD. This was done to ensure that the composition of the leachate (except boron content) was not altered due to the application of Amberlite resin. Amberlite resin was used to prepare dilution solution by removing only boron from leachate. This dilution solution will be referred to as L-B (leachate minus boron) solution through the rest of this thesis. This L-B solution was used for all subsequent dilutions unless indicated otherwise.

3.4. EFFECT OF OPERATIONAL AND ENVIRONMENTAL FACTORS ON BORON ADSORPTION

A series of batch adsorption tests were conducted to evaluate the effect of operating and environmental parameters on adsorption of boron. These included:

1. Effect of drying peat;
2. Effect of shaking;
3. Effect of soil-to-solution ratio;
4. Effect of competing ions and solution composition;
5. Effect of time of contact and kinetics;
6. Effect of pH; and
7. Effect of temperature.

For each case two or more sets of batch adsorption tests at different levels of each parameter were carried out while other parameters were held constant. Each test was repeated a minimum number of 3 times to provide replicates. Then for each case the amount of adsorption obtained at different levels of the parameter of concern were statistically compared.

Figure 3-1 schematically shows how adsorption experiments were conducted. A known quantity (***S***) of adsorbent was added to the solution with a volume of ***Vol*** and initial contaminant concentration of C_i. The mixture was agitated until equilibrium was achieved and then it was filtered. Equilibrium concentration of C_e and final pH of filtrate were measured. It was determined that adsorption of boron and metals was almost complete after 3-4 hrs. A 24 hr period was chosen for conducting adsorption tests to make sure that equilibrium was established.

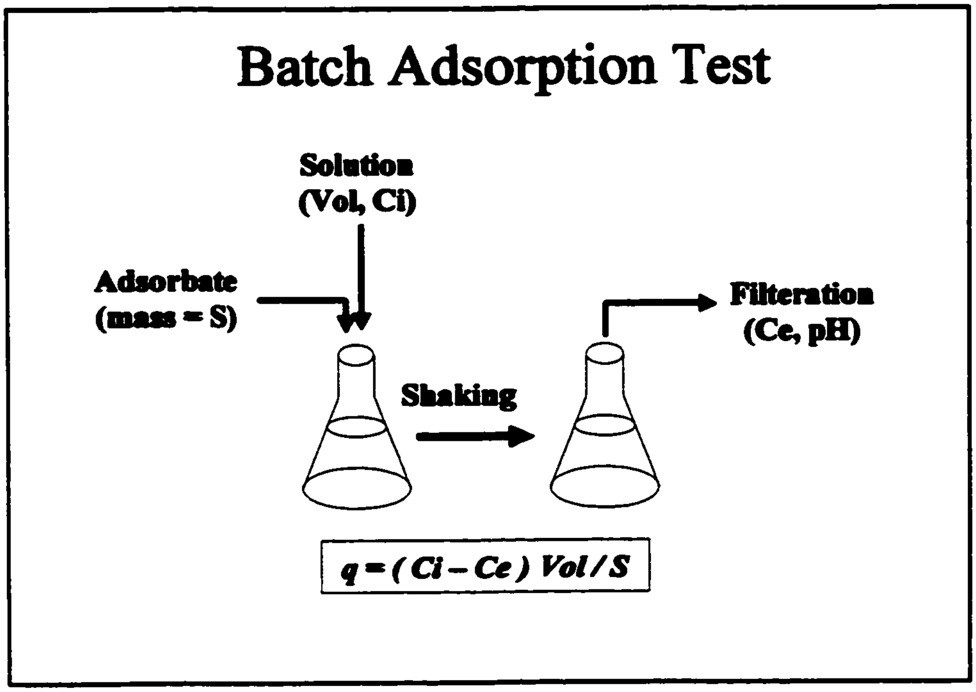


Figure 3-1. Batch adsorption test

For all batch adsorption tests at least three replicates were used. In addition, two blanks were always run to check if any adsorption of elements on the surface of glassware occurs. One control (peat plus L-B solution or DW) was also run to determine if any amount of adsorbate is leached out of peat when in contact with L-B solution or DW.

3.4.1. Effect of drying peat

The adsorption of boron on peat, which was previously dried at a temperature of 105°C, 90°C, 75°C, and air-dried was compared with that of fresh peat as collected. In each case equal amount of fresh peat, 10 or 20 g, was placed in an aluminum dish. One set was dried at the above-specified temperatures while the second set did not receive any treatment (fresh peat). Then batch adsorption tests were carried out using dried and fresh peat samples and the results were compared in order to determine if drying of peat had any significant effect on its adsorption capacity of boron. The reversibility of the drying effect was also investigated by soaking the previously dried peat samples in distilled water for 1 day or two weeks. Then these samples along with samples of fresh peat were used for batch adsorption tests and the results were compared. The reversibility test would help to determine if peat can regain any potential loss of boron adsorption capacity.

3.4.2. Effect of shaking

Two sets of batch adsorption samples under similar initial conditions were subjected to no shaking and shaking at 150 rpm. A similar set of tests with low agitation (50 rpm) and high agitation (200 rpm) was also performed to determine if shaking of batch adsorption samples during the test had any significant effect on boron adsorption process.

3.4.3. Effect of soil-to-solution ratio

The maximum practical ratio for adsorption experiments was measured to be 0.6 g/mL. Two soil-to-solution ratios of 0.1 g/mL and 0.4 g/mL were investigated. Fifty milliliters of leachate was equilibrated with 5 or 20 g of fresh peat. Since peat was acidic and the pH of the solution would change with varying amount of peat, numerous adsorption tests with different dilutions and different amount of 0.1 M NaOH were carried out. Then pairs of samples with identical pH and C_e and different soil-to-solution ratios were used to analyze the effect of soil-to-solution ratio.

3.4.4. Effect of solution composition and competing ions

To assess the effect of solution composition on boron adsorption, two sets of batch adsorption tests were conducted. For the first set leachate was diluted using L-B dilution solution. Fifty millilitres of solution diluted with L-B was added to 10 g of fresh peat to carry out adsorption test. For the second set the same procedure was repeated except that distilled water (DW) was used for dilution instead of L-B dilution solution. In the first set the composition of leachate (except concentration of boron) is unchanged whereas in the second set concentrations of all the leachate constituents are reduced due to the dilution with DW. Several dilutions were prepared by trial and error until equilibrium pH and contaminant concentration in the solution (C_e) of both sets were identical. In this case the only variable was the composition of leachate since all other factors were the same. Then, the results were compared to determine if the change in solution composition had any effect on boron adsorption on peat.

The effect of competing anions on adsorption of boron by peat was also evaluated. Different synthetic solutions (SS) were prepared. SS was used instead of leachate to omit any possible interaction of the competing anions with other constituents in the leachate. The synthetic solutions included DW containing boron and $CaCl_2$, DW containing boron and $Al_2(SO_4)_3$, DW containing boron and $Zn_2(SO_4)_3$, DW containing boron and NH_4SO_4, DW containing boron, $CaCl_2$ and NH_4SO_4. Ten grams of fresh peat was then added to 50 mL of each of these solutions to carry out adsorption tests. The results were compared with those obtained from adsorption tests conducted with DW containing only boron. The comparison of the results would show if adsorption of boron was affected by the presence of other potentially competitive anions such as Cl^- or SO_4^{2-}.

3.4.5. Time effect and kinetics of boron adsorption

To evaluate the effect of duration of batch adsorption test (long-term adsorption) three sets of experiments were carried out. Ten grams of fresh peat were added to 50 mL of leachate. Batch adsorption tests were terminated after 5, 14, and 33 days. These results were compared with those obtained from tests carried out for 24 hrs.

For kinetics of boron adsorption ten grams of fresh peat were added to 50 mL of leachate. The adsorption tests was terminated and the mixture was filtered after 1, 1.5, 3, 5, 10, 20, 30, 50, 90, 120, 180, 300, 420 or 1380 minutes and the filtrate was analyzed by ICP for boron and metals. The pH of the final solution was also measured.

3.4.6. Effect of pH

A preliminary set of batch adsorption tests was carried out to determine if pH had any significant effect on the adsorption of boron. Twelve grams of fresh peat was added to 100 mL of leachate. Three replicates were tested at a pH of 7. Another three replicates were tested at a pH of 7.5. pH of samples in the second set was raised by adding a few drops of 0.1 M NaOH to the leachate before adding the peat. The results of adsorption tests were then statistically compared. The effect of pH was further investigated by running batch adsorption tests at a pH ranging from 7 to 10. These are further explained in the sections on factorial design (two-level and 2nd order).

3.4.7. Effect of temperature

A preliminary set of batch adsorption tests was carried out to determine if temperature had any significant effect on the adsorption of boron. Fifty milliliters of leachate was added to 10 g of fresh peat. Three samples were subjected to a temperature 2°C while another three samples were run at a temperature of 22°C. Comparison of results would indicate if boron adsorption on peat was temperature dependant. The effect of temperature was further investigated by running batch adsorption tests at temperatures of 2°C, 12°C, and 22°C. These are further explained in the sections on factorial design (two-level and 2nd order).

3.5. BATCH ADSORPTION TESTS

After the effect of operational factors was determined, these factors were set at fixed levels for conducting the subsequent batch adsorption tests. For all subsequent tests fresh peat and a soil-to-solution ratio of 0.2-0.4 were used. All tests were conducted for a period of 24 hrs with moderate shaking at 100 rpm. Four sets of batch adsorption tests using 10 g of fresh peat and 50 mL of leachate diluted by L-B at pH values of 7.5, 8, 9, and 10 and room temperature were conducted. The pH of solution was adjusted by addition of 0.1 N NaOH solution to the leachate before addition of peat.

3.5.1. Two-level factorial design

Since it was determined that pH, temperature, and solution composition had significant impact on adsorption of boron it was decided to conduct a two-level factorial design experiment in order to evaluate the relative importance of each of these parameters with respect to others and their interaction if any. Ten grams of fresh peat were added to 50 mL of solution. As shown in Table 3-2, two levels of pH (7.2 and 9.2), two levels of temperature (2 and 22°C), and the use of distilled water versus L-B solution for dilution were examined. pH was adjusted with 0.1 M NaOH. Sample flasks were agitated in a temperature-controlled room set at 2 or 22°C. All samples were replicated at least 3 times.

Table 3-2. Two-level factorial design

Parameter	Lower Level	Higher level
pH	7.2	9.2
Temperature, °C	2	22
Method of dilution	DW	L-B

DW=distilled water used for dilution
L-B= leachate minus boron

3.5.2. Second-order factorial design

In order to find a relationship for boron adsorption as a function of C_e, pH, and temperature a second-order factorial design experiment was carried out. The same procedures as in two-level factorial design were followed except, that each parameter was set at more than two levels. Temperature was set at three levels, 2, 12, and 22°C and pH varied over a range of 7 to 10.2. All samples were replicated at least 3 times.

3.5.3. Alternative adsorbent media

Batch adsorption tests using leachate and Alfred peat, peat moss, two composts (CompostH and CompostT), and Amberlite resin were carried out to evaluate the use of these materials as an alternative boron adsorbing media. Their characteristics were shown in Table 3-1. In the case of Alfred peat, 1, 2, 4, and 8 g of peat and 100 mL of leachate were used for batch adsorption tests. For (commercial) peat moss 3 g of peat moss was added to 50 mL of leachate. L-B solution was used for dilution. Since peat moss was very acidic and caused the pH of the mixture to drop below 6, the pH of the solution was adjusted towards 7 by adding 0.1g $Ca\ (OH)_2$ to each sample. One set of batch adsorption tests with peat at pH=7 was also conducted to compare the results. Batch adsorption tests for CompostH and CompostT were carried out using 500 mL flasks containing 40 or 20 grams of CompostH or CompostT and 50 or 100 mL of a mixture of leachate and L-B solution. To evaluate the effect of pH increase on the adsorption capacity of CompostH, additional tests were conducted by adding 0.15 or 0.25 g of $Ca\ (OH)_2$ to the compost mixture before addition of liquid, which raised the pH to 9. In the case of Amberlite, 0.1 g of Amberlite was added to 100 mL of solution containing different volumes of leachate and L-B solution.

3.5.4. Adsorption of heavy metals (Fe, Pb, and Zn)

The adsorption of Fe, Pb, and Zn was investigated by adding 1, 2, 4, and 8 g of dried peat to 100 mL of leachate. The leachate was spiked for these elements since they were present in low concentrations in the original leachate. Distilled water was used for dilution. After 24 hrs the mixture was filtered and the filtrate was analyzed using ICP method. This set was carried out before it was realized that drying of peat could affect its adsorption capacity.

3.5.5. Desorption tests

The peat samples that were used in the kinetic study tests were washed with distilled water and filtered immediately. This procedure was repeated for a second time and the filtrate was from the second wash was analysed by ICP method to verify if that the soil solution did contain any detectable amount of elements of concern. Then different amounts of distilled water solution were added to the soil mixture and the mixture was agitated for another 48 hrs. The mixture was then filtered and the filtrate was analysed by ICP. The samples were subjected to a second set of desorption test by repeating the previous step for a second time but at a temperature of 90 to 100°C (hot-water extraction).

3.6. COLUMN TESTS

Continuous flow column study provides a more realistic simulation of the proposed engineered wetland. Three different sizes of columns, all of them made of Plexiglass, were used. The first set of columns had 10.2 cm diameter, 11 cm height and a 3.5 cm high leachate reservoir to provide constant hydraulic head. The volume of each cell was 900 cm^3. These will be referred to as "Small columns".

The leachate was spiked with Fe, Pb, and Zn. To produce a homogeneous and uniform medium the peat was dried (at 75-80 °C) and large pieces were crushed or discarded. Peat was then added in layers of 3-5 cm and compacted in the columns to match the field density. Plexiglass top and bottom caps and the top reservoir were screwed to each column with O-rings fitted between them to prevent leakage. A Peristaltic pump was used to continuously pump the leachate into the top reservoirs of columns to maintain a constant head. This is schematically shown in Figure 3-2. Prior to adding any liquid into the columns, CO_2 gas was passed through the columns for 30 minutes and the columns were then saturated with distilled water from the bottom. This procedure helps to prevent any air trapping in the columns. Once all columns were saturated the influent was switched to the spiked leachate. The effluent from each column was measured over time. Also samples from the effluent were collected and analysed for metal concentrations, BOD_5 and COD. From the set of 5 columns one was percolated with distilled water (#5) and the remaining four were percolated with spiked leachate. The columns were disconnected after a predetermined number of pore volumes had passed. The packed peat columns were removed, cut into four slices and squeezed to extrude the pore water.

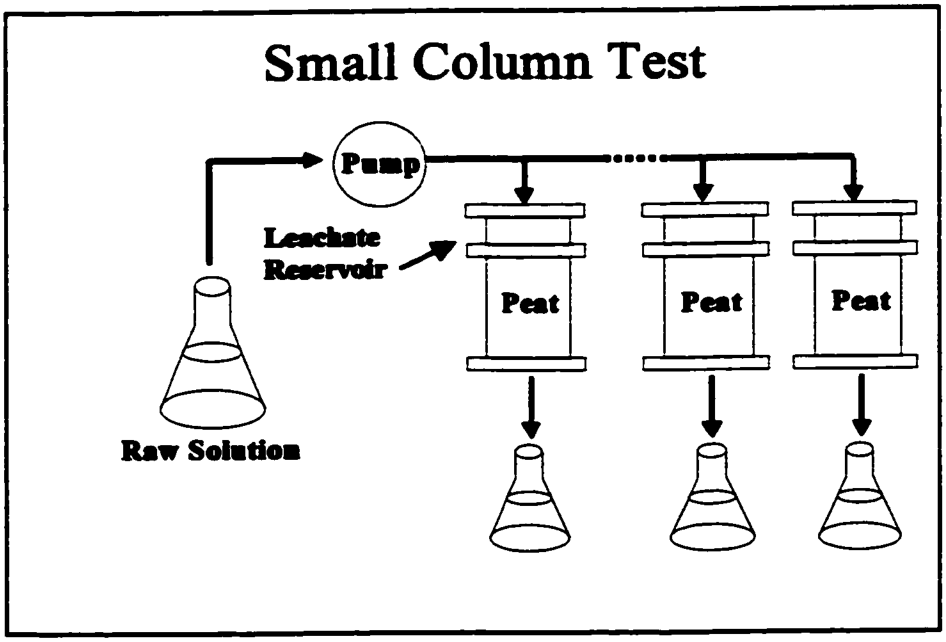


Figure 3-2. Set up of Small Column Tests

The above procedure was found out to be troublesome and inefficient. The main reason was that hydraulic conductivity was changing over time, especially at the beginning of the experiment, and the above system had to be attended and maintained on a continuous basis. In addition the length of the columns were too small to show any profile for boron concentration through the columns. Also, drying of peat was later found to decrease the boron adsorption capacity of peat. Another problem encountered was the growth of algae, which could affect the hydraulic conductivity as well as transport of contaminants. Therefore, it was decided to use larger columns and fresh peat. All columns were covered with clothing to prevent algal growth for subsequent column tests.

The second set of columns had the same configuration as the Small columns, except that their height was 20 cm instead of 11 cm. The operating volume of each column was 1.65 L. The term "Medium" columns will be used to refer to this set of column tests. These columns were used for compost material and peat. Also, the pump was omitted and a holding tank was included instead, to provide a constant head. Fresh peat or compost were placed in layers and compacted. Columns were saturated from the bottom with DW, which was later switched to leachate. Several trials with different degree of compaction were done in order to achieve a hydraulic conductivity in the range of 10^{-3} to 10^{-4} cm/sec. It was not possible to achieve complete saturation by this method and some air pockets were observed in the columns.

Columns used in the third set were 42 cm long and had a diameter of 15.5 cm. The volume of each column was 7.9 L. These will be referred to as "Long columns". In order to achieve complete saturation peat was mixed with DW to make a slurry. Slurry was poured into the columns and pressure was applied from the top by a circular disk. The extra water was allowed to seep through the bottom, which resulted in settlement and compaction of peat. This process was repeated until columns were filled with compacted peat. This process achieved complete saturation. Longer columns also made it possible to install two sampling ports at 1/3 and 2/3 of the length of the columns. The experimental set up is schematically shown in Figure 3-3. Leachate was diluted using B-L solution. A holding tank equipped with a float valve was used to provide constant head. Leachate was distributed through a distribution chamber over the top of the columns. All columns were covered with clothing to

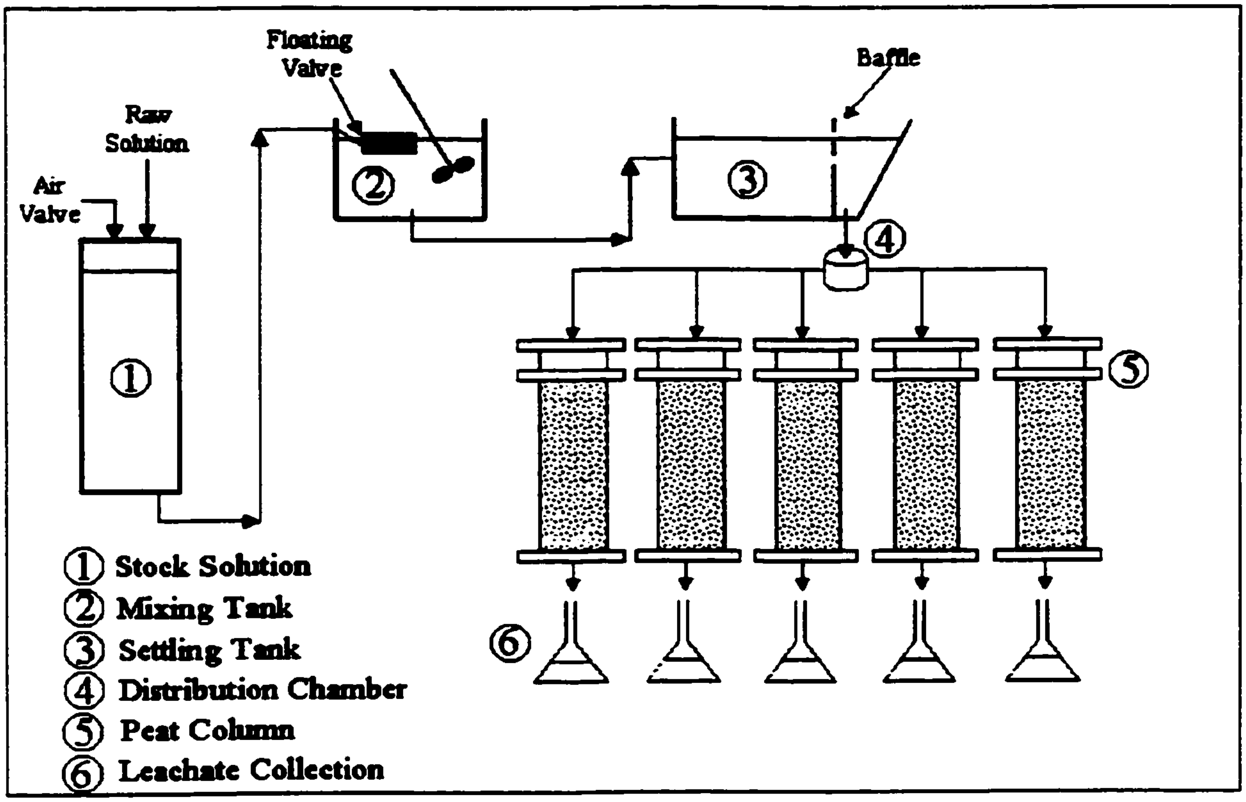


Figure 3-3. Set up of Long Column Tests

prevent algal growth. Three columns were prepared using peat. Three more columns were prepared by mixing peat with lime (1 to 100 ratio) in order to raise the pH. Over time samples from each port were collected and analysed for pH, conductivity, ICP metal scan, and TOC.

Also, to further investigate the adsorption capacity of Amberlite resin, one column with a cross-sectional area of 1 cm^2 and length of 20 cm was packed with the Amberlite resin. Synthetic solution made from boric acid with an intial concentration of 1.7 mM B/L (18.4 mg B/L) was passed through this column using a Peristaltic pump. Boron concentration of the effluent was measured using the ICP method.

3.7. THE HWM LANDFILL SITE AND THE ENGINEERED WETLAND SYSTEM

The Huneault Waste Management (HWM landfill), occupying an area of 40 hectares, has been in operation and serving the Regional Municipality of Ottawa-Carleton since the early 1960's. Since 1971 this landfill has been operating under a certificate of approval from the Ministry of Environment and Energy to receive construction/demolition waste, industrial/commercial/institutional (IC&I) waste, as well as miscellaneous inert material.

The HWM site is located on a thick low permeability (10^{-09} m/sec) Champlain Sea clay deposit, 33.5 m deep in the north and 23 m deep in the south of the landfill, which acts as an aquitard protecting the deep aquifer from being impacted by landfill leachate. The clay deposit is covered by a thin silty sand blanket and is underlain by 0.3 m thick Limestone bedrock at a depth of 25 to 37 m. Shallow groundwater is found in the silty sand layer, which is predominantly horizontal from north to south. The sand layer is 0.6 to 2.0 m deep in the landfill area.

The waste materials received at HWM landfill consist mainly of demolition and construction debris, commercial wastes including paper, cardboard and wood wastes, as well as a variety of packaging, wrapping, textile, plastic, asbestos, contaminated non-hazardous wastes, and other wastes generated within the service area. In 1996, a total of 177,169 tones of materials entered the landfill site of which 50.5% were landfilled, 26.5% were recycled and 23% were used as final cover. Diverted materials consisted of recycled waste such as steel, paper, cardboard, wood and compost material, clean soil, asphalt and brick. The density of compacted solid waste as measured in the field is 1200 kg/m^3 and based on the 1996 fill rate the landfill has 16 to 20 years of operating life remaining (Castonguay, 1997).

In 1991 and 1992, a leachate collection system was installed down-gradient from the landfill along the south property line and west toe of the landfill. In addition, a clay cut-off wall was constructed along the south border to prevent the migration of leachate. A leachate retention pond was also constructed in the southeast corner followed by the construction of a second pond in 1993. So far there has been no off-site discharge of leachate. All leachate has been either re-circulated by infiltration and irrigation or disposed off-site. As a result of recirculating leachate into the waste pile prior to 1997, high pumping rates were experienced. In July 1997, off-site disposal of leachate to the municipal wastewater treatment plant (MWWTP) was initiated resulting in a reduced pumping rate. Construction of final cover over Phase I and II should further reduce the volume of leachate generated.

The site designated for the Engineered Wetland System (EWS) consists of a parcel of land located at the southeast corner of the landfill adjacent to the two existing ponds used for the storage of leachate. This site is approximately 200 m long and 95 m wide. The design of the engineered wetland system consists of four cells, the first one comprising a vertical flow subsurface (VFS) peat filter and the other three cells serving as free water surface (FWS) wetlands. As shown in Figure 3.4, untreated leachate is collected by the leachate collection system and is pumped from manhole number 5 into the retention ponds (Ponds #1 and #2). Leachate is then pumped and distributed over the peat filter by way of spray irrigation. The filtrate is collected at the bottom of the peat filter by a network of subsurface drains and flows by gravity into the FWS wetlands. The collected leachate after passing through the engineered wetland system is re-circulated into the landfill area of the site by either irrigation or infiltration systems. Irrigation during summer could reduce the volume of leachate due to high rates of evapotranspiration.

The peat filter has an average length and width of 103 and 57 m, respectively, providing a surface area of 5870 m^2. The peat filter is underlain by native clay soil. A pervious media consisting of native sand and a series of perforated drainpipes was placed over the base of the peat filter in order to collect the leachate at the base. The total height of the peat filter is approximately 2.0 m, which is 1.4 m for the peat layer and 0.6 m for the sand layer. The drainage pipes used were 100 mm diameter perforated agricultural drainage pipe wrapped in a geotextile filter cloth and spaced 4.6 m apart. Peat obtained from a local source, Casselman, Ontario, was placed over the sand layer. A total of 7,725 tones of peat were used for the construction of the peat filter.

The three FWS wetland cells operate in series and range in size from 1209 to 1595 m^2 for a total of 4374 m^2. The total length of FWS wetlands is 268 m and the average channel width is 12.7 m. The presence of clay soil at shallow depths and the availability of clay for the construction of perimeter berms made it possible to design the constructed wetlands to operate in series and to enhance biodegradation. Such a design should also assist in reducing problems with channelization. Water level control structures insure that a minimum water level is maintained in each cell through the operating period of FWS wetland.

The monitoring system shown in Fig. 3-4 included 5 monitoring wells within the peat filter, MW-1 to MW-5, four locations within the surface water wetlands, SW-1 to SW-4, one location at each pond, Pond#1 and Pond#2, and two locations to check the background concentration of groundwater within the surface water wetlands, W-1 and W-2. In addition, samples from two manholes located at south corners of the peat filter (MHE and MHW) were collected. For each monitoring well within the peat filter there were four sampling levels as shown in Figure 3.4. One level was located in the sand layer at the bottom of the peat filter, designated as D, at a depth of 1.7 m from the surface and the other 3 levels were located within the peat filter at 0.5, 0.9 and 1.2 m from the surface, designated as A, B and C, respectively. Two of these locations, MW-1 and MW-5, were equipped with an additional monitoring well close to the peat surface, 0.25 m below grade. The near surface wells were installed to check for any leakage through the cracks at the peat surface.

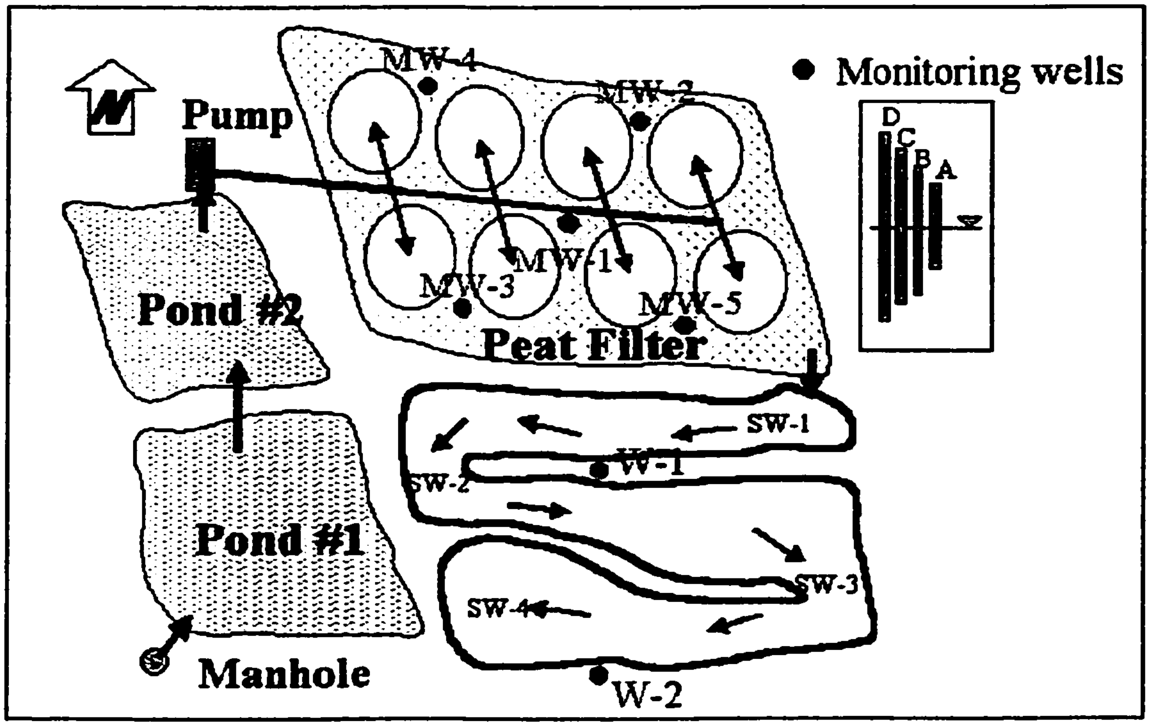


Figure 3-4: Plan View of the Engineered wetland

The monitoring program consisted of the following:

1) Collection of water samples and analysis for ICP metal scan (heavy metals including Pb, Zn, Ni, Cr, Co, Cu, Fe, and calcium, sodium, boron), total carbon (TC), total organic carbon (TOC), dissolved biological oxygen demand (BOD_5), chloride, ammonia nitrogen and total phosphorous (TP).
2) Measuring pH, conductivity, total dissolved solids (TDS) and temperature of the collected samples in the field.
3) Measuring hydraulic conductivity of the peat filter in the field in order to see if there is any clogging due to entrapping of contaminants.
4) Collection and analysis of soil samples from the peat filter to determine the accumulation of contaminants within the peat filter.

Prior to collection of samples, all the monitoring wells were purged to remove stagnant water. pH, conductivity, TDS, and temperature of samples were measured in the field. About 500 mL of sample was collected in plastic bottles and transferred to laboratory for analysis of the remaining parameters. For hydraulic conductivity measurement, slug test was used. The monitoring wells were purged and the recovery of the wells over time was measured. A program, SUPERSLUG, was then used to obtain the values of hydraulic conductivity.

The Huneault engineered wetlands became operational in August of 1995. This system was monitored for two-year period duration (1996-1997). A total number of 14 sets of samples were collected, 8 sets in 1996 and 6 sets in 1997. The monitoring program and collection of samples was conducted over the period of June to November of each year. The EWS was in operation over the period of late May to early November each year and does not operate under freezing weather conditions. The results of monitoring will be presented in Chapter Seven.

3.8. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

The following are the procedures taken during the course of this research project to make sure that the obtained data were reliable and of high quality.

In the case of ICP analysis of samples at least one blank sample, at least two repeats of samples, and at least one standard in addition to conventional standards run for ICP were included in each set of samples to check the precision of the ICP instrument. In the event that there was discrepancy between the results the whole set was disregarded. Also duplicates of two sets of samples were sent to an outside laboratory to check the accuracy of the results. The difference between the results analyzed by both laboratories was statistically insignificant.

To check the effect of type of sampling vials, if any, the use of plastic vials was checked against the glass vials. Both plastic and glass vials proved to be suitable since no adsorption to or leaching from the surface of containers for boron and metals were observed. However, the caps with paper seals were proven not to be suitable. Consequently, caps with plastic or Teflon seals were used. The effect of filtering of samples was also investigated. During the initial laboratory experiments and field monitoring, 3 to 5 samples were analyzed by ICP with and without prior filtering to determine whether filtering of samples would cause any change in the total concentrations of measured parameters. Filtering of samples did not have any significant effect on results.

On two monitoring events, at least two samples were filtered in the field and acidified right after sample collection and the results were compared to those transferred and processed in the lab, which showed that no change in quality of samples occurred during the time between sample collection and processing of samples in the laboratory.

The equipments used for field monitoring were also checked against the laboratory instruments and calibrated if necessary at the beginning and end of each monitoring season to make sure that filed equipments were working properly.

ADSORPTION RESULTS AND MODELING

Chapter 4

The results of batch adsorption experiments described in Chapter 3 are reported and discussed in this chapter. The results of tests described in Section 3.2 for determining whether boron exists in organic or inorganic form within landfill leachate are presented and discussed in Section 4.1. The effect of operational and environmental factors on boron adsorption was systematically investigated and the results are presented in Sections 4.2 through 4.10. These factors included the effect of drying, shaking, soil-to-solution ratio, kinetics, time effect, pH, competing anions, solution composition, and temperature. A new non-linear procedure for estimating the Freundlich adsorption isotherm parameters is presented in Section 4.11. The results of boron adsorption by peat and application of the new code for the determination of parameters of Freundlich equation developed in Section 4.11 are presented in Section 4.12. Based on the results obtained from the effect of factors presented in Sections 4.2 to 4.10 further tests (two-level factorial design experiments) were carried out to assess the importance of pH, temperature, solution composition, and their interactions, which are discussed in Section 4.13. In Section 4.14, an adsorption model which incorporates pH and temperature is developed and used to predict the adsorption of boron by peat. This model will be incorporated in the contaminant transport code developed in Chapter 5. To compare other alternative adsorbing media with peat boron adsorption by another source of peat (Alfred peat), a commercial peat moss, two sources of compost material produced from yard and garden wastes (CompostH and CompostT) and an ion exchange resin (Amberlite) were investigated and the results are shown in Section 4.15. The adsorption of heavy metals from leachate is also investigated and this is discussed in Section 4.16. In Section 4.17 the results of boron adsorption from another source of leachate (Trail Rd leachate) are presented. Desorption of boron is investigated and discussed in Section 4.18. And finally, the chapter is concluded by a summary of the results presented in this chapter.

4.1. BORON SPECIES IN LEACHATE

As mentioned in Chapter 2 although it is reported that organo-boron compounds represent a tiny fraction of the industrial boron compounds in use, however, no attempt has been made so far to determine which boron species are present in a complex solution such as landfill leachate. Leachate contains an enormous number of organic and inorganic compounds, some of them with unknown molecular and chemical characteristics. In addition, in the majority of adsorption studies reported in the literature, a synthetic solution made of boric acid was used. Thus, it was decided to determine if any boron organic compounds are present in the landfill leachate.

The organic extraction method utilizing dichloromethane or chloroform as the organic solvent proved to be ineffective in separating boron organic compounds, if any, from landfill leachate. Similar tests for extraction of boron from synthetic solution (SS) revealed that boron forms some type of a bond with these organic solvents. As a result, it was not possible to draw any conclusion whether separated boron from leachate was coming from inorganic or organic source. However, it was observed that both solvents at different pH values (a pH range of 8–10) removed similar amounts of boron from leachate and synthetic solution. This similar behavior could be an indication that boron within the leachate has the same inorganic composition as in the synthetic solution.

The extracts from leachate and SS by organic solvents were further analyzed by a Gas Chromatography Mass Spectroscopy (GCMS) analyzer. No boron was detected in the extracts from either of leachate and SS. The fact that no boron was detected in the case of SS shows that the bond between inorganic boron (boric acid or borate ion) and organic solvent is weak and is broken during the volatilization step. Thus, the same process should occur if boron in the leachate is in the inorganic form. Since no boron was detected in extracts from leachate, either boron is in inorganic form, or it is associated with very large and stable organic molecules resisting volatilization during analysis.

An anion exchange resin named Amberlite IRA-743 (produced by Rohm and Haas Company) was also used to separate any boric acid and borate ions from the leachate and synthetic solution. Amberlite-743 is an anion exchange resin, which is claimed to specifically remove borate and boric acid under a variety of conditions without adsorbing other anions. Additional information on this resin is presented in Appendix A. As an initial step it was decided to check if Amberlite removes other anions and organic compounds other than boron. Therefore, leachate samples were put in contact with Amberlite resin for a period of 24 hrs. Leachate was analyzed before and after this treatment for COD, Cl^-, and SO_4^{2-} results presented in Table 4-1. The results of paired t-test (α=0.05), see Table 4-2, show that there was no significant differences for any of these parameters except SO_4^{2-}. P(T<=t) is the probability that the t value be greater than or equal to the measured t statistics (t Stat). The difference for SO_4^{2-} is on average 5.3%. This indicates that Amberlite does not remove any organic compounds or anions tested except SO_4^{2-} (only 5.3%). Amberlite reduced boron concentration to 0.2 mg/L compared to an initial boron concentration of 8.5 mg/L. Thus less than 2% of initial boron remained in the solution. This implies that the amount of organic boron compounds, if any, is less than 2% and insignificant.

Table 4-1. COD, Cl^-, and SO_4^{2-} concentrations within leachate before and after using Amberlite

COD (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)	
Before	**After**	**Before**	**After**	**Before**	**After**
175	163	272	287	150	144
181	146	283	295	155	145
158	157	269	275	146	138

Table 4-2. Results of paired t-test (α=0.05) for COD, Cl^-, SO_4^{2-} before and after treatment with Amberlite

	COD (mg/L)		Cl^- (mg/L)		SO_4^{2-} (mg/L)	
	Before	After	Before	After	Before	After
Mean	171.33	155.33	274.67	285.67	150.33	142.33
Variance	142.33	74.333	54.33	101.33	20.33	14.33
Observations	3	3	3	3	3	3
df	2		2		2	
t Stat	1.597		4.151		6.926	
P(T<=t)	0.251		0.504		0.02	
t Critical	4.302		4.302		4.302	

4.2. EFFECT OF DRYING

To investigate the effect of drying peat on the adsorption of boron two sets of preliminary adsorption tests using leachate and synthetic solution were carried out. Peat was dried at a temperature of 105°C. The results are summarized in Table 4-3. Since there were only two replicates and for the case of SS neither C_e nor dry mass of peat was constant, the results cannot be compared statistically. However, the amounts of boron adsorbed (q) qualitatively show that adsorption on fresh peat is higher than dried peat.

Table 4-3. Effect of drying peat at 105 °C on boron adsorption

	Synthetic Solution (SS)			Leachate		
	Mass (DM)	*Ce* (mg/L)	*q* (mg/g)	Mass (DM)	*Ce* (mg/L)	*q* (mg/g)
Fresh Peat	2	13.5	0.075	2.5	5	0.050
Fresh Peat	1.9	12.9	0.111	2.5	4.9	0.054
Dried Peat	2.9	13.7	0.045	3.3	5	0.037
Dried Peat	2.8	14.1	0.031	3.4	4.8	0.040

In the next step it was decided to run more replicates under similar conditions on fresh peat and peat dried at a temperature of 90°C, below the boiling temperature water, to see if there is any impact due to drying of peat at this temperature. A temperature of 85°C is recommended in the literature as a suitable level for drying peat without affecting its structure (MacFarlane, 1969). The results are presented in Table 4-4. The results were compared statistically by doing a t-test, see Table 4-5. To conduct the t-test, a F-test was performed first to see if the variances from the two sets of samples could be pooled together and perform a t-test with equal variances, otherwise a t-test with unequal variances should be carried out. The results at a pH of 7 show that boron adsorption by peat dried at a temperature 90°C is significantly different from boron adsorption on fresh peat (p (T<=t) = 0.016). The same result was obtained for samples tested at a pH of 7.5 thus showing that drying at 90°C significantly reduces the boron adsorption capacity of the peat.

Table 4-4. The effect of drying peat at 90 °C on boron adsorption (*q*, mg/g)

	pH= 7.0			pH= 7.5		
	#1	#2	#3	#1	#2	#3
Fresh Peat	0.075	0.081	0.086	0.094	0.097	0.105
Dried Peat	0.055	0.056	0.057	0.066	0.067	0.072

Table 4-5. t-test (unequal variance, α=0.05), T=90 °C

	Fresh Peat	Dried Peat
Mean	0.0809	0.0560
Variance	2.95E-05	6.98E-07
Observations	3	3
df	2	
t Stat	7.888	
P(T<=t)	0.016	
t Critical	4.303	

A third set of batch adsorption tests with leachate was carried out with peat dried at a temperature of 75°C, air-dried peat, and fresh peat. The results are shown in Table 4-6. Also, the results of t-test (α=0.05) are presented in Table 4-7. It shows that drying of peat 75°C and even at room temperature significantly reduces the adsorption capacity of peat.

Table 4-6. Effect of drying (75°C and air dried) on *q* (mg B/g)

Fresh Peat	Dried at 75°C	Air Dried
0.0590	0.0442	0.0492
0.0573	0.0457	0.0521
0.0598	0.0486	0.0475

Table 4-7. t-test (equal variance, α=0.05), peat dried at 75°C and air dried

	Fresh Peat	Dried at 75°C	Fresh Peat	Air-dried
Mean	0.0587	0.0462	0.0587	0.0496
Variance	1.62E-06	4.96E-06	1.62E-06	5.38E-06
Observations	3	3	3	3
Df	4		4	
t Stat	8.485		5.955	
P(T<=t)	0.001		0.004	
t Critical	2.132		2.131	

The reversibility of the drying effect was also investigated by soaking peat samples dried in the previous step (at 90°C) for 1 day and two weeks. Results of the t-test, shown in Table 4-8, show that the adsorption capacity of peat reached the original level, i.e. the same as fresh peat, only for the samples saturated in water for at least two weeks. For samples saturated in water for one day the results were significantly different. This shows that complete saturation and restoring of dried peat is a slow process. Thus if peat is dried prior to any batch adsorption tests or column studies, it should be saturated in water for a sufficiently long period of time (in this case at least two weeks) in order to restore its full adsorption capacity for boron. Similar results were obtained from field measurements by Lischeid (2000) as water content of peat increased for days after dry season under steady state conditions. Due to these findings all subsequent experiments, except some preliminary experiments which had been already conducted, were carried out using fresh peat (stored in plastic bags at 4 °C).

Table 4-8. t-test (equal variance, $\alpha=0.05$) for the effect of time on saturation of peat

	Fresh Peat	Dried Peat (Saturated 14 days)	Fresh Peat	Dried Peat (Saturated 1 day)
Mean	0.0879	0.0818	0.0879	0.0560
Variance	3.474E-05	4.484E-05	3.474E-05	6.982E-07
Observations	3	3	3	3
df	4			2
t Stat	1.175			9.287
P(T<=t)	0.153			0.006
t Critical	2.132			2.920

4.3. EFFECT OF SHAKING

Two sets of batch adsorption samples under similar conditions (leachate with fresh peat, pH=7.0, and temperature = 22 °C) were subjected to no shaking and shaking at 150 rpm. The amounts of boron adsorbed as well as the results of the t-test are presented in Table 4-9. There was no significant difference between the results obtained from samples subjected to shaking with those that were not shaken. A similar set of tests with low agitation (50 rpm) and high agitation (200 rpm) were also performed and did not show a significant difference.

Table 4-9. Effect of shaking on q (mg B/g)

q (mg/g)		Results of t-test (equal variance, α=0.05)		
Shaking	No-shaking		No-shaking	Shaking
0.177	0.145	Mean	0.154	0.153
0.161	0.184	Variance	0.00068	0.00069
0.128	0.134	Observations	3	3
		df	4	
		t Stat	0.016	
		P(T<=t)	0.980	
		t Critical	2.132	

4.4. EFFECT OF SOIL-TO-SOLUTION RATIO

As mentioned in the literature review, soil-to-solution ratio could affect adsorption. The maximum practical ratio for adsorption experiments with peat was measured to be 0.6 g/mL. Since peat is acidic and the pH of the solution would change with varying amount of peat used, numerous adsorption tests with different amounts of dilution and different amount of 0.1 N NaOH at two soil-to-solution ratios of 0.1 and 0.4 were carried out. Out of numerous samples, pairs of samples with the same pH and C_e were selected (presented in Table 4-10) and a paired t-test was performed. By doing this, the experimental conditions that could affect adsorption, i.e. pH and C_e, are set at the same level and the only difference between the samples in each pair is the soil-to-solution ratio.

Table 4-10. Results of soil-to-solution ratio effect on *q*

Replicates	Ratio= 0.1 g/mL	Ratio= 0.4 g/mL	pH	C_e
#1	0.0556	0.0720	7.3	5.8
#2	0.0578	0.0426	7.1	4.2
#3	0.0499	0.0475	6.9	4.4
#4	0.0850	0.0483	7.0	4.7
#5	0.0786	0.0694	7.1	5.8
#6	0.0595	0.0684	6.9	6.0

Table 4-11 presents the outcome of the paired t-test. The results show that there is no significant difference between the two, or in other words, soil-to-solution ratio does not have any impact on the adsorption capacity of boron on peat. For subsequent adsorption tests a soil-to-solution ratio in the range of 0.2 to 0.4 was used.

Table 4-11. t-test for soil-to-solution ratio effect (α=0.05)

Soil-to-solution ratio	0.1 g/mL	0.4 g/mL
Mean	0.0644	0.0850
Variance	0.0002	0.00018
Observations	6	6
Df	5	
t Stat	0.830	
P(T<=t)	0.445	
t Critical	2.571	

4.5. ADSORPTION KINETICS

Adsorption kinetics experiments were carried out using peat and leachate. The experiments were repeated for a second time that showed very similar results. Figure 4-1 illustrates the change of C_e and pH versus time for the first trial. The exponential curves fitted to the data points, which show the trend of change in pH and C_e, are presented on the graph as well. The results from the other trial are presented in Appendix B. Most of adsorption occurred within 2.5 hours. As mentioned in Chapter 3, all adsorption tests were conducted for a period of 24 hours, except the tests on adsorption kinetics and long-term adsorption tests. The rate of change of C_e was very fast at the beginning and then slowed down as adsorption proceeded.

The pH increased as more adsorption occurred. The increase in pH should be due to the release of the hydroxyl ions being replaced by adsorbed borate ions. If pH of solution is plotted against boron concentration of solution, Figure 4-2, it can be seen that there is a negative correlation between the two showing a decrease in boron concentration (increase in boron adsorption) with increasing pH. As mentioned in literature review, Metwally et al. (1974) also reported on positive correlation of boron adsorption and OH^- release by Al and Fe hydroxide and concluded that anion exchange was the main mechanism for boron sorption.

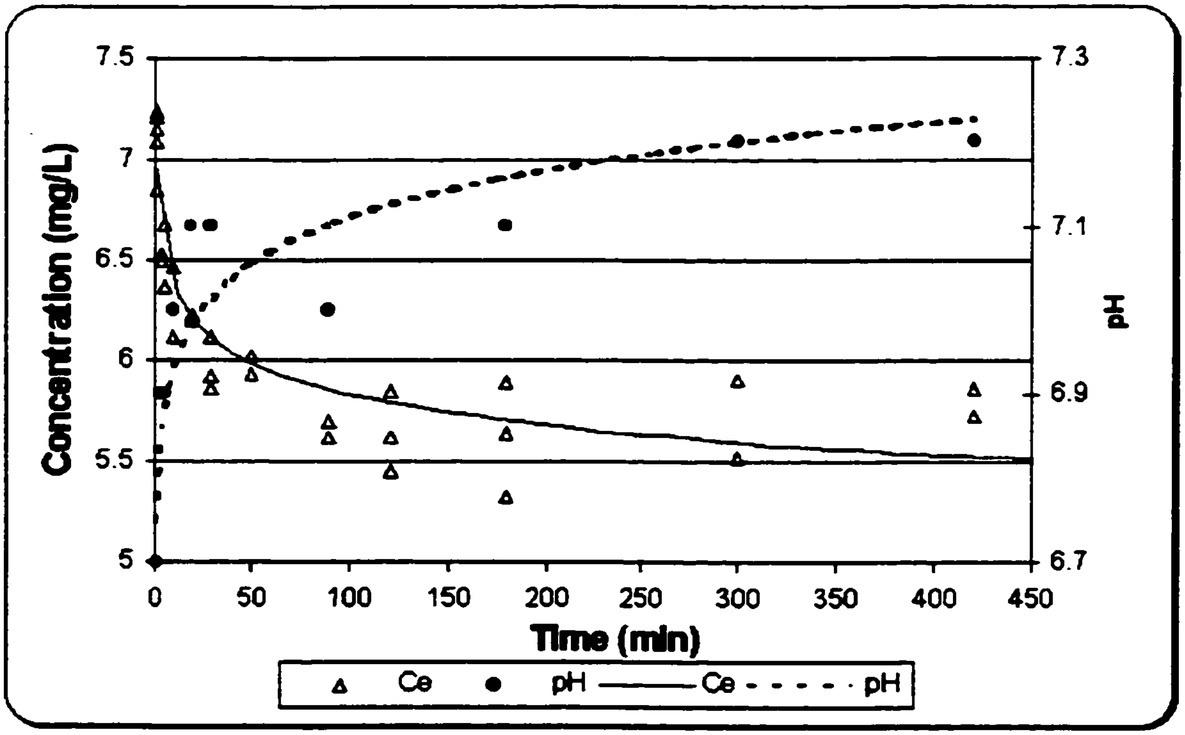


Figure 4-1: Kinetics of boron adsorption by peat

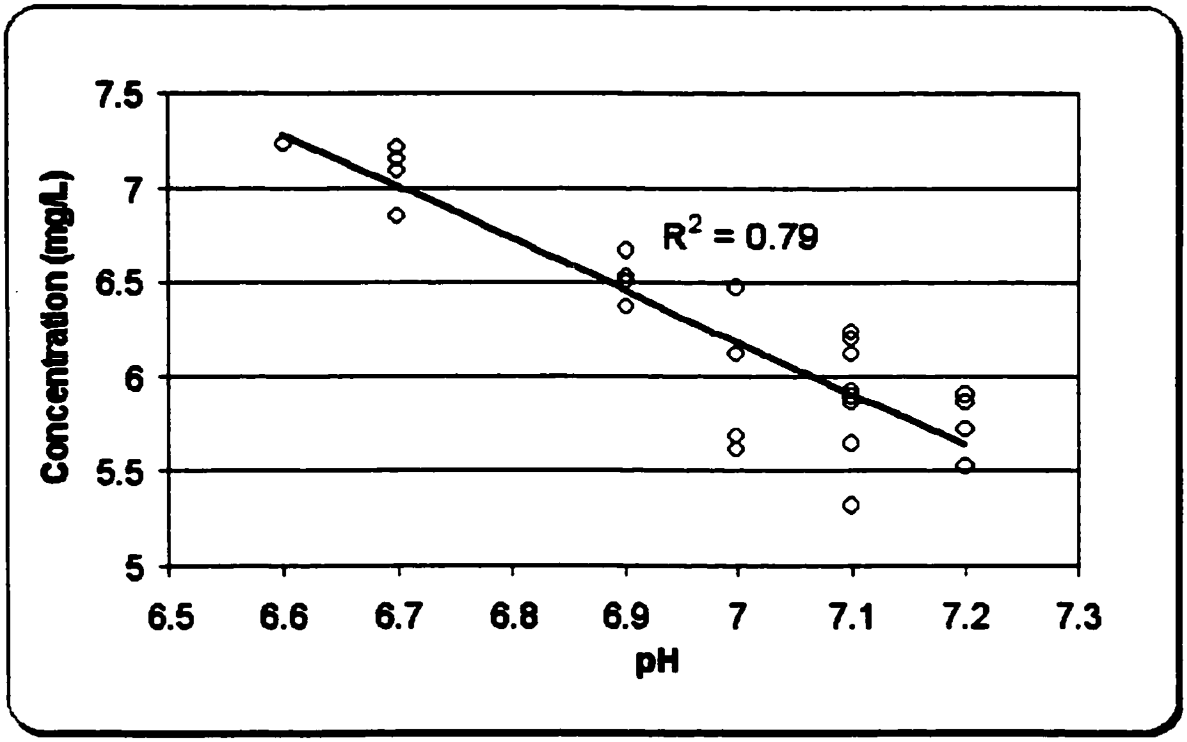


Figure 4-2: Correlation between pH and boron conc. for kinetics study

The collected data were plotted for the zero, 1st, and 2nd order reactions. The 2nd order reaction describes the kinetics of boron adsorption better than the other two since the plot of data showed a better linear fit to the transformed equation, see Figure 4-3. For a 2nd order reaction, the plot of $1/C_e$ vs. t would yield a straight line with a slope equal to reaction rate constant (Snoeyink and Jenkins, 1980). The reaction rate constant was 0.0003.

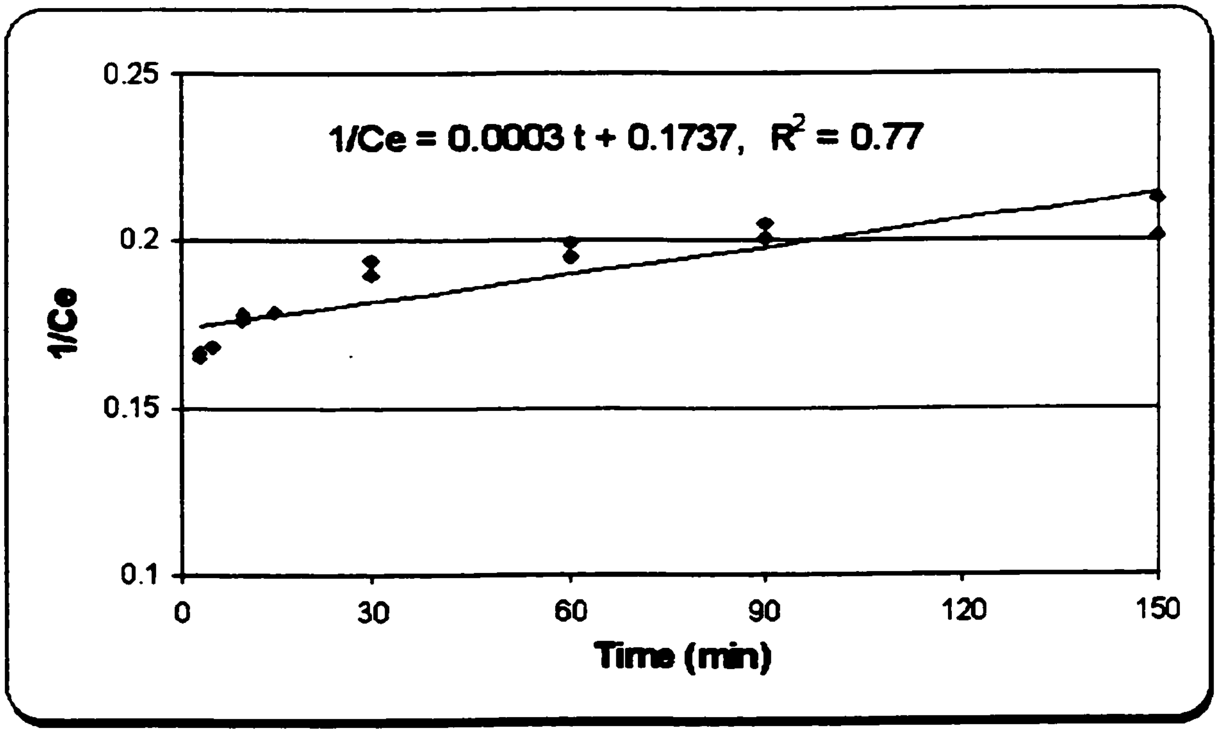


Figure 4-3: Second order plot of kinetics data

4.6. EFFECT OF ADSORPTION TIME

As mentioned previously, it is reported that for clay soils boron adsorption increases with time even after the initial equilibrium is established. To investigate whether similar mechanism could occur in the case of boron adsorption on peat, three sets of experiments were carried out. For each set three samples were filtered after 24 hrs and three samples were filtered after 5 days, 14 days, or 33 days and the amount of adsorption was compared statistically. All conditions were the same (leachate with fresh peat, pH=7.0, and temperature = 22°C) except the duration of the tests. The results are shown in Table 4-12. For all three cases with durations of 5 days, 14 days, and 33 days there was no significant difference between the amounts of adsorption measured and the amounts of adsorption obtained for 24 hr tests, see Table 4-13. Thus, the adsorption of boron on peat, unlike some clay soils, does not increase over time after the initial equilibrium is established.

Table 4-12. Effect of time on boron adsorption (*q*, mg B/g)

First Set		Second Set		Third Set	
1 day	5 days	1 day	14 days	1 day	33 days
0.0700	0.0846	0.1469	0.1160	0.0576	0.0837
0.0771	0.0925	0.1360	0.1420	0.0769	0.0735
0.0654	0.0717	0.1265	0.1381	0.0660	0.0852

Table 4-13. Results of t-test (equal variance, α=0.05) for the effect of time on *q*

	1 day	5 days	1 day	14 days	1 day	33 days
Mean	0.0708	0.0829	0.1365	0.1322	0.0668	0.0808
Variance	3E-05	0.0001	0.0001	0.0002	9.32E-05	4.05E-05
Observations	3	3	3	3	3	3
df	4		4		4	
t Stat	1.737		0.424		2.094	
P(T<=t)	0.157		0.693		0.104	
t Critical	2.132		2.132		2.776	

4.7. EFFECT OF pH

The amounts of boron adsorbed at two pH levels, 7 and 7.5, were already presented in Table 4-4. Table 4-14 shows the results of t-test for adsorption of boron on fresh peat at these two pH levels. The increase of 0.5 units in pH was enough to significantly (at α=0.05) affect the adsorption of boron. This indicates that pH has a very strong effect on boron adsorption. The effect of pH will be further investigated in Sections 4-13 and 4-14.

Table 4-14. t-test (Equal variance, α=0.05) for the effect of pH

	PH=7.0	PH=7.5
Mean	0.0810	0.0988
Variance	2.95E-05	2.85E-05
Observations	3	3
df	4	
t Stat	4.045	
P(T<=t)	0.016	
t Critical	2.132	

4.8. EFFECT OF COMPETING ANIONS

One set of batch adsorption tests was carried out with a synthetic solution (SS) only containing boron. Additional batch adsorption tests were carried out using SS containing boron and $CaCl_2$, boron and $Al_2(SO_4)_3$, boron and $Zn_2(SO_4)_3$, boron and NH_4SO_4, as well as boron and combination of $CaCl_2$ plus NH_4SO_4. These chemicals were added in order to see if the presence of other anions such as Cl^- and SO_4^{2-} has any effect on the adsorption of boron on peat. The pH of the solutions with $Al_2(SO_4)_3$ and $Zn_2(SO_4)_3$ was higher than the remaining solutions (7.5 vs. 6.5). This makes it impossible to statistically compare the results; hence related results were not used. The amounts of boron adsorption from different solutions are presented in Table 4-15. The outcome of t-test is shown in Table 4-16. The addition of individual anions and their combination had no significant effect on adsorption of boron on peat. These results are similar to the ones reported by Goldberg et al. (1996), Goldberg and Glaubig (1986a), and Bingham and Page (1971). They showed that boron adsorption by clay soil was not affected by high concentrations of silicon, nitrate, sulphate, molybdate, and phosphate. These researchers suggested that boron adsorption sites are very specific and the presence of other anions does not have any effect on boron adsorption.

Table 4-15. The effect of competing anions on boron adsorption (*q*, mg B/g)

Replicate	SS	SS+$CaCl_2$	SS+NH_4SO_4	SS++
#1	0.0550	0.0528	0.0688	0.0653
#2	0.0615	0.0533	0.0643	0.0733
#3	0.0665	0.0515	0.0678	0.0643

SS= Synthetic Solution containing boron, SS++= SS plus $CaCl_2$ plus $NH_4\ SO_4^{2-}$

Table 4-16. Results of t-test (α=0.05) for the effect of anions on *q*

	SS	SS+$CaCl_2$	SS	SS+NH_4SO_4	SS	SS++
Mean	0.0610	0.0525	0.0610	0.0669	0.0610	0.0676
Variance	3.32E-05	8.1E-07	3.325E-05	5.4537E-06	3.33E-05	2.43E-05
Observations	3	3	3	3	3	3
Df	2		4		4	
t Stat	2.523		1.632		1.5031	
P(T<=t)	0.128		0.178		0.207	
t Critical	4.303		2.132		2.132	

4.9. EFFECT OF SOLUTION COMPOSITION

To assess the effect of solution composition on boron adsorption two sets of batch adsorption tests were conducted. For the first set leachate was diluted by L-B solution. As explained in Chapter 3, L-B solution was prepared by removing boron from leachate using Amberlite resin. Therefore, when L-B solution is used for dilution the composition of leachate, except boron content, is not changed. For the second set distilled water (DW) was used for dilution. For both cases several dilutions were prepared by trial and error until equilibrium pH and *Ce* of both sets were identical. Thus, the only difference between the two sets was the composition of solution. The results as well as outcome of t-test are summarized in Table 4-17. Adsorptions of boron for the two scenarios were significantly different. This means that the composition of solution has a significant effect on boron adsorption on peat. This is consistent with electrical double layer theory explained in the previous chapter: adsorption increases as the ionic strength of the solution increases. This indicates that the common method of using distilled water for preparing dilutions for adsorption tests is not appropriate. As a result, for all subsequent experiments L-B solution was used for any dilution. This ensures that the composition of solution (except boron concentration) would not change due to dilution.

Table 4-17. Effect of solution composition on boron adsorption (t-test with equal variance, α=0.05)

q (mg/g)		Results of t-test		
L + L-B	L + DW		L	L + DW
0.037	0.023	Mean	0.03938	0.02542
0.034	0.027	Variance	5.3E-05	4.1E-06
0.048	0.026	Observations	3	3
		df	4	
		t Stat	3.20701	
		P(T<=t)	0.03268	
		t Critical	2.13185	

L= leachate

4.10. EFFECT OF TEMPERATURE

The amounts of boron adsorbed by at two temperature levels, 2 and 22°C, for similar pH and equilibrium concentration, as well as the results of t-test are presented in Table 4-18. It shows that adsorption of boron on fresh peat at these two temperature levels were significantly different. Also, it was observed that temperature increase had a negative effect on boron adsorption, as the mean value of boron adsorption at 22°C is lower than the value at 2°C (0.1205 mg B/g vs. 0.1354 mg B/g).

Table 4-18. Effect of temperature on q (equal variance, α=0.05)

q (2 °C)	q (22 °C)	Results of t-test		
			2 °C	22 °C
0.1319	0.1276	Mean	0.1354	0.1205
0.1343	0.1177	Variance	1.75E-5	3.17E-5
0.1400	0.1162	Observations	3	3
		df	4	
		t Stat	3.44	
		P(T<=t)	0.026	
		t Critical	2.776	

4.11. ADSORPTION ISOTHERM PARAMETERS ESTIMATION

As mentioned in Section 2.5.8, in the linearized transformation of the Freundlich and Langmuir isotherm equations some of the basic assumptions of the least square method are violated. Some non-linear regression programs such as the one (ISOTHERM) by Kinniburgh (1986) have been developed to address this issue. Although these procedures are improvements over linear least square method, they are not 100% correct. There is a fine and delicate flaw in the non-linear regression method used by Kinniburgh (1986) and others. The problem stems from the way dependent and independent variables are defined.. In linear and non-linear regression analysis used so far, q and C_e are defined as dependent and independent variables, respectively. q is calculated according to equation 4-1.

$$q = (C_i - C_e)\frac{V}{S} \qquad (4\text{-}1)$$

where C_i is the initial concentration, C_e is the equilibrium concentration, S is the mass of adsorbent, and V is the volume of solution used in batch adsorption test. However, closer examination of Equation 4-1 shows that C_e is used in the calculation of q from experimental data, in other words, inherent in the value of q is information on C_e. This means that C_e is being regressed against itself when q is chosen as the dependent variable. Sweeney et al. (1982) noted this problem and they presented a procedure for obtaining the estimates of isotherm parameters by choosing C_e as dependent variable, S as independent variable, and C_i and V as constants. However, the more proper way would be to choose C_e as dependent and C_i as independent variable since C_i is set (independent variable) at the beginning of the experiment, C_e is measured as a response variable at the end of experiment, and V and S can be accurately measured in the laboratory. In addition, the procedure presented by Sweeney et al. (1982) is inefficient and needs 3 or 4 sets of initial estimates of parameters. It acts like a trial and error or a search method. Three or four sets of initial estimates of parameters have to be provided; the set that produces largest error is rejected and based on the remaining sets a new set is chosen. This procedure is repeated until a pre-established termination criterion is met.

Considering the issues raised above it was decided to develop a new non-linear procedure and a new computer code for non-linear regression analysis of C_e against C_i. Gauss-Newton method was used to carry out non-linear regression (Bates and Watts, 1988; Box and Draper, 1987). This approach is not very straightforward and uses an iterative method for obtaining the parameter estimates. If C_e is chosen as dependent variable, the general model could be defined as:

$$C_e = f(C_i, K, 1/n) + \varepsilon \qquad (4\text{-}2)$$

where f is the expectation function, C_i is the independent variable, K and $1/n$ are parameters, and ε is the error term. To obtain least-square estimates, we must find the values of K and $1/n$ that minimize the sum squares of residuals (SSR).

$$SSR\ (K, 1/n) = \sum \{C_e - f(C_i, K, 1/n)\}^2 \qquad (4\text{-}3)$$

Equating first derivatives of Equation 4-3 with respect to parameter K and $1/n$ to zero yields a set of equations that contain function f and its first derivatives with respect to parameter K and $1/n$, which are non-linear. In the Gauss-Newton method the function f is expanded as a Taylor series for parameters K_1 and $1/n_1$ to the first-order term about initial guess values of K_o and $1/n_o$. Then a linear least-squares is used to obtain K_1 and $1/n_1$. The procedure is repeated with K_1 and $1/n_1$ replacing the initial guess values and so on until a convergence criterion is met. More details on the Gauss-Newton approach can be obtained from Bates and Watts (1988).

To follow the above procedure we need to find the form of function f and its derivatives with respect to parameters K and $1/n$. If q in Equation 4-1 is replaced by Freundlich equation and all the terms are moved to one side, the following equations are obtained.

$$q = (C_i - C_e)\frac{V}{S} = KC_e^{1/n} \qquad (4\text{-}4)$$

$$\left(\frac{KS}{V}\right)C_e^{1/n} + C_e - C_i = 0 \qquad (4\text{-}5)$$

Noting that Equation 4-5 has the form $G(K,f(C_i, K,1/n)$, we can determine the derivative of Equation 4-5 with respect to K as:

$$\frac{\partial G}{\partial K}=\left(\frac{\partial G}{\partial K}\right)_f+\frac{\partial G}{\partial f}\frac{\partial f}{\partial K} \tag{4-6}$$

$$\left(\frac{S}{V}\right)C_e^{1/n}+\left(\frac{KS(1/n)}{V}\right)C_e^{(1/n)-1}\frac{\partial C_e}{\partial K}+\frac{\partial C_e}{\partial K}=0$$

which can be solved for $\partial C_e / \partial K$:

$$\frac{\partial C_e}{\partial K}=-\frac{(S/V)\ C_e^{1/n}}{1+\dfrac{KS(1/n)}{V}\ C_e^{(1/n)-1}} \tag{4-7}$$

Similarly we can obtain the derivative of Equation 4-5 with respect to $(1/n)$:

$$\left(\frac{KS}{V}\right)\left((1/n)C_e^{1/n-1}\frac{\partial C_e}{\partial(1/n)}+C_e^{1/n}LnC_e\right)+\frac{\partial C_e}{\partial(1/n)}=0 \tag{4-8}$$

$$\frac{\partial C_e}{\partial(1/n)}=-\frac{(KS/V)\ C_e^{1/n}Ln(C_e)}{1+\dfrac{KS(1/n)}{V}\ C_e^{(1/n)-1}} \tag{4-9}$$

As it can be seen from Equations 4-7 and 4-9, to obtain the value of derivatives the value of C_e is needed. Thus, at each iteration equation 4-5 should be solved for C_e. A new computer code called NLPEFM (Non-Linear Parameter Estimation for Freundlich Model) was developed that executes the above procedure. Figure 4-4 shows a flow chart of this computer code. One of the drawbacks of the Gauss-Newton method is that it may converge slowly. Good initial guess values could on the other hand accelerate the convergence. NLPEFM includes a subroutine that calculates initial guess values by carrying out a linear regression analysis, thus providing good initial guess values. During each iteration, Equation 4-5 is solved for C_e numerically. This value is substituted back into Equations 4-7 and 4-9 to calculate the derivatives of C_e. Linear regression is then used to obtain a set of improved parameter values. The procedure is repeated until a pre-set criterion for convergence is met.

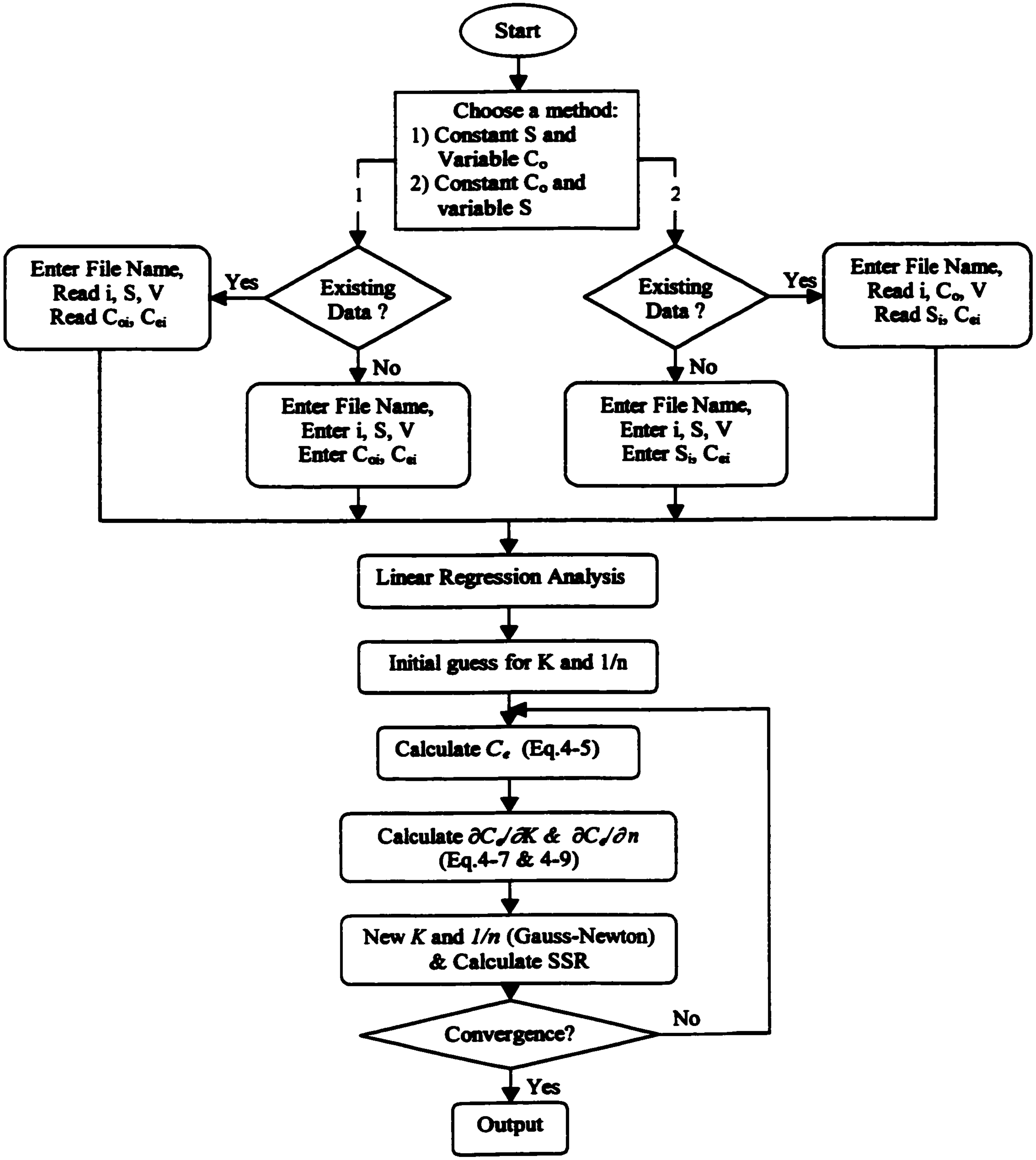


Figure 4-4: Flowchart of NLPEFM computer code

A second computer code called NLISOTHERM was also developed, which carries out a non-linear regression analysis of q vs. C_e. NLISOTHERM was developed in order to compare the results of regression of C_e against C_i with that of q against C_e. Both NLPEFM and NLISOTHERM were developed in such a way that they give the user options of creating and saving new input files or reading previously created input files. Both programs produce output files which contain the values of parameters K and $1/n$ as well as the sum square of residuals (SSR).

To demonstrate that NLPEFM is superior to linear regression and non-linear regression method of q vs. C_e, NLPEFM program was used to find the parameters K and $1/n$ for 3 sets of data on adsorption of boron by organic soil, peat moss, and compost material. Then the results were compared with those obtained by linear regression and NLISOTHERM methods. The first set of data was presented by Huettl (1976). The results obtained from NLPEFM program along with the results from linear regression and NLISOTHERM are presented in Figure 4-5.

Linear method is clearly showing weakness in describing the data, especially at higher concentrations. Although both NLISOTHERM and NLPEFM show big improvements over linear method, the output from NLPEFM shows lower deviations from the data points compared with NLISOTHERM. The parameters estimates as well as the sum square of residuals (SSR) are presented in Table 4-19. SSR of C_e, SSR(C_e) values for NLISOTHERM and NLPEFM show a 91.5% and 97.5% reduction compared to linear regression results. Also, the SSR of C_e value obtained by NLPEFM is 71% lower than the one obtained by the NLISOTHERM method, which shows NLPEFM is far superior to NLISOTHERM for this set of data. Parameter estimates for K and $1/n$ obtained by NLPEFM are 49% higher and 16% lower than those obtained by NLISOTHERM, respectively.

Table 4-19. Parameters estimates and SSR obtained for Huettl (1976) data

	K	*1/n*	SSR (C_e)
Linear Regression	0.0055	1.075	80.358
Non-linear Regression NLISOTHERM (q vs. C_e)	0.0091	0.741	6.814
Non-linear Regression NLPEFM (C_e vs. C_i)	0.0136	0.624	1.969

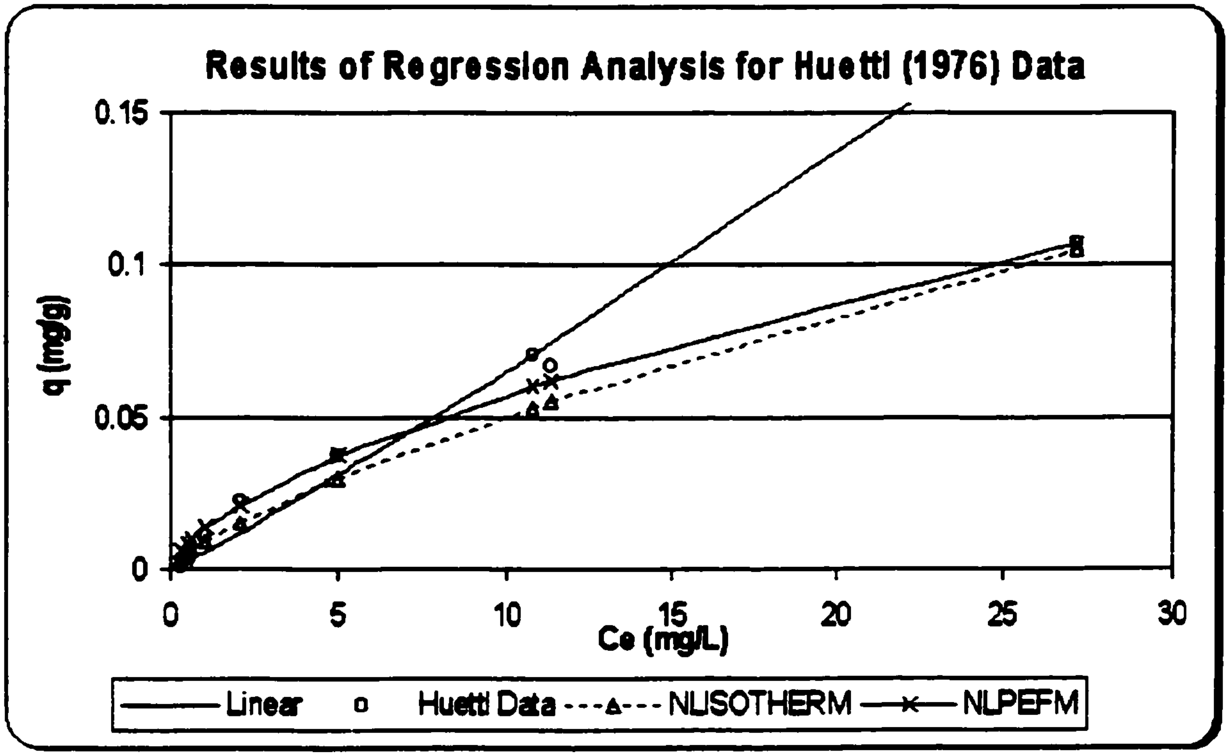


Figure 4-5: Comparison of NLPEFM, NLISOTHERM, and linear regression results for Huettl (1976) data

The second set of data was obtained as part of this research work. Peat moss was used to remove boron from leachate. The adsorption isotherms are shown in Figure 4-6. The parameters estimates as well as sum square of residuals (SSR) for the case of peat moss are presented in Table 4-20. The improvements are not as great as previous example; however, NLPEFM method shows 15% improvements for SSR of C_e and 7% difference for the estimate of $1/n$ compared to the linear method. The SSR(C_e) and estimate of $1/n$ obtained by NLPEFM were only 2% and 3% less than those obtained by NLISOTHERM.

Table 4-20. Parameters estimates and SSR obtained for commercial peat moss

	K	*1/n*	SSR (*q*)	SSR (C_e)
Linear Regression	0.01653	0.4487	1.4×10^{-5}	0.0155
Non-linear Regression NLISOTHERM (q vs. C_e)	0.01646	0.4225	1.3×10^{-5}	0.0134
Non-linear Regression NLPEFM (C_e vs. C_i)	0.01652	0.416	1.3×10^{-5}	0.0132

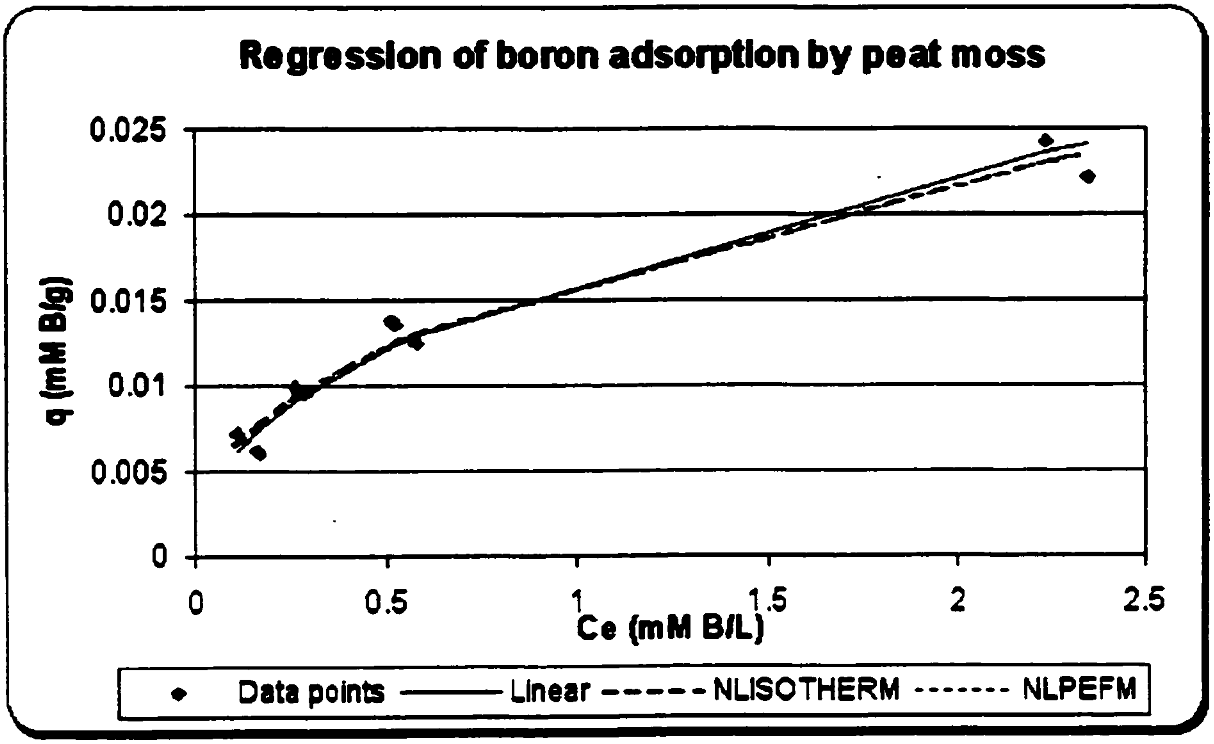


Figure 4-6: Comparison of NLPEFM, NLISOTHERM, and linear regression results for Peat moss (author's) data

The above case is a scenario where the effect of linearization of the equation on the estimates of parameters is not very significant (only 7% for $1/n$). However, it should be noted that SSR obtained by both NLPEFM and NLISOTHERM regression methods is 15% lower than SSR obtained by linear regression. This case is presented to show that at times results from non-linear and linear regression analysis could be very close. However, this is not always the case and it depends on the nature of the data and its variation. Nonetheless, the new non-linear regression analysis (NLPEFM code) appears to be an improved method of analysing adsorption isotherm data, and it is used for analysis of all adsorption isotherm data presented in this thesis.

The third set of data was the results of adsorption of boron from landfill leachate by CompostT, as presented in Table 4-21. NLPEFM and NLISOTHERM show 13% and 12% reduction in SSR (C_e), respectively. Also, the parameter estimates obtained NLPEFM for K and $1/n$ are 25% lower and 53% higher than those obtained by linear regression. Contrary to the previous case, for this set of data SSR (C_e) obtained by NLPEFM and NLISOTHERM are very close (less than 1% difference), the difference in values of parameters K and $1/n$ is much higher (10% for K and 12% for $1/n$). Also, the difference in SSR between linear and non-linear methods is low, 13%, however the differences in parameters estimates are higher, 20-33% for K and 36-53% for $1/n$.

Table 4-21. Parameters estimates and SSR obtained for CompostT

	K	$1/n$	SSR (C_e)
Linear Regression	0.00614	0.366	0.5076
Non-linear Regression NLISOTHERM (q vs. C_e)	0.00513	0.499	0.4480
Non-linear Regression NLPEFM (C_e vs. C_i)	0.00462	0.561	0.4434

The above three sets of data were chosen to show different scenarios that could be encountered when dealing with adsorption data and prove that regardless of the SSR values it is necessary to use the correct procedure to obtain parameters K and $1/n$. It is also worth noting that the parameter estimates obtained by these three procedures could vary significantly. Therefore, the values reported in the literature should be used cautiously as they could be misleading. The above results show the superiority of NLPEFM procedure. It is surprising that the majority of the results reported in the literature are based on simple linear regression.

4.12. ADSORPTION OF BORON BY PEAT

The program NLPEFM was used to determine the parameters *K* and *1/n* for the adsorption of boron from leachate by peat at different pH values. The results are summarized in Table 4-22. The model predictions were in good agreement with experimental results as the correlation factor for C_e values were between 0.98 to 0.99. Data points as well as the adsorption isotherms obtained by NLPEFM program are presented in Figure 4-7. It can be seen that pH has a profound effect on adsorption of boron. Adsorption increases as pH increases from 7.5 to 9.0 and then drops by further increase in pH.

Table 4-22. Parameters estimates obtained for adsorption of boron by peat at different pH values

	NLPEFM parameters estimates	
	K	*1/n*
pH=7.5	0.0154	0.859
pH=8.0	0.0314	0.741
pH=9.0	0.0423	0.688
pH=10.0	0.0349	0.768

Over the range of 0.1 to 0.9 mM B/L, the adsorption of boron by peat showed 180 to 310% increase when pH was raised from 7.5 to 9.0. The same trend has been reported by other researchers for the adsorption of boron by clay soils. Using the Freundlich parameters obtained, at C_e of 1 mM B/L the adsorption capacity of peat is 15 to 42 mM B/Kg peat. This is in good agreement with boron adsorption capacity of 100 mM B/Kg at an equilibrium concentration of 2.5 mM B/L for humic acids extracted from peat reported by Meyer and Bloom (1997).

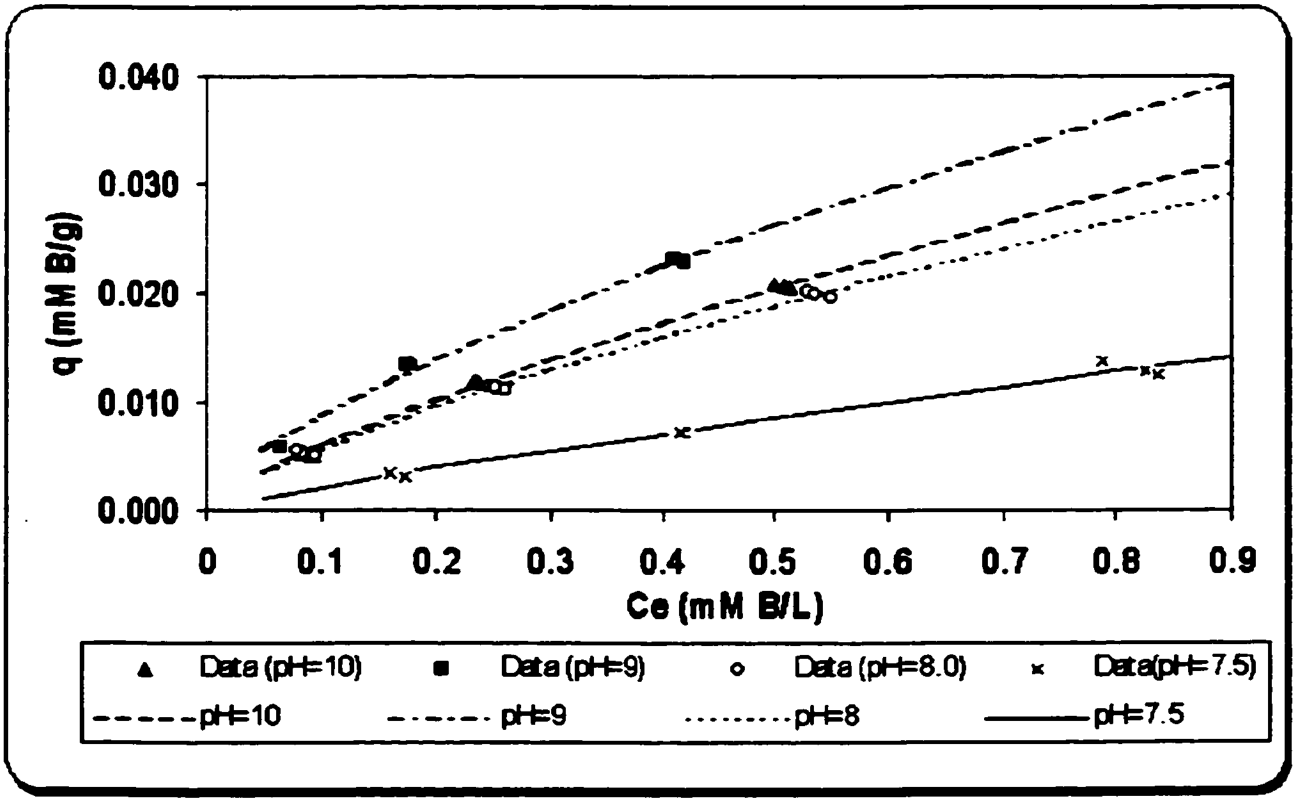


Figure 4-7: Freundlich isotherms for boron adsorption on peat

The effect of pH is better illustrated when adsorption curves are drawn with respect to pH, as in Figure 4-8. The pH effect becomes more obvious at higher equilibrium concentrations of boron. As mentioned in Chapter 2, with increasing pH the concentration of $B(OH)_4^-$ increases which results in higher amounts of adsorption. However, at pH levels above the range of 9-10, high concentrations of OH^- ions result in a decrease in boron adsorption due to competition effect.

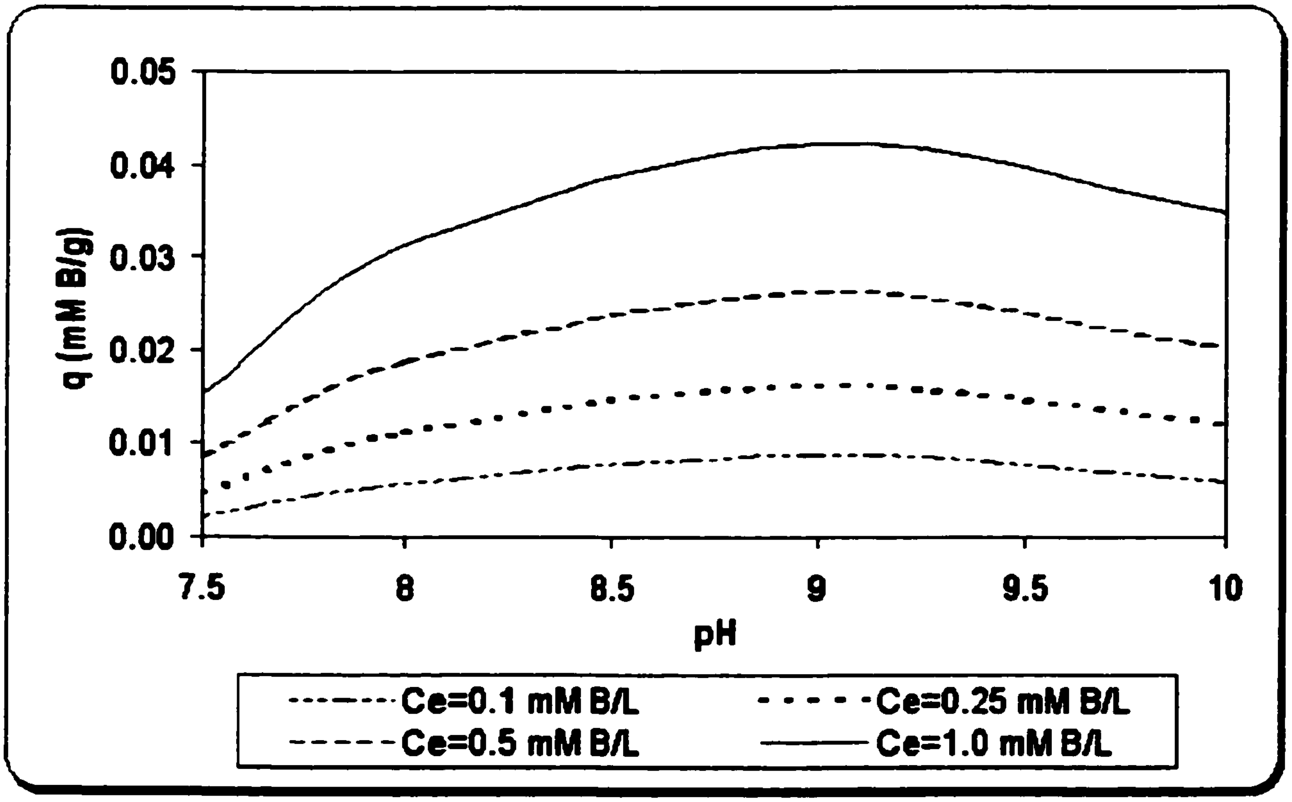


Figure 4-8: The effect of pH on adsorption of boron by peat

4.13. TWO-LEVEL FACTORIAL DESIGN

In the earlier sections of this chapter, the effect of a number of parameters on the adsorption of boron was investigated by statistical comparison of the batch adsorption tests results. Based on the findings some of these parameters including drying, soil-to-solution ratio, shaking, and contact time were fixed for all subsequent tests. To further assess the effect of pH, temperature, and solution composition by a more rigorous method and based on a larger number of tests, a two-level factorial design experiment was conducted. In addition to its use as a screening tool, two-level factorial design can provide information on the relative importance of each parameter with respect to others and show if there is any interaction between parameters of concern. Table 4-23 indicates the lower and upper levels of each parameter. To simplify the calculation and comparison of the individual or joint influence of parameters the lower and upper values are coded and these are shown in Table 4-23.

Table 4-23. Two-level factorial design

Parameter	Level	Coded level
PH	7.2	-1
	9.2	1
Temperature	2	-1
	22	1
Solution composition	DW	-1
	L-B	1

DW=distilled water used for dilution

A complete two-level factorial design model has the following form.

$$E(q) = \beta_0 + \beta_1\, pH + \beta_2\, Temp + \beta_3\, Comp + \beta_{12}\, pH \bullet Temp + \beta_{13}\, pH \bullet Comp + \beta_{23}\, Temp \bullet Comp + \beta_{123}\, pH \bullet Temp \bullet Comp + \varepsilon \qquad (4\text{-}10)$$

where $E(q)$ is the expected value of response (adsorption here) and pH, $Temp$, and $Comp$ represent independent variables pH, temperature, and solution composition respectively. β_0 represents the overall mean, $\beta_{1,2,3}$ are the principal effects, $\beta_{12,13,23}$ are the 2-way interactions between factors, β_{123} is the 3-way interaction, and ε is the random error.

To construct the confidence intervals and test the adequacy of the model, one needs an estimate of variance of error. The variance of error can be obtained from replicates. Thus, each operating condition was replicated between 2 to 5 times. The results are presented in Table 4-24. The outcome of the regression analysis is presented in Table 4-25. The confidence intervals for all interaction terms contain zero and therefore these terms may be deleted from the model. After deleting these terms, the regression analysis was repeated with the remaining parameters, which did not change the parameters.

$$E(q) = 0.0093 + 0.0019\, pH - 0.0008\, Temp + 0.0005\, Comp \qquad (4\text{-}11)$$

The significance of the model inadequacy was tested by comparing the value of r ratio, as defined below, with an $F_{v1,v2,\alpha}$ distribution at desired probability level (α=0.05).

Table 4-24. Experimental results for Two-level factorial design

No.	pH	Temp	Comp	pH•Temp	pH•Comp	Temp•Comp	pH•Temp•Comp	q (mM B/g)
1	-1	-1	1	1	-1	-1	1	0.00808
1	-1	-1	1	1	-1	-1	1	0.00793
1	-1	-1	1	1	-1	-1	1	0.00832
1	-1	-1	1	1	-1	-1	1	0.00870
1	-1	-1	1	1	-1	-1	1	0.00863
2	-1	-1	-1	1	1	1	-1	0.00803
2	-1	-1	-1	1	1	1	-1	0.00825
3	1	-1	1	-1	1	-1	-1	0.01221
3	1	-1	1	-1	1	-1	-1	0.01244
3	1	-1	1	-1	1	-1	-1	0.01297
4	1	-1	-1	-1	-1	1	1	0.01172
4	1	-1	-1	-1	-1	1	1	0.01104
4	1	-1	-1	-1	-1	1	1	0.01145
5	-1	1	1	-1	-1	1	-1	0.00685
5	-1	1	1	-1	-1	1	-1	0.00581
5	-1	1	1	-1	-1	1	-1	0.00786
5	-1	1	1	-1	-1	1	-1	0.00799
6	-1	1	-1	-1	1	-1	1	0.00591
6	-1	1	-1	-1	1	-1	1	0.00671
6	-1	1	-1	-1	1	-1	1	0.00574
7	1	1	1	1	1	1	1	0.01182
7	1	1	1	1	1	1	1	0.01090
7	1	1	1	1	1	1	1	0.01076
8	1	1	-1	1	-1	-1	-1	0.00912
8	1	1	-1	1	-1	-1	-1	0.00956

Table 4-25. Parameters estimate for Two-level factorial design

	Coefficients	Lower 95%	Upper 95%
β_0	0.009269	0.009021	0.009518
β_1	0.001841	0.001593	0.002089
β_2	-0.000834	-0.001082	-0.00059
β_3	0.000519	0.000271	0.000767
β_{12}	-2.747E-05	-0.000276	0.000221
β_{13}	0.000219	-2.94E-05	0.000467
β_{23}	0.000188	-6.02E-05	0.000436
β_{123}	-1.609E-05	-0.000264	0.000232

$$r = \frac{\sum_{u=1}^{n}(q_{ave}-E(q))^2 / \left\{n-p-\sum_{i=1}^{l}(m_i-1)\right\}}{\sigma^2_p} \qquad (4\text{-}12)$$

where n= number of data points, p= number of parameters in model, l number of sets of replicates, m_i number of data points in the i'th set of replicates, q_{ave} mean value, and $E(q)$ is the value of fitted response. $v1=n-p-\sum(m_i-1)$ and $v2 = \sum(m_i-1)$ are degrees of freedom (df) associated with σ_p^2. Based on the replicates, σ_p^2 was calculated to be 3.18 x 10^{-7} with 17 df. The numerator was calculated to be 4.578 x 10^{-7}. Therefore, the value of r is equal to 1.44 (=4.578/3.18), which compares to $F_{4,17,\ \alpha=0.05}$ = 2.96. Since the value of r is less than $F_{v1,v2,\ \alpha=0.05}$ the model does not display any lack of fit or any significant inadequacy. The adequacy of the model was further tested by plotting residuals vs. all the parameters. The plot of residual for C_e is shown as an example in Figure 4-9. The residual plot does not show any evidence of a systematic behavior or specific trend, suggesting that the fitted model provides an adequate representation of the data.

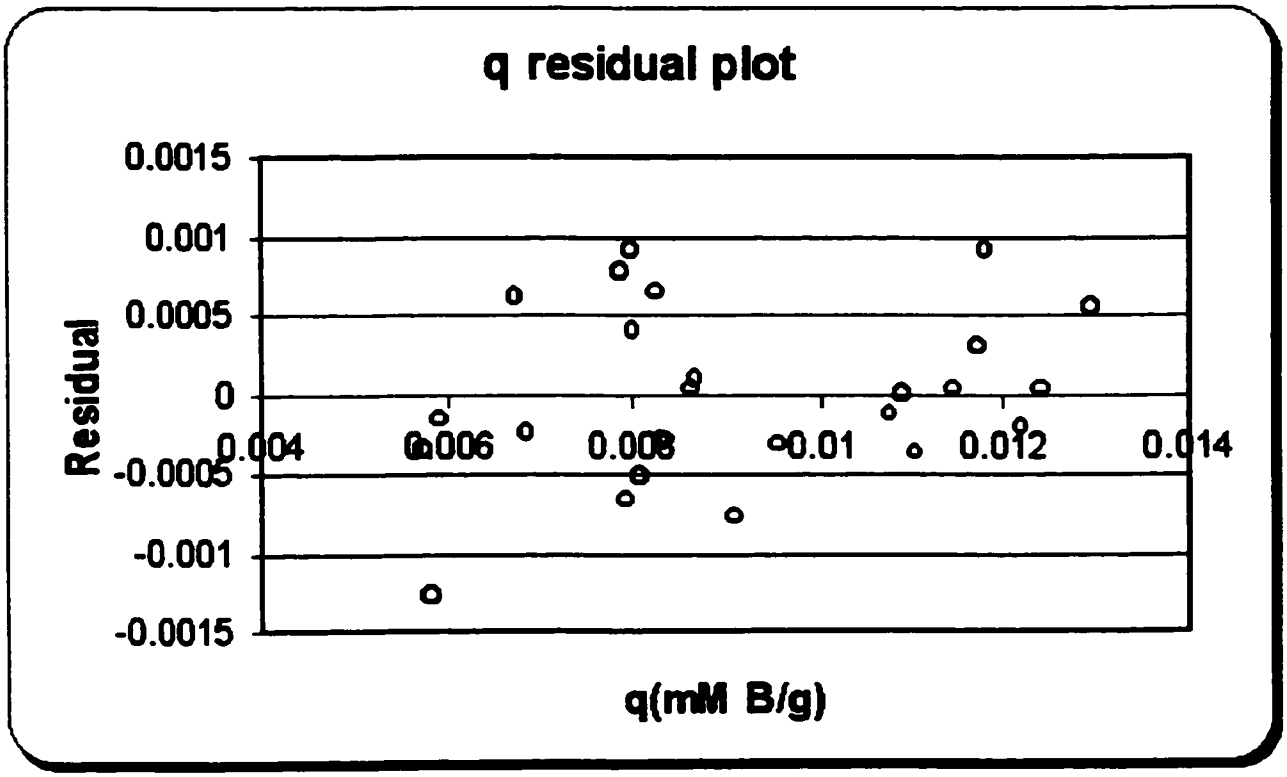


Figure 4-9: Plot of residuals for two-level factorial design

The ratio Q, as defined below, can be used to test whether the model can be further simplified by deleting any of the terms.

$$Q = \frac{1}{\sigma_p} \frac{(SSR\ of\ reduced) - (SSR\ of\ original)}{(\#\ of\ parameters\ of\ original) - (\#\ of\ parameters\ of\ reduced)} \tag{4-13}$$

The ratio Q is compared with $F_{v1,v2,\alpha}$. $v1$ is the difference in the number of estimated parameters in the reduced and original model; $v2$ is the df associated with σ_p^2. σ_p was obtained by pooling the estimates of variances from replicates and had a value of 3.18×10^{-7} with df=17. Since composition and pH term had the lowest parameters, they were omitted from the model one at a time, which resulted in a Q value of 19.4 and 45.8, respectively. These compares with $F_{1,17,\alpha=0.05} = 4.45$. Q is higher than F value in both cases showing that deletion of each term results in an inadequate model.

Comparison of the coefficient of Equation 4-11 shows that pH has the strongest influence on boron adsorption since its coefficient is 2.2 times and 3.5 times greater than the coefficients of temperature and solution composition terms, respectively. Also, positive values of coefficients for pH and solution composition terms show that these parameters have a positive correlation with boron adsorption. Thus, boron adsorption increases with pH increase and not using DW for dilution of leachate. In the case of temperature, the coefficient is negative showing that boron adsorption decreases as temperature increases.

4.14. SECOND (2^{nd}) ORDER DESIGN MODEL

Two-level factorial design is not intended to provide definitive models of process behavior since it does not yield information about possible quadratic or higher degree behavior of the operating parameters. In two-level factorial design each operating parameter is only tested at two levels. If a polynomial model is to be used to model the response function, then it must be of at least second degree and each operating variable has to be tested at least at three levels, hence a three-level design. The drawback is an unacceptably larger number of runs for large number of operating variables. It was decided to develop a model to describe the adsorption of boron, which incorporates the effect of pH and temperature in addition to equilibrium concentration. The solution composition parameter assessed in the previous step was omitted since it was shown that diluting leachate by DW and the resulting change in the chemistry of the leachate had a significant effect on adsorption of boron. All the subsequent tests were carried out using L-B for dilution. Therefore, the model to be fitted to the experimental data has the following form.

$$E(q)= \beta_0 + \beta_1\, pH + \beta_2\, Temp + \beta_3\, C_e + \beta_{11}\, pH^2 + \beta_{22}\, Temp^2 + \beta_{33}\, C_e^2 + \beta_{12}\, pH \bullet Temp + \beta_{13}\, pH \bullet C_e + \beta_{23}\, Temp \bullet C_e + \beta_{123}\, pH \bullet Temp \bullet C_e + \varepsilon \qquad \textbf{(4-14)}$$

where *E(q)* is the expected value of response and *pH*, *Temp*, and C_e represent independent variables of pH, temperature, and equilibrium concentrations. Experimental results of adsorption tests as well as the value of pH, temperature, and concentration equilibrium are summarized in Table 4-26.

Table 4-27 shows the estimates of the parameters obtained by regression analysis. The results of the regression analysis shows that only the confidence interval for term β_{22} contains zero and therefore this term may be deleted from the model. This term was omitted and the regression analysis was repeated.

Table 4-26. Second order factorial design

	pH	Temp	C_e	q (mM B/g)		pH	Temp	C_e	q (mM B/g)
1	9.5	2	0.05	**0.00622**	13	7.5	12	0.37	**0.00845**
1	9.5	2	0.05	**0.00621**	14	9.1	12	0.37	**0.02398**
1	9.5	2	0.05	**0.00618**	14	9.1	12	0.37	**0.02397**
2	9	2	0.13	**0.01435**	14	9.1	12	0.38	**0.02372**
2	9	2	0.13	**0.01431**	15	9	22	0.06	**0.00579**
2	9	2	0.14	**0.01414**	15	9	22	0.06	**0.00579**
3	8.0	2	0.15	**0.01393**	15	9	22	0.06	**0.00579**
3	8.0	2	0.15	**0.01386**	16	10	22	0.09	**0.00513**
3	8.0	2	0.15	**0.01379**	16	10	22	0.09	**0.00513**
4	9.2	2	0.16	**0.01244**	16	10	22	0.09	**0.00508**
4	9.2	2	0.15	**0.01297**	17	9.1	22	0.17	**0.01324**
5	10.3	2	0.22	**0.01220**	17	9.1	22	0.17	**0.01323**
5	10.3	2	0.22	**0.01215**	17	9.1	22	0.18	**0.01314**
5	10.3	2	0.22	**0.01212**	17	9	22	0.18	**0.01182**
6	7.2	2	0.31	**0.00870**	18	10	22	0.23	**0.01181**
6	7.2	2	0.31	**0.00863**	18	10	22	0.23	**0.01175**
6	7.2	2	0.32	**0.00832**	18	10	22	0.24	**0.01171**
7	9.5	2	0.33	**0.02501**	19	8.1	22	0.25	**0.01132**
7	9.5	2	0.34	**0.02495**	19	8.1	22	0.25	**0.01130**
7	9.5	2	0.35	**0.02449**	19	8.1	22	0.26	**0.01110**
8	7.4	2	0.36	**0.00866**	20	7.4	22	0.34	**0.00799**
8	7.4	2	0.36	**0.00855**	20	7.4	22	0.34	**0.00786**
8	7.4	2	0.36	**0.00852**	20	7.4	22	0.38	**0.00685**
9	9.5	2	1.18	**0.04909**	21	9.1	22	0.41	**0.02310**
9	9.5	2	1.54	**0.04026**	21	9.1	22	0.41	**0.02302**
9	9.5	2	1.55	**0.03988**	21	9.1	22	0.42	**0.02284**
10	9.1	12	0.15	**0.01379**	22	10	22	0.50	**0.02087**
10	9.1	12	0.16	**0.01369**	22	10	22	0.51	**0.02062**
10	9.1	12	0.16	**0.01364**	22	10	22	0.51	**0.02048**
11	8.0	12	0.19	**0.01273**	23	8.1	22	0.53	**0.02013**
11	8.0	12	0.20	**0.01265**	23	8.0	22	0.54	**0.01995**
11	8.0	12	0.21	**0.01245**	23	8.1	22	0.55	**0.01958**
12	10.2	12	0.23	**0.01186**	24	7.2	22	0.45	**0.00532**
12	10.2	12	0.23	**0.01179**	24	7.2	22	0.60	**0.00754**
12	10.2	12	0.24	**0.01157**	24	7.2	22	0.60	**0.00724**
13	7.5	12	0.36	**0.00869**	24	7.2	22	0.59	**0.00706**

Table 4-27. Parameters estimates for 2nd order design

	Coefficients	*Lower 95%*	*Upper 95%*
β_0	-0.2552	-0.2930	-0.2173
β_1	0.0656	0.0580	0.0732
β_2	-0.0030	-0.0038	-0.0021
β_3	-0.2083	-0.2608	-0.1558
β_{11}	-0.0041	-0.0044	-0.0037
β_{33}	-0.0347	-0.0381	-0.0312
β_{12}	0.0003	0.0002	0.0004
β_{13}	0.0306	0.0249	0.0364
β_{23}	0.0099	0.0073	0.0125
β_{123}	-0.0011	-0.0014	-0.0009

The significance of the model inadequacy was tested by comparing the value of R ratio with an $F_{v1,v2,\alpha=0.05}$ distribution the same way as in two-level factorial design. σ_p was obtained by pooling the estimates of variances from replicates and had a value of 1.23×10^{-6} with df=44. The value of r is 0.9, which compares to $F_{14,44,\alpha=0.05} = 1.97$. This shows that the model does not display any lack of fit or any significant inadequacy. In the next step the possibility of deleting some of the terms was investigated. However, further deletion of any of the remaining terms resulted in the lack of fit of the model. The adequacy of the model was further tested by plotting of residuals vs. all the parameters. The plot of residuals for C_e and q are shown as examples in Figures 4-10 and 4-11. The plots of residuals do not show any evidence of a systematic behavior or specific trend, suggesting that the fitted model provides an adequate representation of the data. Therefore, the final form of the regression model is as indicated below.

$$E(q) = -0.2552 + 0.0656\ \mathrm{pH} - 0.0030\ \mathrm{Temp} - 0.2083\ C_e - 0.0041\ \mathrm{pH}^2 - 0.0347\ C_e^2 + 0.0003\ \mathrm{pH} \bullet \mathrm{Temp} + 0.0306 \mathrm{pH} \bullet C_e + 0.0099\ \mathrm{Temp} \bullet C_e - 0.0011\ \mathrm{pH} \bullet \mathrm{Temp} \bullet C_e$$

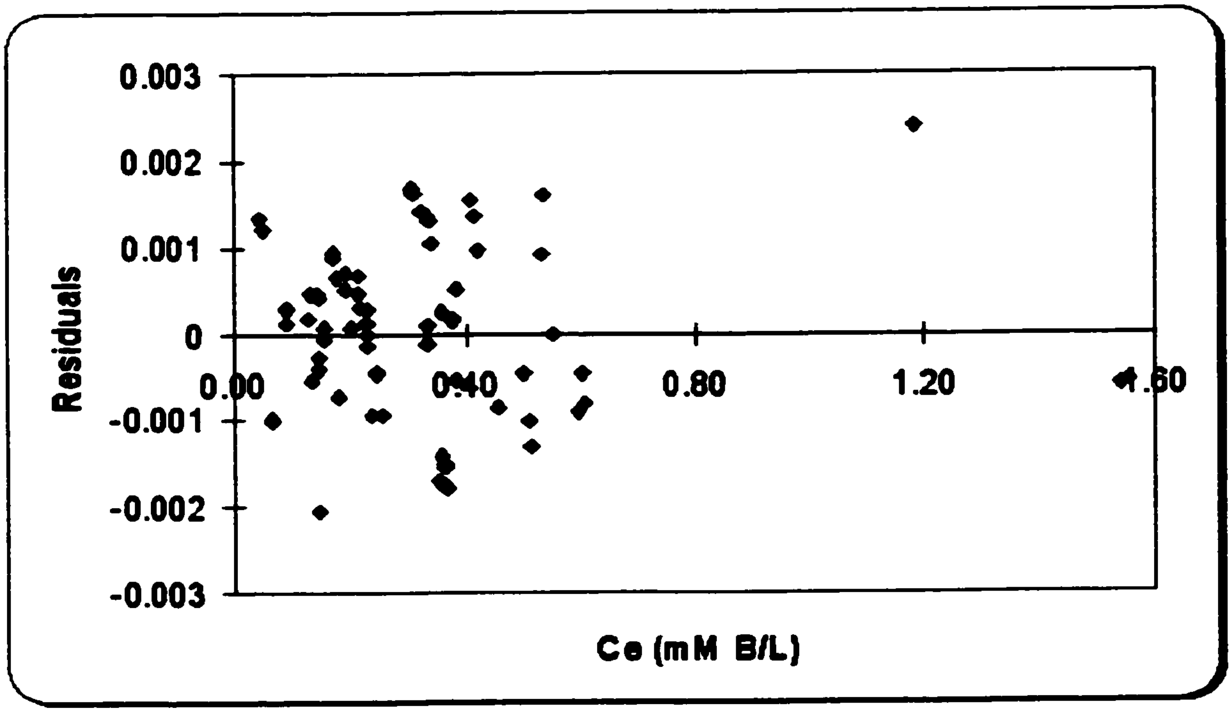


Figure 4-10: Plot of residuals vs. C_e for 2nd order factorial design

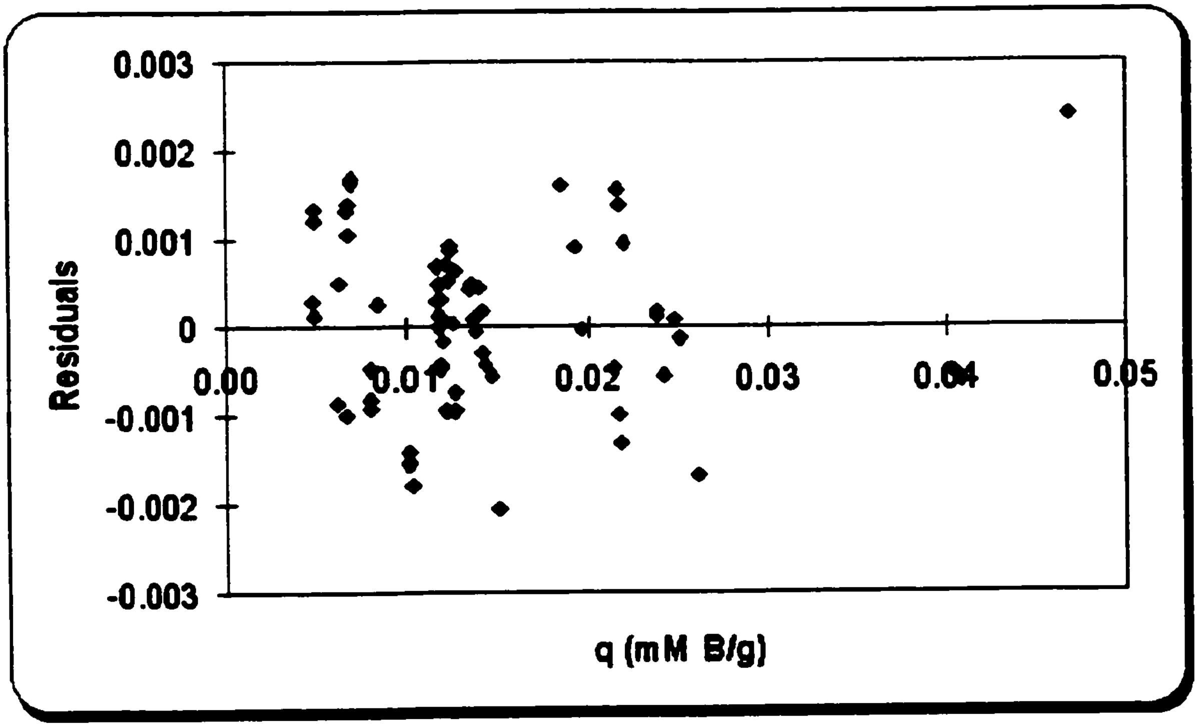


Figure 4-11: Plot of residuals vs. q for 2nd order factorial design

Figure 4-12 compares the fitting of the above model with those obtained by Freundlich model as well as some of the experimental points at two pH values. The plot shows very good agreement between the experimental points and the 2nd order design model. There is also a very good agreement between the output of the 2nd order design model and Freundlich isotherms.

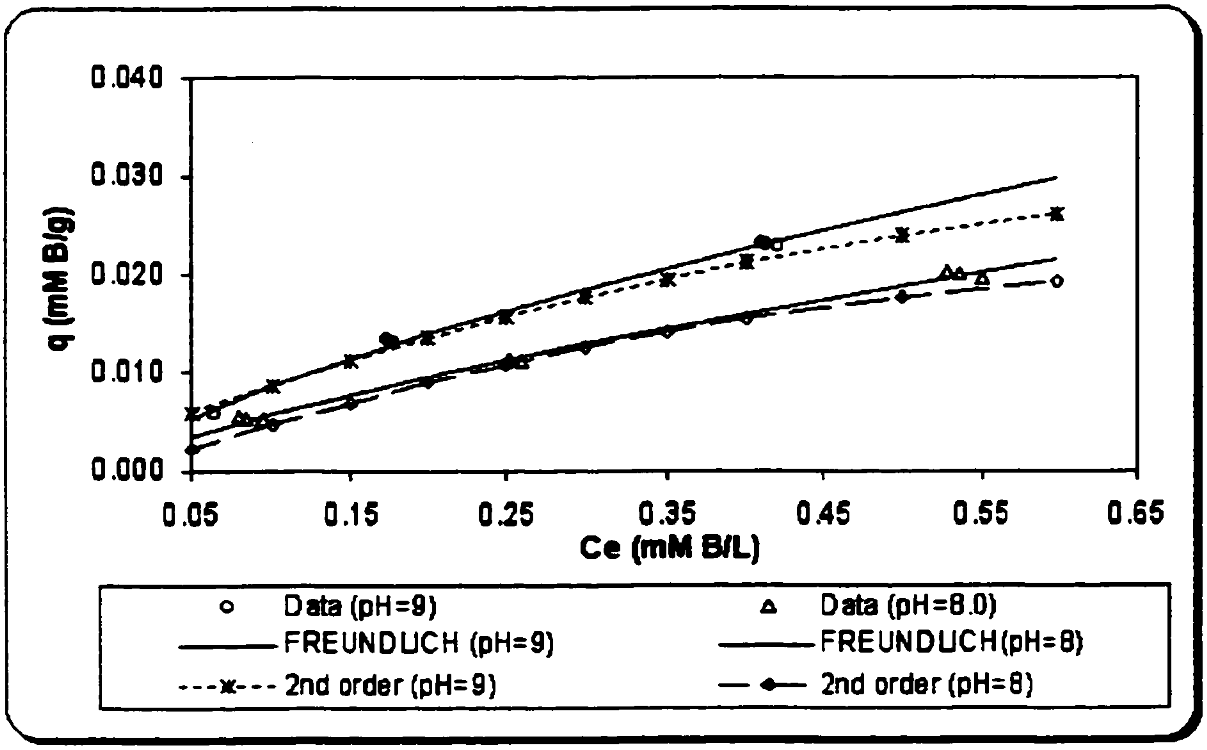


Figure 4-12: Plot of adsorption results from NLPEFM and 2nd order design vs. experimental data

Since Freundlich isotherms are only available at a temperature of 22 °C and a pH of 7.5, 8, 9, and 10, the experimental points under these conditions were selected and the SSR for both methods were calculated, see Table 4-28. SSR for Freundlich and the 2nd order design models were 1.4 x 10^{-5} and 2.1 x 10^{-5}, respectively. Although SSR for Freundlich isotherms model is less than that of the 2nd order design, it should be noted that the 2nd order design model has many advantages over Freundlich adsorption model. The 2nd order design can predict the adsorption at any pH and temperature while adsorption isotherms obtained by Freundlich are applicable for specific pH and temperature for which they were developed.

Table 4-28. SSR for Freundlich and 2^{nd} order design for data points at Temp=22 °C

pH	Temp	C_e	q	$E(q)_{2nd}$	$\{q-E(q)_{2nd}\}^2$	$E(q)_{Fr}$	$\{q-E(q)_{Fr})\}^2$
9	22	0.06	**0.00579**	**0.00678**	9.761E-07	**0.00643**	4.025E-07
9	22	0.06	**0.00579**	**0.00679**	9.962E-07	**0.00644**	4.177E-07
9	22	0.06	**0.00579**	**0.00679**	1.014E-06	**0.00644**	4.31E-07
10	22	0.09	**0.00513**	**0.00484**	8.555E-08	**0.00554**	1.638E-07
10	22	0.09	**0.00513**	**0.00484**	8.122E-08	**0.00554**	1.691E-07
10	22	0.09	**0.00508**	**0.00495**	1.635E-08	**0.00563**	2.998E-07
9.1	22	0.17	**0.01324**	**0.01232**	8.573E-07	**0.01270**	2.951E-07
9.1	22	0.17	**0.01323**	**0.01235**	7.627E-07	**0.01274**	2.388E-07
9.1	22	0.18	**0.01314**	**0.01251**	4.061E-07	**0.0129**	5.94E-08
9	22	0.18	**0.01182**	**0.01256**	5.427E-07	**0.01321**	1.946E-06
10	22	0.23	**0.01181**	**0.01153**	7.731E-08	**0.01133**	2.289E-07
10	22	0.23	**0.01175**	**0.01163**	1.404E-08	**0.01141**	1.171E-07
10	22	0.24	**0.01171**	**0.01171**	9.312E-13	**0.01155**	5.767E-08
8.1	22	0.25	**0.01132**	**0.0117**	1.806E-07	**0.01129**	8.623E-10
8.1	22	0.25	**0.01130**	**0.01177**	2.199E-07	**0.01131**	1.496E-10
8.1	22	0.26	**0.01110**	**0.01205**	8.924E-07	**0.01157**	2.148E-07
7.4	22	0.34	**0.00799**	**0.00668**	1.716E-06	**0.00605**	3.781E-06
7.4	22	0.34	**0.00786**	**0.00681**	1.112E-06	**0.00612**	3.031E-06
7.4	22	0.38	**0.00685**	**0.00634**	2.569E-07	**0.00674**	1.141E-08
9.1	22	0.41	**0.02310**	**0.0216**	2.372E-06	**0.02287**	5.129E-08
9.1	22	0.41	**0.02302**	**0.02166**	1.87E-06	**0.02299**	9.587E-10
9.1	22	0.42	**0.02284**	**0.02188**	9.093E-07	**0.02328**	1.951E-07
10	22	0.50	**0.02087**	**0.0213**	2.133E-07	**0.02042**	1.996E-07
10	22	0.51	**0.02062**	**0.02163**	1.022E-06	**0.02073**	1.346E-08
10	22	0.51	**0.02048**	**0.02179**	1.687E-06	**0.02090**	1.741E-07
8.1	22	0.53	**0.02013**	**0.01923**	8.186E-07	**0.01958**	3.034E-07
8.0	22	0.54	**0.01995**	**0.01834**	2.576E-06	**0.01978**	3.146E-08
8.1	22	0.55	**0.01958**	**0.01959**	2.694E-10	**0.02018**	3.689E-07
				SSR	2.1E-05	**SSR**	1.4E-05

Also, the 2^{nd} order design produces one equation for the whole domain while a group of equations have to be developed in the case Freundlich model is used. In addition, collection of experimental data for the 2^{nd} order design is much easier and needs much less effort. The reason is that in the case of using Freundlich isotherm the conditions such as pH has to be constant. When leachate is diluted or different mass of adsorbent, especially in the case of peat, is used pH might change and it might be necessary to find the correct configuration for each test by trial and error. In addition, the 2nd order design model could be developed with less number of experiments. For the 2nd order design developed in this section 72 experimental points were used. Considering the same configuration, i.e. 3 temperatures, 4 pH values, and four experimental points with 3 replicates for each condition, 144 experimental points would be needed to develop Freundlich equations to cover the whole domain.

Figure 4-13 illustrates the comparison of the 2nd order model with Freundlich isotherms as a function of pH. It is apparent that the 2nd order model is in good agreement with adsorption isotherms obtained by the Freundlich model. It is also capable of describing the adsorption of boron as a function of pH as it has the same trend showing a maximum value at a pH of about 9.

The effect of temperature is depicted in Figure 4-14. The 2nd order model shows an increase in boron adsorption as temperature decreases. This follows the same trend observed

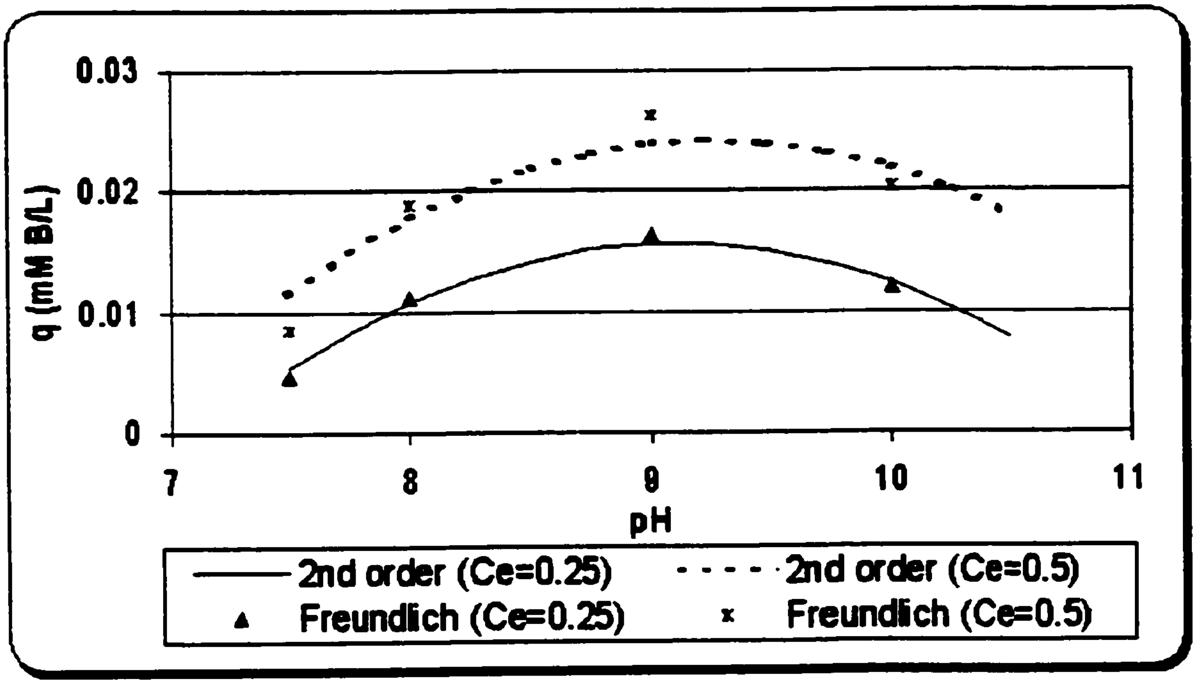


Figure 4-13: Results from 2nd order model and NLPEFM vs. pH

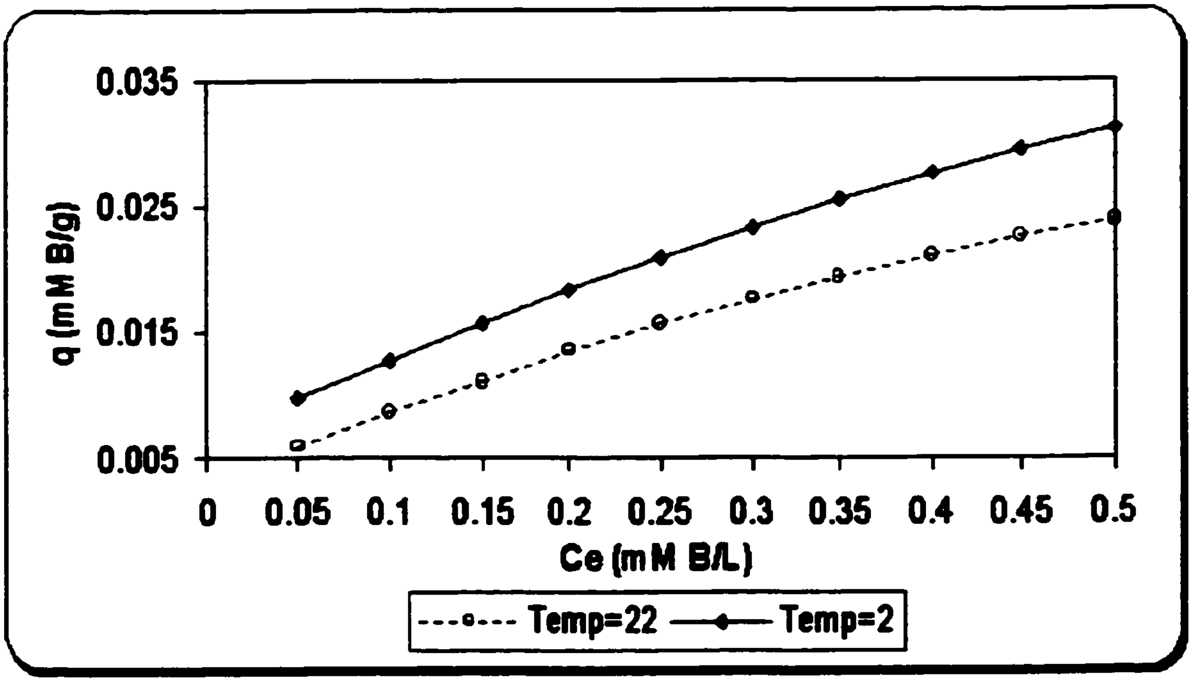


Figure 4-14: The effect of temperature on boron adsorption by peat

from experimental data. Figure 4-15 is the plot of another set of experimental data at pH of 9.5. As it is seen the adsorption increases with increasing C_e until it reaches a peak value and then it drops. Such a behavior observed in experimental points is probably due to reaching the maximum adsorption level and/or the compounded effect of interaction between pH, temperature, and C_e and cannot be described by Freundlich model. This also shows the superiority of the developed 2nd order model over Freundlich isotherm model.

In summary, the developed 2nd order model can describe the adsorption process very well and has the advantage of incorporating the effect of pH and temperature, thus removing the need for developing different sets of isotherm equations under different environmental conditions. Such a model can be incorporated in contaminant transport model in order to account for the adsorption term.

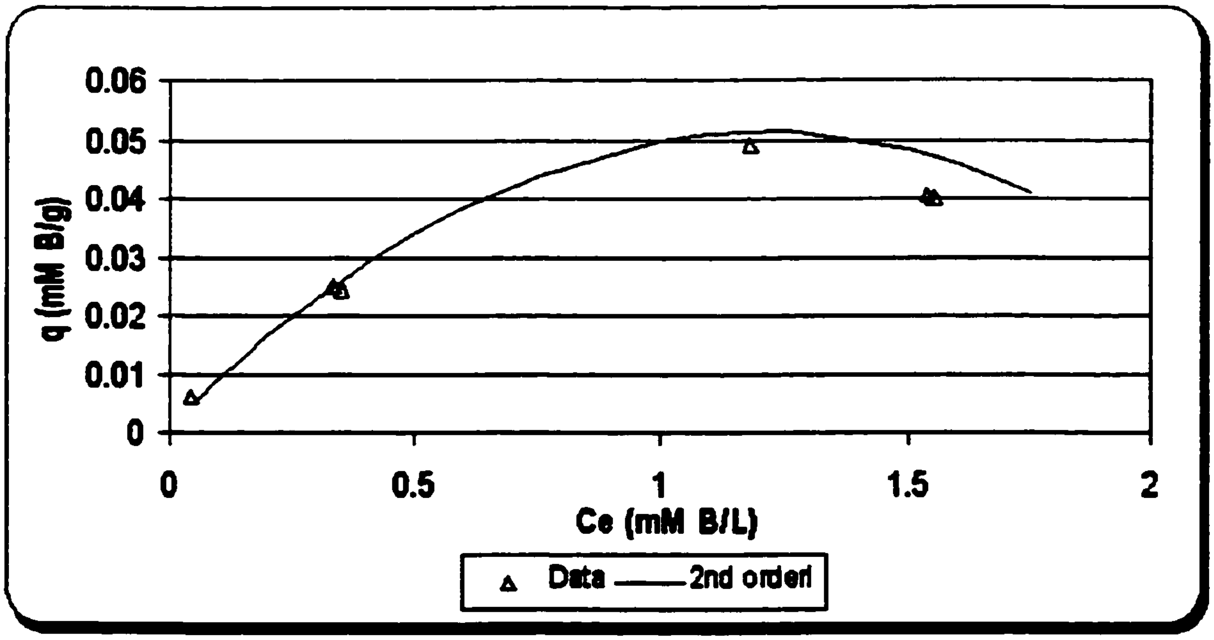


Figure 4-15: Results of regression analysis at temp = 2 °C & pH=9.5

4.15. USE OF ALTERNATIVE ADSORBING MEDIUM

Two sources of compost (CompostH and CompostT), two sources of peat (Alfred peat and commercial peat moss), and Amberlite-743 ion exchange resin were used as alternative adsorbing medium. The characteristics of these materials are described in Chapter 3. The adsorption of boron by these materials is discussed in this section.

4.15.1. Adsorption on Compost Materials

Composts produced at Huneault Waste Management (HWM) landfill and Trail Road landfill were used as the two sources of compost, and there are called CompostH and CompostT, respectively. Both composts were passed through a 3/8 " sieve (9.5 mm) to remove large pieces of wood in order to have a more uniform and homogeneous material for subsequent tests. NLPEFM program developed in a previous section was used to find the parameters estimates of Freundlich isotherm model by non-linear regression analysis. These parameters along with the regression factors for each case are summarized in Table 4-29. As mentioned in Chapter 3, one set of batch adsorption tests were run at pH of 7. The parameters obtained for peat under pH values of 7.0 and 7.5 (Section 4.12) are included as well.

Table 4-29. Results obtained by non-linear regression

Medium	pH	*K*	*1/n*	R^2
CompostH	8.0	0.0016	0.86	0.91
CompostH	9.0	0.0029	0.60	0.98
CompostT	7.8	0.0021	1.02	0.99
Peat	7.5	0.0154	0.86	0.98
Peat	7.0	0.0135	1.17	0.97

As an example, the data points along with the results of non-linear regression obtained by NLPEFM program for CompostT are presented in Figure 4-16. Adsorption isotherms for CompostH and CompostT are compared in Figure 4-17. At low concentrations adsorption capacity was the same. At higher concentrations (1 mM B/L) CompostT showed as much as

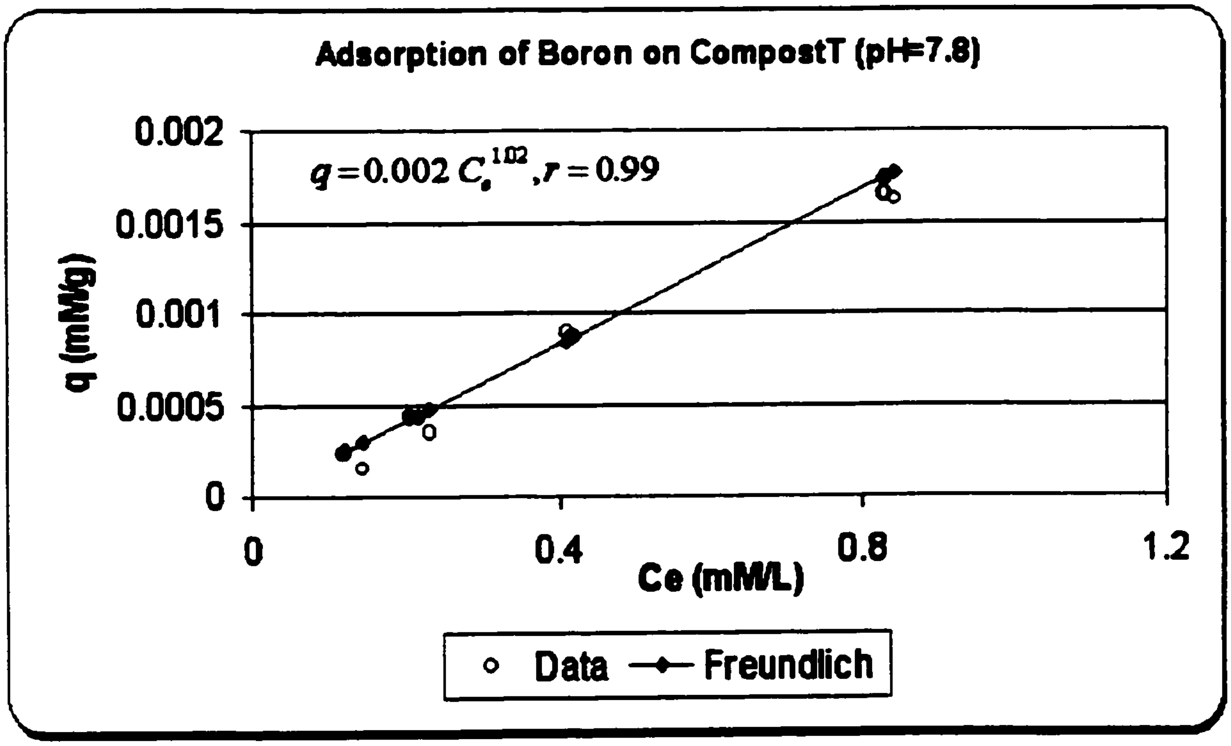


Figure 4-16: Freundlich isotherm for boron adsorption on CompostT

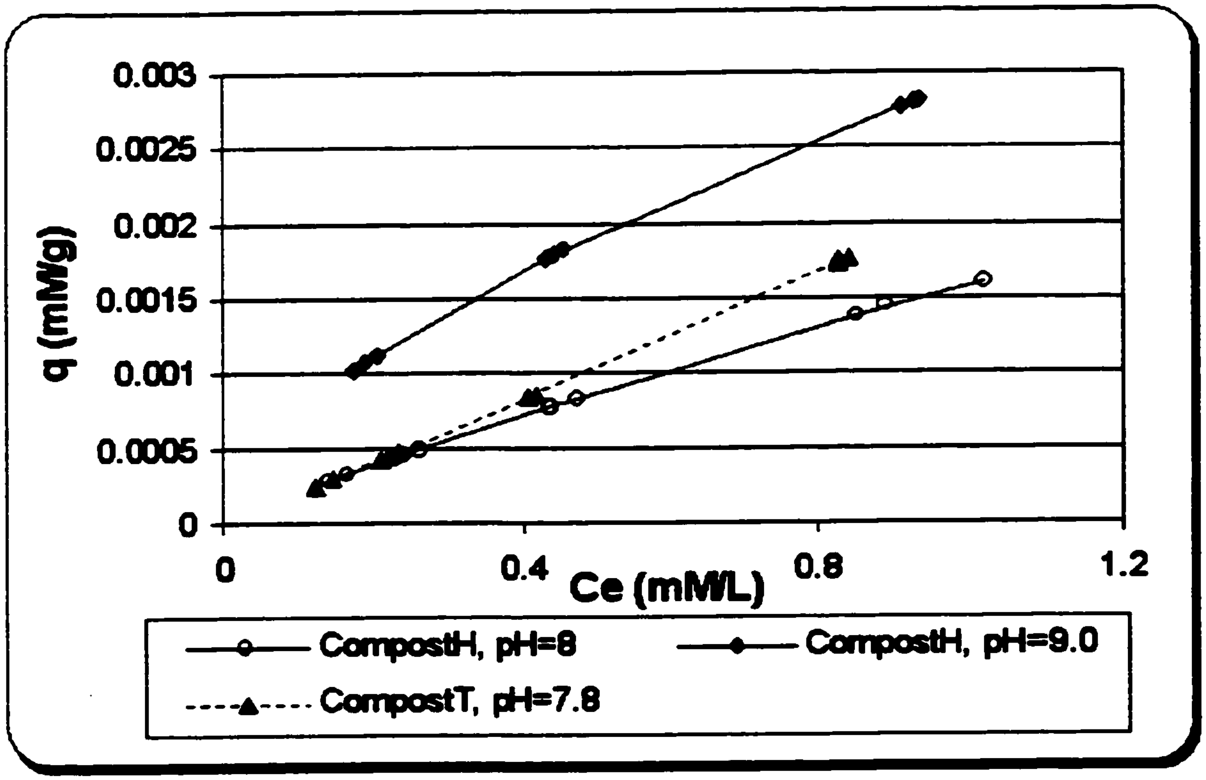


Figure 4-17: Comparison of boron adsorption by CompostH vs. CompostT

30% increase in boron adsorption capacity. In another set of experiments pH was raised to pH=9 by adding of lime to the compost (1 to 130 ratio). The result of increasing pH on adsorption of boron on CompostH is also shown in Figure 4-17. The effect of pH increase (from 8 to 9) was very significant as boron adsorption increased between 85 to 170% over the concentration range of 0.2 to 0.9 mM B/L (2.2 to 9.7 mg B/L). The enhancement of boron adsorption observed here conforms to the results presented for peat earlier (Figure 4-8) showing a strong positive effect for pH.

Comparison of the adsorption parameters estimates presented in Table 4-29 shows that boron adsorption capacity of peat is greater than the boron adsorption capacity of compost material. The value of *1/n* for both peat and CompostH at pH of 8 is the same (0.86), however the value of *K* for peat is about 10 times greater than that of CompostH even at a higher pH. Figure 4-18 compares boron adsorption isotherms of peat with CompostH.

Adsorption capacity of peat was tremendously greater than CompostH. Even at a lower pH of 7.5, peat showed 900% greater boron adsorption compared to CompostH at a pH of 8. This should be due to higher organic matter content of peat with respect to compost material.

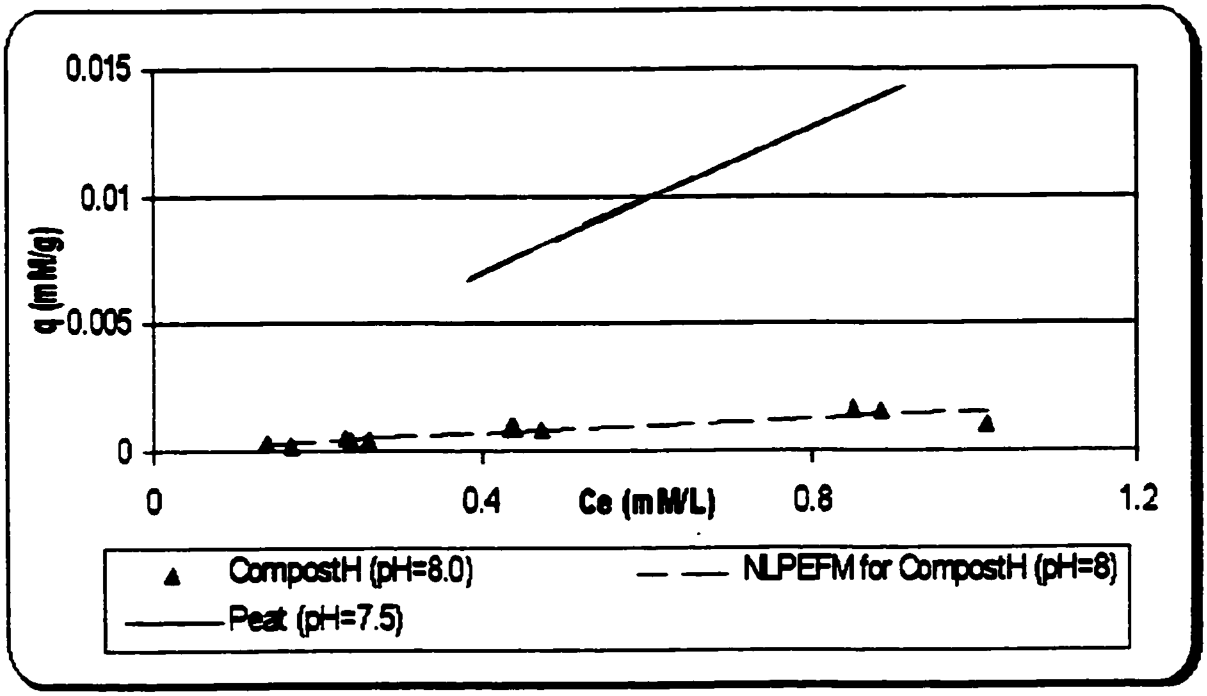


Figure 4-18: Comparison of boron adsorption by CompostH vs. Peat

Some additional adsorption tests with both CompostH and CompostT material and synthetic solution made of boric acid were carried out. As in the case of leachate, both compost materials showed similar adsorption capacity for boron over the range of measured equilibrium concentrations. Figure 4-19 shows the comparison of the adsorption of boron from synthetic solution and leachate. The adsorption of boron from leachate was 10 to 135% greater than that of synthetic solution over the range 0.1 to 0.9 mM B/L (1.1 to 9.7 mg B/L). This result conforms to the results obtained for peat showing that the ionic strength of the solution has a positive effect on the adsorption of boron.

In summary, the results obtained show that both compost sources have relatively similar capacity for boron adsorption. Comparison of results for the two composts with peat

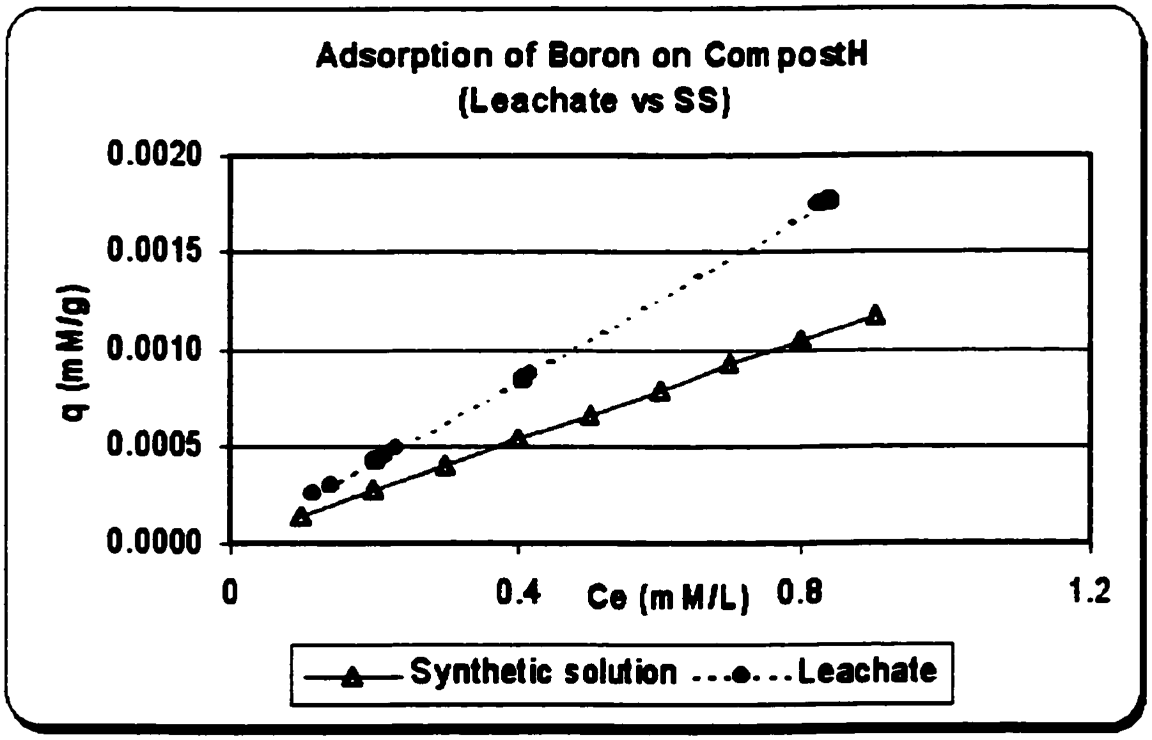


Figure 4-19: Comparison of boron adsorption from SS vs. Leachate

reveals that peat soil has much greater adsorption capacity for boron. Also, pH had a significant impact on adsorption of boron by both composts and peat soil.

4.15.2. Adsorption of boron on Alfred peat

Freundlich isotherm parameters estimates were obtained by non-linear regression analysis (NLPEFM). The plot of the boron adsorption isotherm is presented in Figure 4-20. Leachate was spiked for the adsorption tests on Alfred peat and thus a different range of equilibrium concentration is observed. Nevertheless, the trend of both curves shows that Alfred peat had lower boron adsorption capacity. This again should be due to lower organic content of Alfred peat compared to peat.

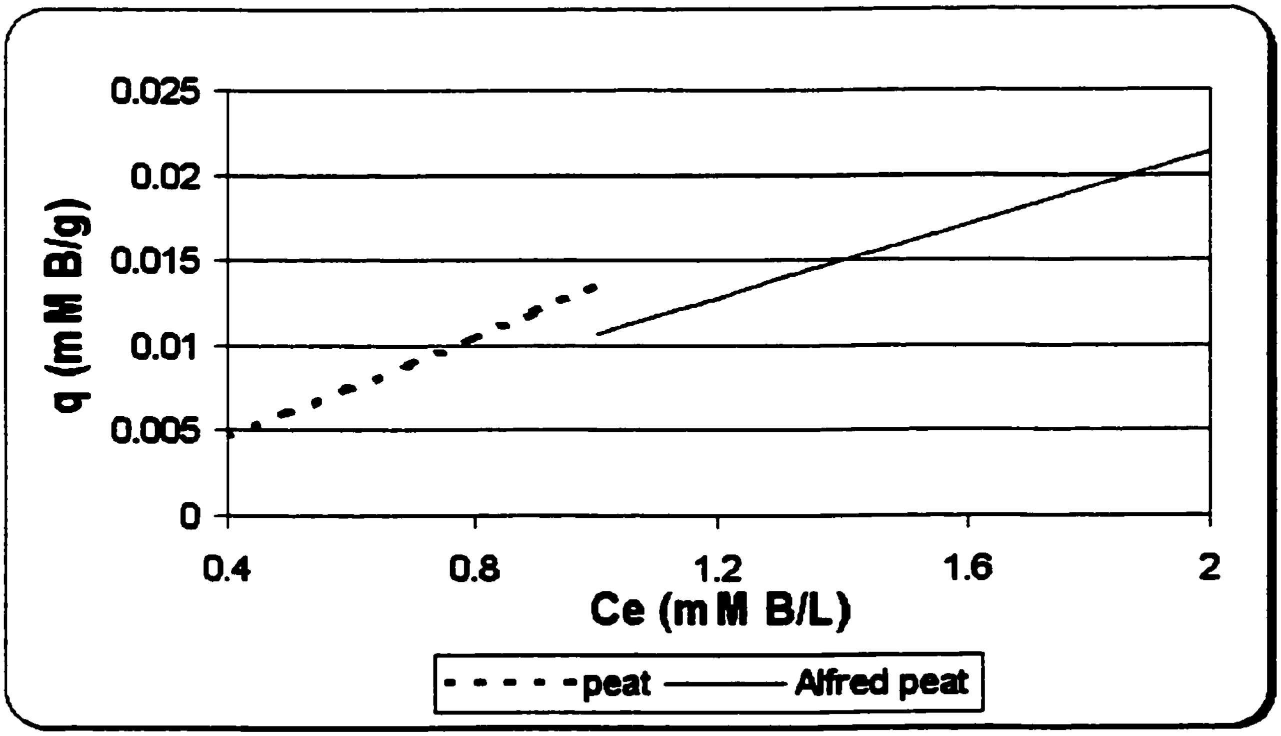


Figure 4-20: Comparison of boron adsorption by peat vs. Alfred peat

4.15.3. Adsorption of boron on peat moss

The characteristics of the commercial peat moss were described in Chapter 3. The parameters estimates of Freundlich isotherm model were obtained by using non-linear regression analysis (NLPEFM). The boron adsorption isotherms for peat moss along with peat are presented in Figure 4-21. It is apparent from this figure that commercial peat moss outperforms the peat used in this study. Over the concentration range of 0.1 to 0.6 mM B/L (1.1 to 6.5 mg B/L) the commercial peat moss shows an 85 to 550% increase in boron adsorption. Higher organic content of the commercial peat moss could be the main reason for this. In fact if the organic content of the two composts, peat, Alfred peat, and commercial peat moss are compared, as indicated in Table 4-30, it can be seen that there is a positive correlation between the organic content and the adsorption capacity for boron. Boron adsorption was calculated for two equilibrium concentrations using the parameters obtained by non-linear regression analysis (NLPEFM program) and their correlations with respect to volatile solid contents were

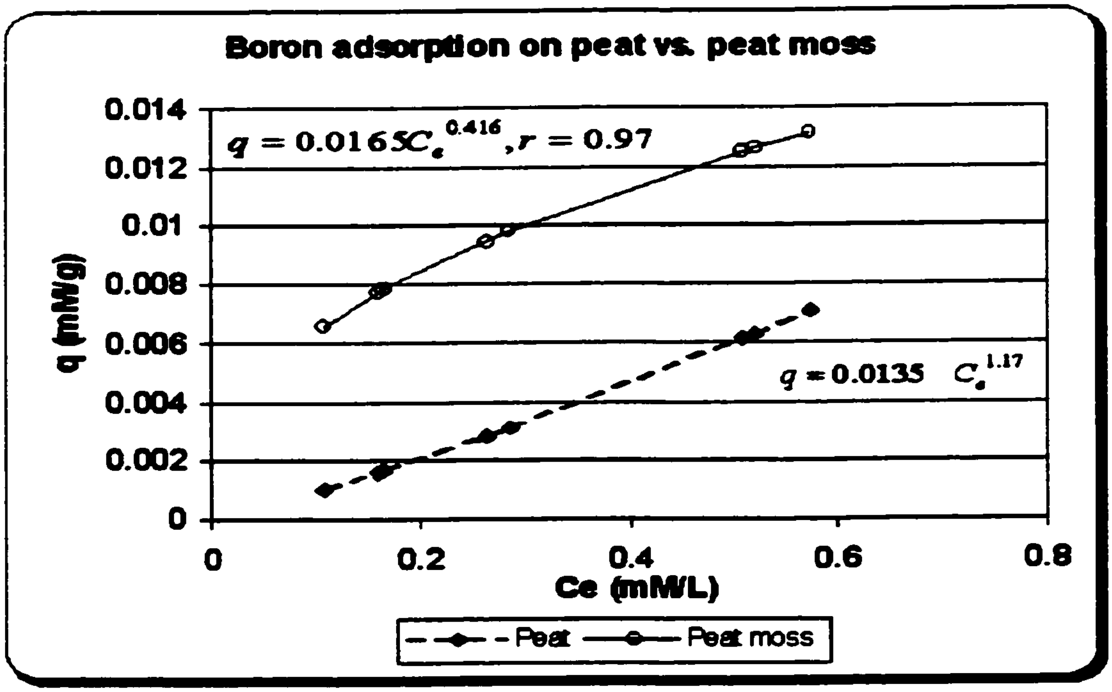


Figure 4-21: Comparison of boron adsorption by peat (pH=7) vs. peat moss

calculated, which showed a correlation factor of 0.92 and 0.98 at equilibrium concentrations of 0.5 and 1.0 mM B/L, respectively. If the amount of boron adsorption is normalized with respect to volatile solids content of these materials, at C_e of 1.0 mM B/L boron adsorption is within the range of 0.5 to 1.7 mM B/kg of VS.

Table 4-30. Correlation between organic content and adsorption of boron (mM B/g)

	%VS	q (mM B/g) Ce=0.5	q (mM B/g) Ce=1.0
CompostH	29.4	0.0009	0.0016
CompostT	18.3	0.0010	0.0021
Alfred peat	70.1	0.0054	0.0107
Peat (pH=7)	84.4	0.0060	0.0135
Peat Moss	97.2	0.0124	0.0165
Correlation Factor		0.92	0.98

4.15.4. Adsorption of boron on Amberlite Anion Exchange Resin

Adsorption of boron by Amberlite was investigated and Freundlich isotherm parameters were obtained by the NLPEFM program. Figure 4-22 shows these results along with adsorption data for peat. The adsorption capacity of peat is almost negligible when compared to that of

Amberlite resin. At a concentration of 0.5 mM B/L, Amberlite shows more than 100 times greater boron adsorption than peat. The result is promising as Amberlite provides a much higher adsorption capacity for boron. As shown previously, the other advantage of Amberlite is that it specifically removes boron without adsorbing other anions or organic compounds. The drawback is that its use requires the setup of ion exchange columns, which have to be operated and maintained. The columns also have to be regenerated once the capacity is exhausted. Nevertheless, it may offer an economically feasible alternative, which is worth investigating.

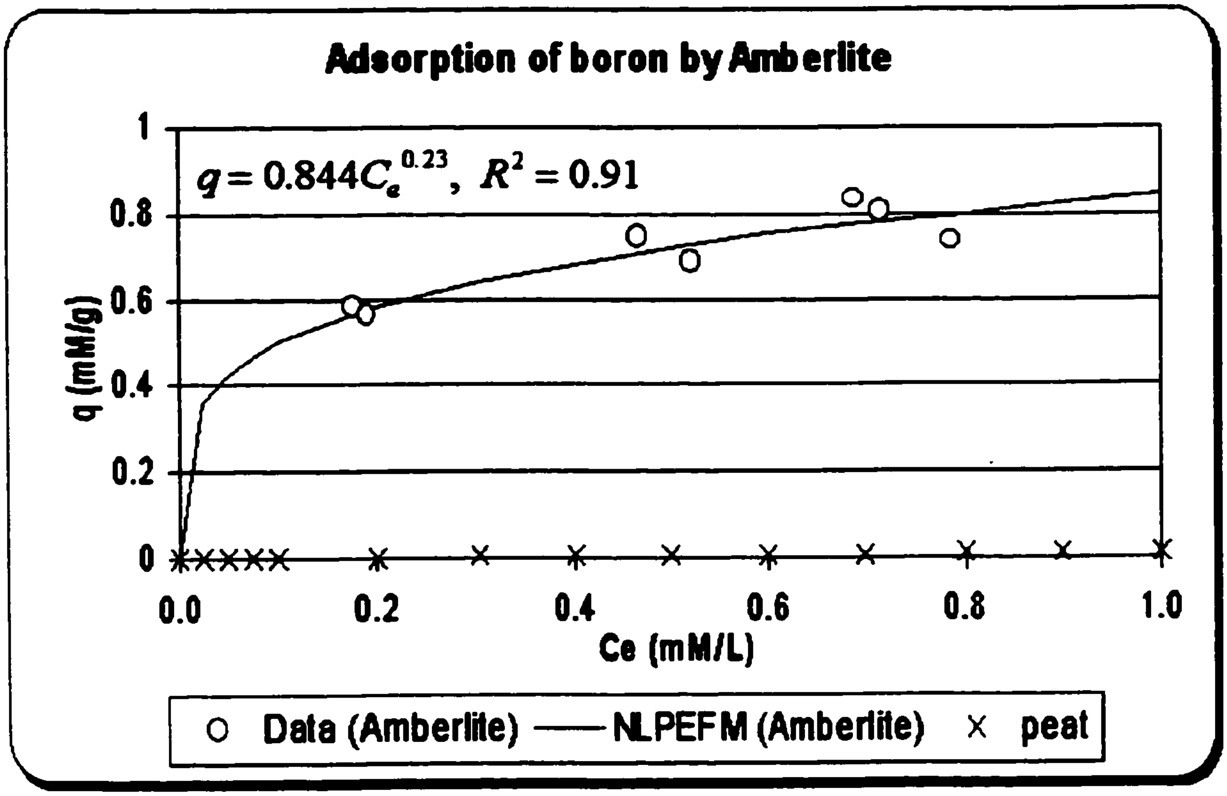


Figure 4-22: Comparison of boron adsorption by peat vs. Amberlite

4.16. ADSORPTION OF IRON, LEAD, AND ZINC

To evaluate the effectiveness of the peat in removing other elements from leachate a set of batch adsorption tests with spiked leachate (for Fe, Pb, and Zn) was carried out. The concentrations of Fe, Pb, and Zn were raised to 4.4, 3.7, and 11 mg/L respectively.

Adsorption isotherms of Fe, Pb, and Zn, presented in Figure 4-23, show that peat is also effective in removing metals from leachate. The results obtained by NLPEFM are summarized in Table 4-31. Comparison of the *K* values shows that the adsorption of metals is greater than boron. Among metals, adsorption of Zn by peat was significantly greater than Fe and Pb.

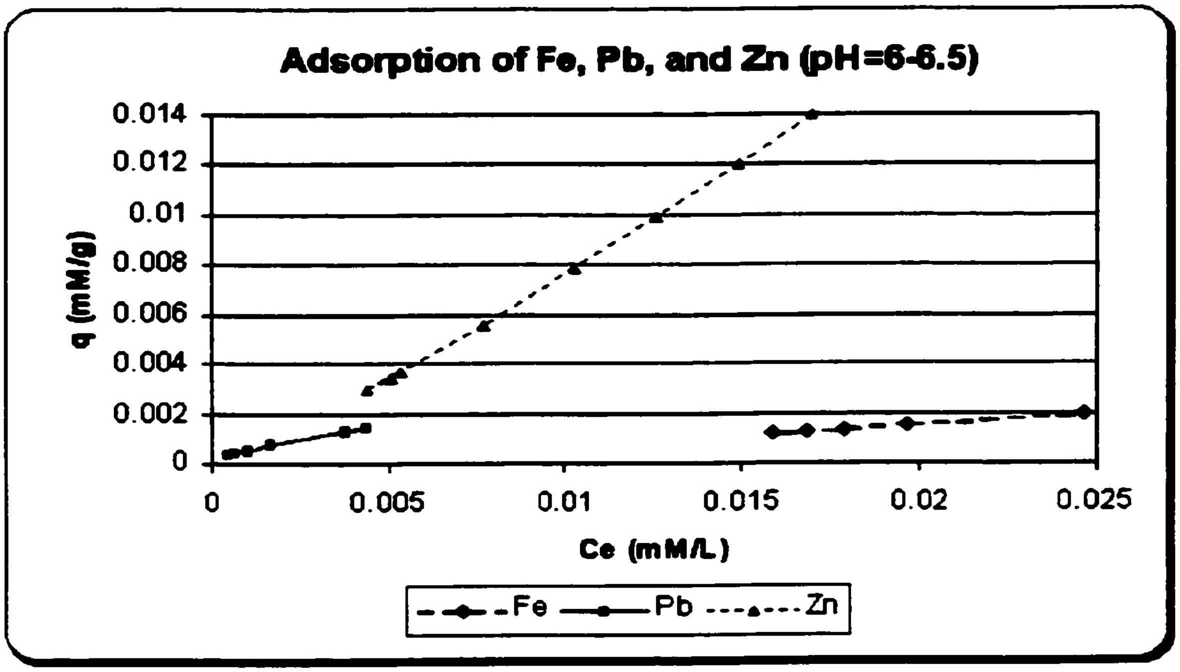


Figure 4-23: Adsorption of Fe, Pb, and Zn by peat

Table 4-31. Results of non-linear regression analysis for B, Fe, Pb, and Zn

	K	*1/n*	R^2
Boron	0.0135	1.17	0.93
Iron	0.1252	1.12	0.76
Lead	0.0589	0.69	0.98
Zinc	1.644	1.17	0.92

4.17. BORON ADSORPTION FROM TRAIL ROAD LEACHATE

As mentioned in Chapter 3, another source of leachate, collected from Trail Road landfill, was also tried as a source of leachate. Trail Road leachate contained an average boron concentration of 8.2 mg/L, which is within the range of boron concentrations measured at Huneault Waste Management (HWM) landfill. Figure 4-24 shows the experimental points for adsorption tests as well as the fitted adsorption isotherms obtained by NLPEFM for Trail Rd leachate and HWM leachate at pH of 8. The pH of the adsorption tests for Trail Rd leachate was 7.8, therefore it is compared with the HWM leachate at a pH of 8. The results are very similar showing that the adsorption of boron from both source of leachate is consistent and almost the same. In fact the statistical comparison of the results (paired t-test at α=0.05) showed that there was no significant difference between the results.

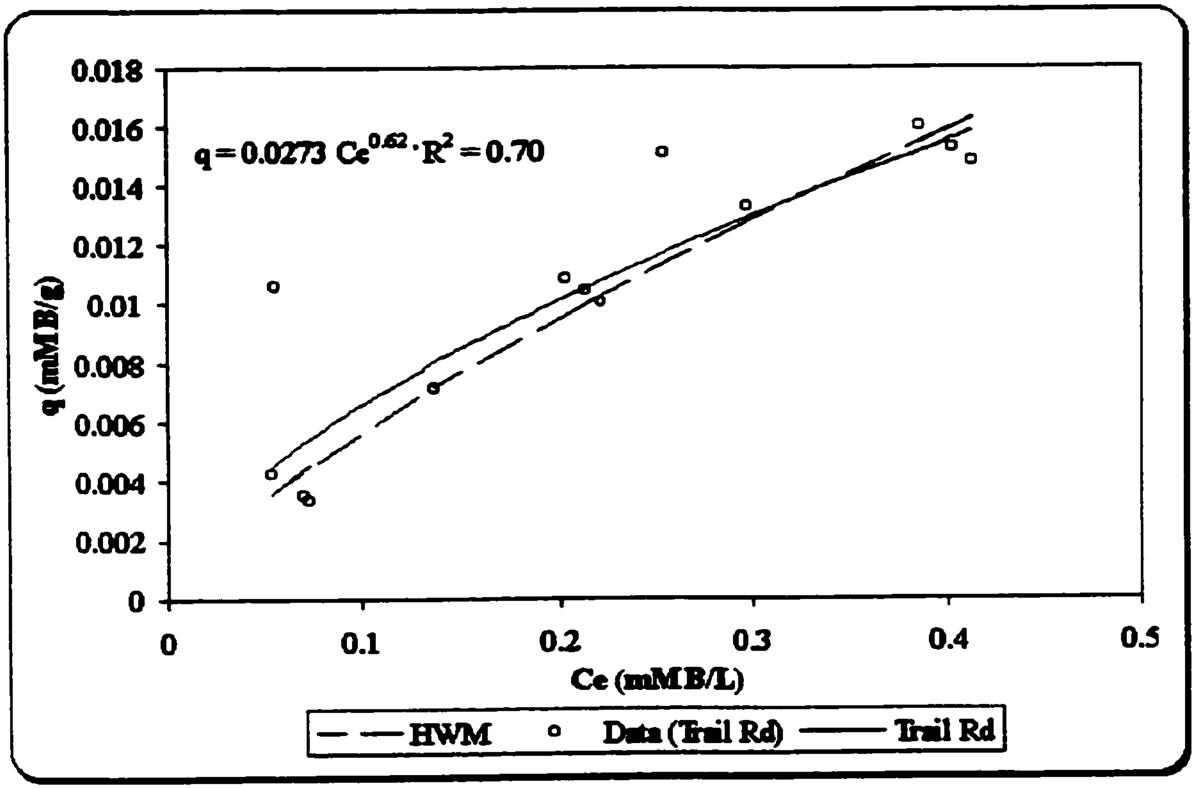


Figure 4-24: Comparison of boron adsorption from HWM and Trail Rd leachates

4.18. BORON DESORPTION

The peat samples used in the kinetic study were twice washed with distilled water and filtered immediately to remove any boron from soil solution. Then DW was added to the samples and the samples were agitated for 48 hrs. The samples were subjected to a second set of desorption test at a temperature of 90 to 100°C (hot-water extraction). The amounts of adsorbed boron in each case were calculated by doing a mass balance. Desorption of boron by DW showed significant hysteresis as only between 24% to 45% of the adsorbed boron was desorbed. As mentioned in Chapter Two, boron desorption hysteresis is related to organic carbon. Hot water extraction was effective in enhancing boron desorption as between 60% to 90% of the adsorbed boron was released when samples were subjected to both desorption steps, i.e. first with DW and then followed by hot water.

4.19. SUMMARY

This section summarizes the results of laboratory tests discussed in this chapter. Boron content of leachate was shown to be mainly in the inorganic form. Shaking, soil-to-solution ratio, and long-term adsorption did not have any significant effect on the adsorption of boron by peat. However, drying of peat, solution composition, temperature and pH significantly affected the adsorption of boron by peat. Saturation of dried peat and restoration of its full boron adsorption capacity is a slow process and takes at least two weeks. It was shown that the new non-linear regression procedure (NLPEFM) for determining the Freundlich model coefficients was superior to linear and previous non-linear procedure. Boron adsorption kinetics showed that most of adsorption occurs within 2.5 hours, and was best described by a second order reaction rate. The adsorption of boron by peat increases with increasing pH until a pH of 9 and then it drops with further increase in pH. Two-level factorial design experiments showed that pH had the strongest effect on boron adsorption followed by temperature and composition of leachate. Second order design experiments provided a quadratic equation for describing boron adsorption in terms of pH, temperature and their interactions. This equation was able to predict the behavior of boron adsorption by peat under different pH and temperature conditions. Also, collection of experimental data for the 2nd order design proved to be much easier and needed much less effort compared to determining the Freundlich adsorption isotherm parameters at the same pH and temperature levels. The adsorption capacity of peat for boron was greater than that of CompostT, CompostH, and Alfred peat but lower than that of commercial peat moss. There was a strong correlation between adsorption capacity and organic contents of these materials, which could explain these results. Amberlite-743 Anion Exchange Resin showed more than 100 times greater adsorption of boron than peat. Peat also proved to be effective in removing metals and it showed greater adsorption capacities of for Fe, Pb, and Zn than boron. Adsorption of boron from HWM leachate was consistent with that of Trail Rd landfill. Boron desorption displayed hysteresis but hot water extraction was effective in enhancing boron desorption.

NUMERICAL MODELING OF SOLUTE TRANSPORT

Chapter 5

This chapter deals with the development of numerical methods and a new computer code for transport of contaminants through subsurface. After this new computer code is validated and verified it will be used to simulate the results of laboratory column tests as well as the performance of the peat filter in the field, which are the subjects of Chapters 6 and 7.

Starting with the general equation of continuity and substituting for advection, dispersion and adsorption terms the following equation for the transport of reactive solutes in one dimension is obtained:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\frac{\partial S}{\partial t} \qquad (5\text{-}1)$$

where C is the solute concentration (mM or mg/L), D is the coefficient of hydrodynamic dispersion (m^2/ sec.), v is the average linear ground water velocity (m/sec.), θ is the effective porosity (vol./vol.), ρ_b is dry bulk density (dry mass of solids/vol.), and S is the concentration of adsorbed material in solid phase (mM or mg/g). As it was mentioned in Chapter 2, often an ideal case of linear adsorption is assumed and a parameter named Retardation factor, R, is incorporated into the equation of solute transport to address the adsorption term, as shown in the following equation:

$$\frac{\partial C}{\partial t} = \frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} \qquad (5\text{-}2)$$

$$\text{where} \qquad R = \left(1 + \frac{\rho_b}{\theta}k_d\right), \quad k_d = \frac{dS}{dC}$$

But in the case of boron adsorption S (C) in not linear and therefore dS/dC is a function of C, which makes (5-2) non-linear. The new code that is introduced later in this chapter can incorporate non-linear adsorption into the transport model.

5.1. RATIONAL

As indicated in Chapter 2 contaminant adsorption on soils could deviate from the linear relationship. Other limitations to this approach were also discussed in Chapter 2. Therefore, it was decided to develop a new computer code that could handle non-linear adsorption case and incorporate any adsorption equation such as Freundlich or the 2nd order equation developed in Chapter 4. Besides handling non-linear adsorption, the effect of pH and temperature (in the case of 2nd order equation), is incorporated in the numerical model and solved using the new computer code. Since the fluid flow in the column tests as well as in the peat filter is essentially one dimensional, the computer code is also developed for one dimension.

Two basic assumptions for development of (5-2) are: 1) the adsorption process is instantaneous; and 2) the adsorption process is reversible. The first assumption is approximately valid in the case of Boron adsorption, because, as was shown previously, the sorption process takes place over a matter of hours, whereas transport processes over a matter of several days or weeks. On the other hand, the second assumption is more problematic. As indicated in the previous chapter, boron sorption by peat is hysteretic and partly irreversible, which implies that dS/dC is actually a function of $C(x,t)$. For the purpose of modeling the column tests and the EWS, the hysteretic and irreversible behavior of boron adsorption is ignored and this is a limitation of the model. This implies that the model cannot predict the transport of boron if the peat filter or columns are to be subjected to boron free water or leachate. In order to incorporate this hysteretic behavior of boron adsorption another equation has to be developed and incorporated into the model, which can describe desorption of boron.

5.2. NUMERICAL METHODS

A finite difference approach was chosen to approximate differential equations. Indices *i* and *j* represent distance and time, respectively. A Crank-Nicolson method was used since it does not have the instability problems associated with the explicit methods. In this method, the partial differentials of C with respect to x are centered at *j-1/2* and partial differentials of C with respect to t are centered at *i*, as shown in the following equation.

$$\left(\frac{\partial C}{\partial t}\right)_{ij} = D\left(\frac{\partial^2 C}{\partial x^2}\right)_{ij-\frac{1}{2}} - v\left(\frac{\partial C}{\partial x}\right)_{ij-\frac{1}{2}} - \frac{\rho_b}{\theta}\left(\frac{\partial S}{\partial t}\right)_{ij} \tag{5-3}$$

This equation can be expanded as follows:

$$\begin{aligned}\frac{C_{ij}-C_{ij-1}}{\Delta t} = {} & \frac{D}{2}\left(\frac{C_{i-1j}-2C_{ij}+C_{i+1j}}{\Delta x^2}\right)+\frac{D}{2}\left(\frac{C_{i-1j-1}-2C_{ij-1}+C_{i+1j-1}}{\Delta x^2}\right) \\ & -\frac{v}{2}\left(\frac{C_{i+1j}-C_{i-1j}}{2\Delta x}\right)-\frac{v}{2}\left(\frac{C_{i+1j-1}-C_{i-1j-1}}{2\Delta x}\right)-\frac{\rho_b}{\theta}\left(\frac{S_{ij}-S_{ij-1}}{\Delta t}\right)+\varepsilon\end{aligned} \tag{5-4}$$

Equation (5-3) is 2nd order in distance and 1st order in time. Thus to solve this equation 3 initial and boundary conditions are required. For initial condition concentration at all points are set at zero. This implies that concentration of solute at all locations within the peat filter or columns are initially zero. As one boundary condition, concentration at x=0 is set equal to influent concentration (C_0). This implies that concentration of solute, for example boron, at the surface of peat filter or top of the columns are known and equal to concentration of influent leachate. The other boundary condition is that C remains unchanged far from the inlet. These boundary and initial conditions can mathematically be expressed as:

$$\begin{aligned} &C(x, t=0)=0; && C_{i1}=0 && \text{for } i=1,\ldots,I \\ &C(x=0, t)=C_0; && C_{1j}=C_0 && \text{for } j=2,\ldots,J \\ &C(x=\infty, t)=0; && C_{Ij}=0 && \text{for } j=2,\ldots,J \end{aligned} \tag{5-5}$$

Considering these initial and boundary conditions, all the terms in Equation 5-4 with *j-1* indices are associated with the previous time step and are known. If the known quantities along with constant parameters are grouped together and Equation 5-4 is rearranged so that concentration at each node is expresses in terms of the concentrations at adjacent node, the following equation will be obtained:

$$aC_{ij} = bC_{i-1j} + dC_{i+1j} + \alpha_{ij} \tag{5-6}$$

Where coefficients *a*, *b*, *d*, and α_{ij} are defined as:

$$\begin{aligned} a &= 1+\frac{D\Delta t}{\Delta x^2} \\ b &= \frac{D\Delta t}{2\Delta x^2}+\frac{v\Delta t}{4\Delta x} \\ d &= \frac{D\Delta t}{2\Delta x^2}-\frac{v\Delta t}{4\Delta x} \end{aligned} \tag{5-7}$$

$$\alpha_{ij} = (2-a)C_{ij-1} + bC_{i-1j-1} + dC_{i+1j-1} - \frac{\rho_b}{\theta}(S_{ij} - S_{ij-1})$$

For even time and space discretization intervals *a*, *b*, and *d* are constant and independent of *i* and *j*. For now the adsorption term, the last term in the equation for α, is ignored and only advection and dispersion processes (A-D) are considered. Once the procedure and numerical methods for A-D are developed, the adsorption process will added and incorporated in to the model. If Equation 5-6 is written for each node (i), a group of equations will be obtained. To solve these equations an approach similar to the one suggested for modeling of heat transfer by Patankar (1980) was used. If Equation 5-6 is written for *i*=2, it will have the following form:

$$aC_{2j} = bC_{1j} + dC_{3j} + \alpha_{2j} \tag{5-8}$$

However C_{1j} is known since it is a boundary condition. Therefore, it is possible to reduce this to a relation between C_{2j} and C_{3j}. If Equation 5-6 is written for *i*=3, it will be a relation between C_{2j}, C_{3j}, and C_{4j}. C_{2j} however can be expressed in terms of C_{3j} as explained in the previous step. Therefore, a relationship between C_{3j} and C_{4j} will be obtained. Thus one can define a general forward-substitution relationship for each point such as:

$$C_{ij} = P_i C_{i+1j} + Q_i \tag{5-9}$$

If Equation 5-9 is written for *i-1*, Equation 5-10 will be obtained.

$$C_{i-1j} = P_{i-1} C_{ij} + Q_{i-1} \tag{5-10}$$

Now substituting Equation 5-9 in Equation 5-10 and rearranging the resulting equation to look like Equation 5-9, the coefficients P_i and Q_i will be obtained as:

$$P_i = \frac{d}{a-bP_{i-1}}, \quad and \quad Q_i = \frac{\alpha_{ij} + bQ_{i-1}}{a-bP_{i-1}} \tag{5-11}$$

If Equation 5-8 is rearranged to look like Equation 5-9, P_2 and Q_2 will be obtained as:

$$P_2 = \frac{d}{a}, \quad and \quad Q_2 = \frac{\alpha_{2j} + bC_{1j}}{a} \qquad \textbf{(5-12)}$$

The values of P_2 and Q_2 are known. Therefore, Equation 5-11 can be used to calculate the values of all subsequent P_i and Q_i. At the other end, for point I-1, the Equation 5-9 will look like:

$$C_{I-1j} = P_{I-1}C_{Ij} + Q_{I-1} \qquad \textbf{(5-13)}$$

C_I is set equal to zero as a boundary condition. Thus, C_{I-1j} is equal to Q_{I-1}. Therefore, one can set C_{I-1j} equal to Q_{I-1} and use Equation 5-9 to back calculate the values of concentrations at all points.

A new computer code called SOLTRAN (in FORTRAN) was developed which carries out the above procedure and calculates the concentration of solute at all points over time. The flowchart presented in Figure 5-1 shows the structure of this program. SOLTRAN was developed in such a way that it gives the user the option of creating and saving new input file or reading previously created input file. Also, it provides the option of defining constant or variable influent concentrations. The values of I, J, dx, dt, D, v, ρ_b, and 2 are the input parameters that have to be specified by the user when prompted.

Using the procedure described above, for each time step SOLTRAN calculates the concentrations of solutes at all nodes considering advection and dispersion (A-D) only. For reactive solutes, at the end of each time step SOLTRAN adjusts solute concentration at each node to satisfy a mass balance between the liquid and solid phase, i.e. the change in solute mass in liquid phase has to be equal to the change in solute mass in the solid phase. The above approach decouples the A-D from the reaction term. The latter normally tends to slow the advective and dispersive processes and the net result is that some solute mass advances by A-D before being retarded by adsorption. This produces an error and causes the solute profile to be slightly ahead of where it should be. However, for small time step the error is insignificant and the above method offers great potential because it is much, much simpler than trying to solve a non-linear partial differential equation.

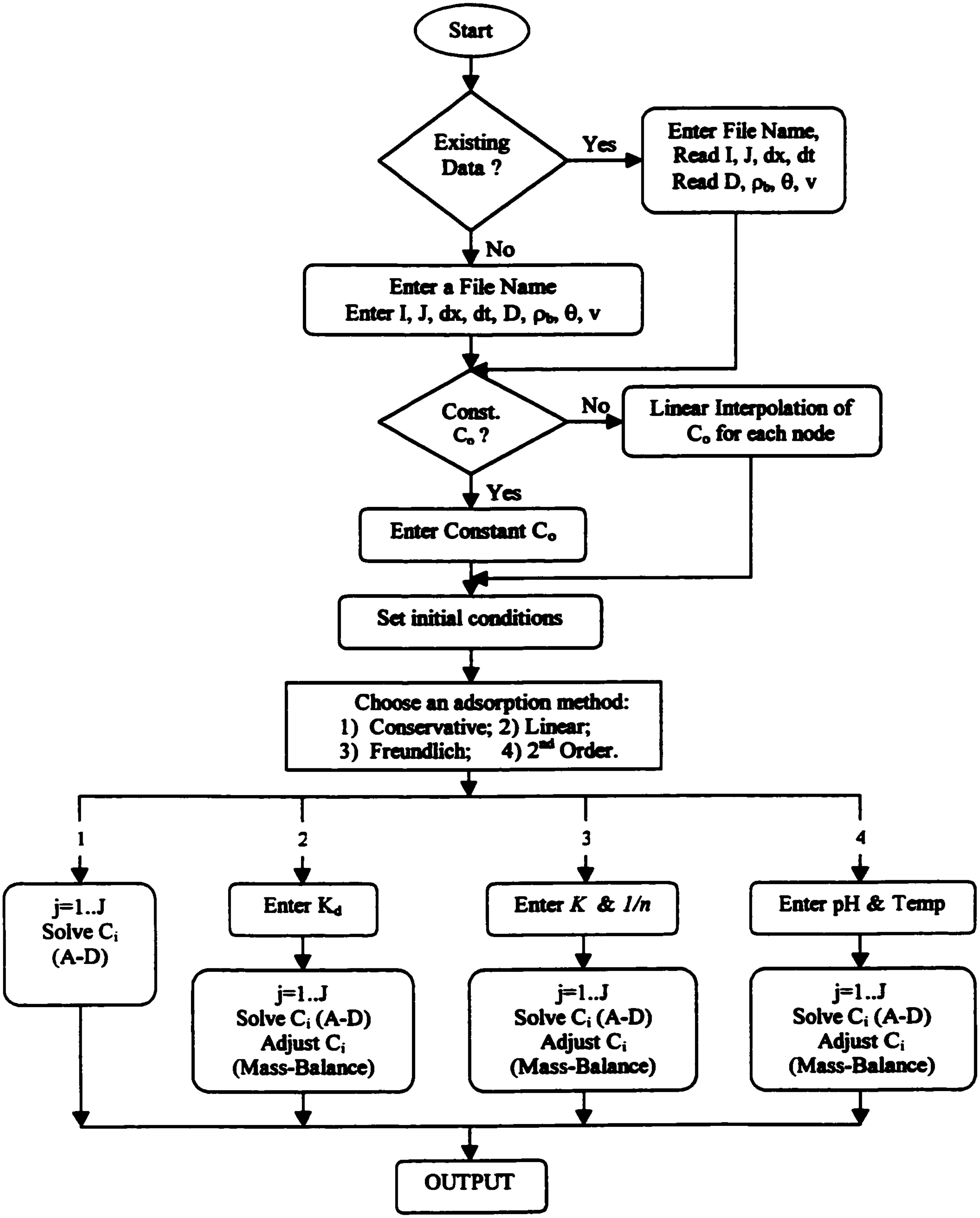


Figure 5-1: Flowchart of SOLTRAN computer code

If the concentration calculated by considering only A-D is shown by C_{adv}, the solute mass balance between the liquid and solid phase for the unit volume can be expressed as:

$$(C_{adv} - C_{ij})\,\theta = \rho_b\,(S_{ij} - S_{ij-1}) \qquad \textbf{(5-14)}$$

Equation 5-14 is solved for C_{ij} to obtain the adjusted concentration at each node. As far as adsorption is concerned SOLTRAN can handle zero adsorption (conservative or non-reacting solute), linear adsorption, non-linear Freundlich, and any general adsorption equation such as the 2nd order equation developed in Chapter 4. For linear adsorption the k_d value has to be entered when prompted. For Equation 5-14 the term S_{ij} is replaced by k_dC_{ij}. If the Freundlich isotherm is chosen, the program will ask for the Freundlich isotherm parameters, *K* and *1/n*. If the term S_{ij} in Equation 5-14 is replaced by Freundlich equation, the resulting equation will be non-linear and has to be solved numerically for C_{ij}. In the case of the general adsorption equation, pH and temperature have to be entered as input as well. SOLTRAN is capable of handling variable pH and temperature profiles. The mass balance equation is handled similar to the Freundlich case, except that the 2nd order equation is used instead of Freundlich equation.

The model, in this form, presumes that pH or temperature is not affected by the sorption process. If a pH front develops as a result of the boron sorption front, then pH should technically be adjusted and the appropriate chemical species would need to be modeled using a separate A-D, which might include other processes.

5.3. CODE VERIFICATION

Code verification refers to the comparison of the numerical solution obtained by the model with one or more analytical solutions or other numerical solutions. This step ensures that the computer program, SOLTRAN in this case, accurately solves the equations that constitute the mathematical model. The SOLTRAN code was checked against the analytical solution developed by Ogata-Bank (Fetter, 1994), which is given by:

$$C = \frac{C_0}{2}\left[erfc\left(\frac{x - vt}{2\sqrt{Dt}}\right) + \exp\left(\frac{vx}{D}\right) erfc\left(\frac{x + vt}{2\sqrt{Dt}}\right)\right] \qquad \textbf{(5-15)}$$

where C is the solute concentration at some distance x, C_0 is the initial solute concentration at x=0, v is the average linear ground water velocity, t is the time, and D is the longitudinal dispersion coefficient. The Ogata-Bank analytical solution is based on the following boundary and initial conditions:

$$\begin{aligned} &C(x, t = 0) = 0 \\ &C(x = 0, t) = C_0 \\ &C(x = \infty, t) = 0 \end{aligned} \qquad \textbf{(5-16)}$$

If solute undergoes mixing at $x=0^+$, just inside the inlet of the column, then a type III boundary condition would be more appropriate. However, in the error induced due to assuming a type I boundary condition in 1-D is very small. The third condition in Equation 5-16 assumes a semi-infinite domain. This is different from the assumption made in the procedure used in SOLTRAN where domain is not semi-infinite. For this reason, one must select a column length such that the contaminant front does not reach the downgradient boundary. If the contaminant does reach the downgradient boundary, the boundary condition impacts the solution and the numerical solution no longer follows the Ogata-Banks analytical solution.

Results of simulation of concentration profiles for a column with influent concentration of 1 mM/L for a conservative element such as chloride and $D = 5\text{x}10^{-5}$ cm^2/sec, $v = 5\text{x}10^{-5}$ cm/sec, and t= 30,000 sec generated by SOLTRAN as well as Ogata-Bank analytical solution are presented in Figure 5-2. Also, Break Through Curves (BTC) for the same conditions at x=2 cm are presented in Figure 5-3. The values for D and v were chosen based on the values obtained in the laboratory column tests, which are presented in a later section in this chapter. Both figures show that SOLTRAN program accurately solves the governing equations and produces results that are very close to those obtained by Ogata-Bank analytical solution.

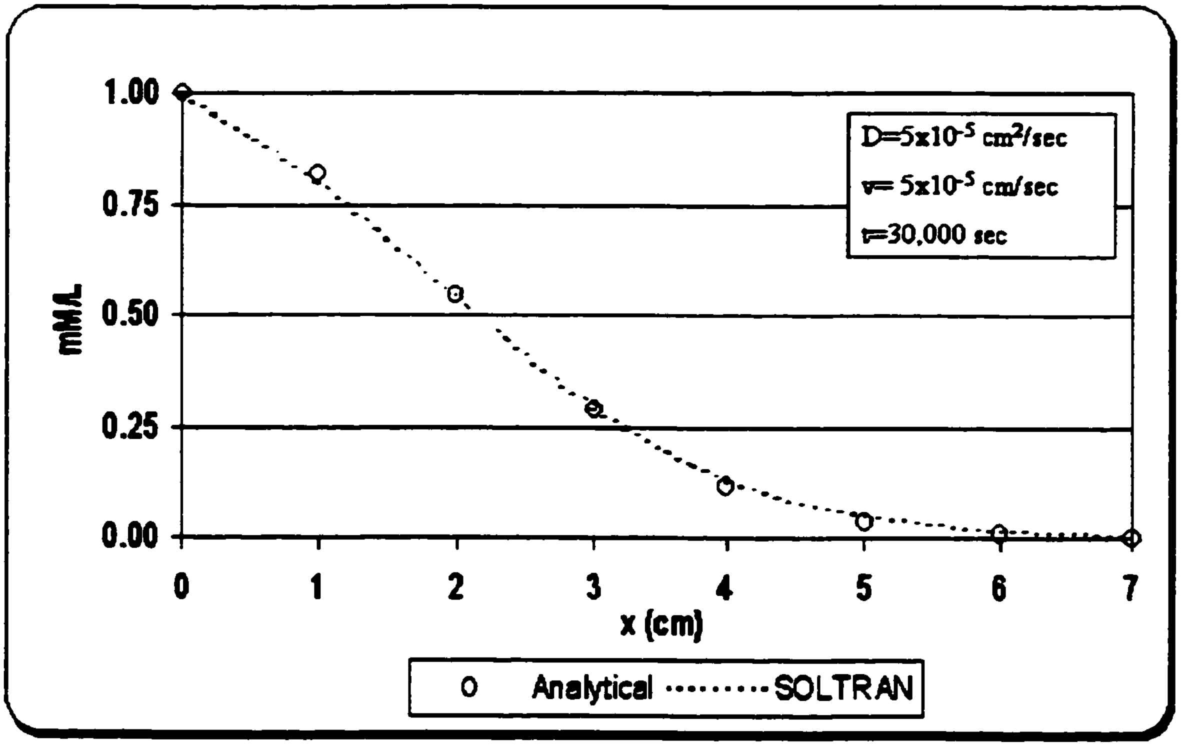


Figure 5-2: Comparison of concentration profiles obtained by SOLTRAN and Analvtical solutions for a conservative

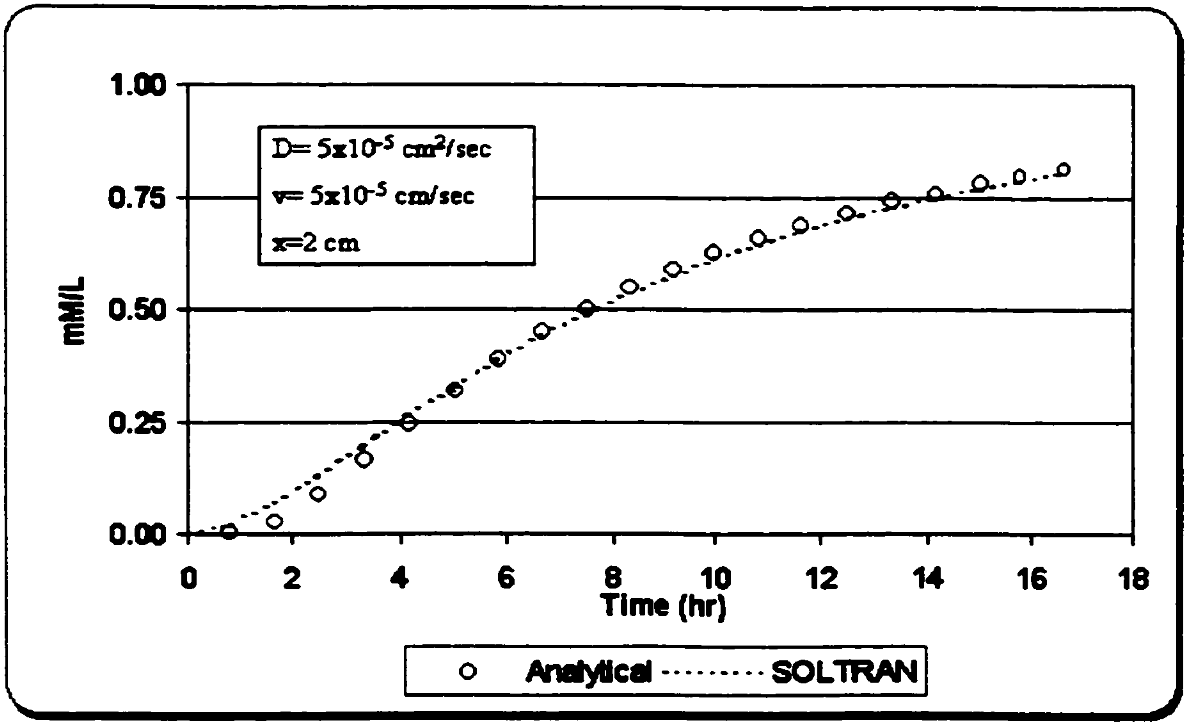


Figure 5-3: BTCs obtained by SOLTRAN and analytical solutions

Zheng and Bennett (1995) recommended a number of statistical measures for goodness of fit including the correlation factor, the mean of residual errors (MRE), and the mean of absolute residual error (MARE). The correlation factors between the results obtained by SOLTRAN and analytical solution for concentration profiles and BTCs presented in Figures 5-2 and 5-3 were 0.9997 and 0.9991, respectively. The MARE for concentration profiles and BTCs were 1.1x10^{-2} mM/L and 1.5x10^{-2} mM/L, respectively, which are very small compared to influent concentration of 1 mM/L.

To verify SOLTRAN for the case of reactive (adsorbing) contaminants, the same conditions as above, i.e. C_o =1 mM/L of a reactive element, D = 5x10^{-5} cm^2/sec, v= 5x10^{-5} cm/sec and t= 60,000 sec were used. A linear adsorption case, with K_d= 0.015 L/g, was assumed. In addition, ρ_b (dry bulk density) and θ were set equal to 0.1 g/cm^3 and 0.8. The values assumed for K_d, ρ_b, and θ are within the range observed in the laboratory column tests. If the values of K_d, ρ_b, and θ are substituted in Equation 5-2 for retardation factor, a value of R=2.9 is obtained. To use Ogata-Bank equation for this case the values of D and v should be divided by retardation factor to get the analytical solution for the reactive solute. Figure 5-4 shows the concentration profiles generated by SOLTRAN along with analytical solution. Results obtained by analytical solution are in good agreement with the concentration profile produced by SOLTRAN. The correlation factor between the results obtained by SOLTRAN and analytical solution was 0.9995, which is very close to 1. Also, the MARE was 1 x10^{-2} mM/L, which is very small compared to influent concentration of 1 mM/L. This shows that SOLTRAN accurately predicts the concentration profiles of reactive solutes in the case of linear adsorption. It also indicates that the error associated with decoupling of the A-D from adsorption is small. The concentration profile of a non-reactive solute is presented in Figure 5-4 as well, which indicates the retarding effect of adsorption for reactive solutes.

As in the case of non-reactive solute, the BTCs, presented in Figure 5-5, obtained by SOLTRAN and analytical solution are also in good agreement with each other; correlation factor and MARE were 0.9998 and 5.7 x10^{-3} mM/L, respectively.

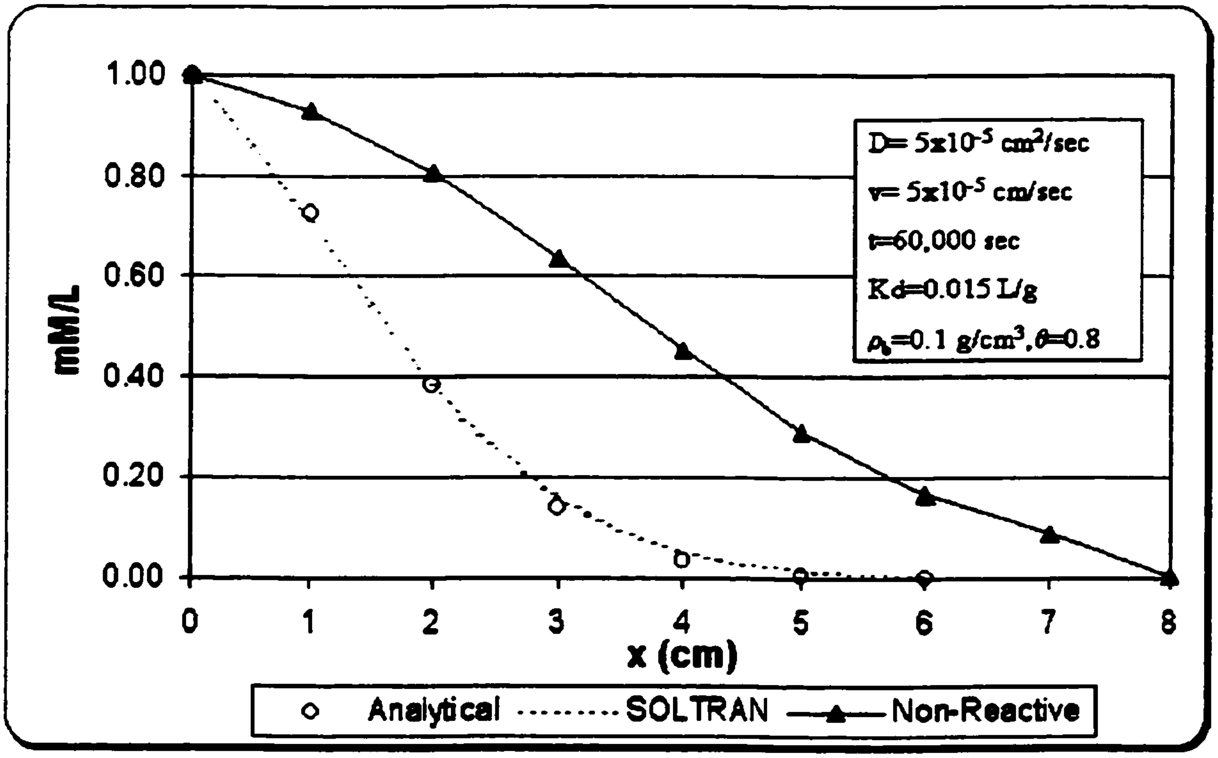


Figure 5-4: Comparison of concentration profiles obtained by SOLTRAN and analytical solutions for a reactive (linear) element

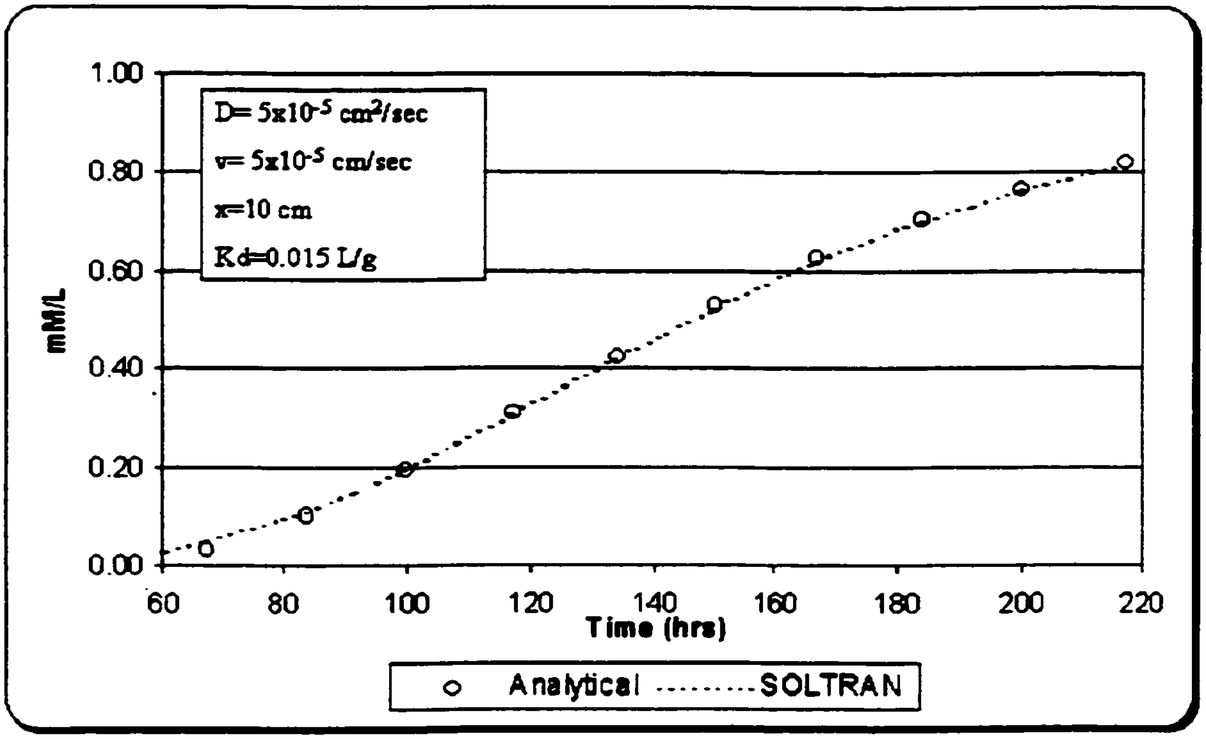


Figure 5-5: Comparison of BTCs obtained by SOLTRAN and analytical solution for Linear adsorption isotherms

To verify that SOLTRAN produces accurate results for the case of Freundlich adsorption model, the results obtained by SOLTRAN for a Freundlich adsorption isotherm with $1/n$=1 and K equal to K_d of the previous simulation for linear adsorption were compared, and these are presented in Figure 5-6. The results for a Freundlich isotherm with $1/n$=1 are the same as the results obtained for linear adsorption with a K_d value equal to the value of K parameter of Freundlich adsorption equation. Thus SOLTRAN accurately produces the results for Freundlich adsorption case. The procedure for the 2nd order design is similar to the Freundlich except that the 2nd order design equation developed in Chapter 4 is used instead of the Freundlich equation and the input parameters are pH and temperature instead of K and $1/n$ and all other required parameters (D, v, ρ_b, θ) are the same as the previous case.

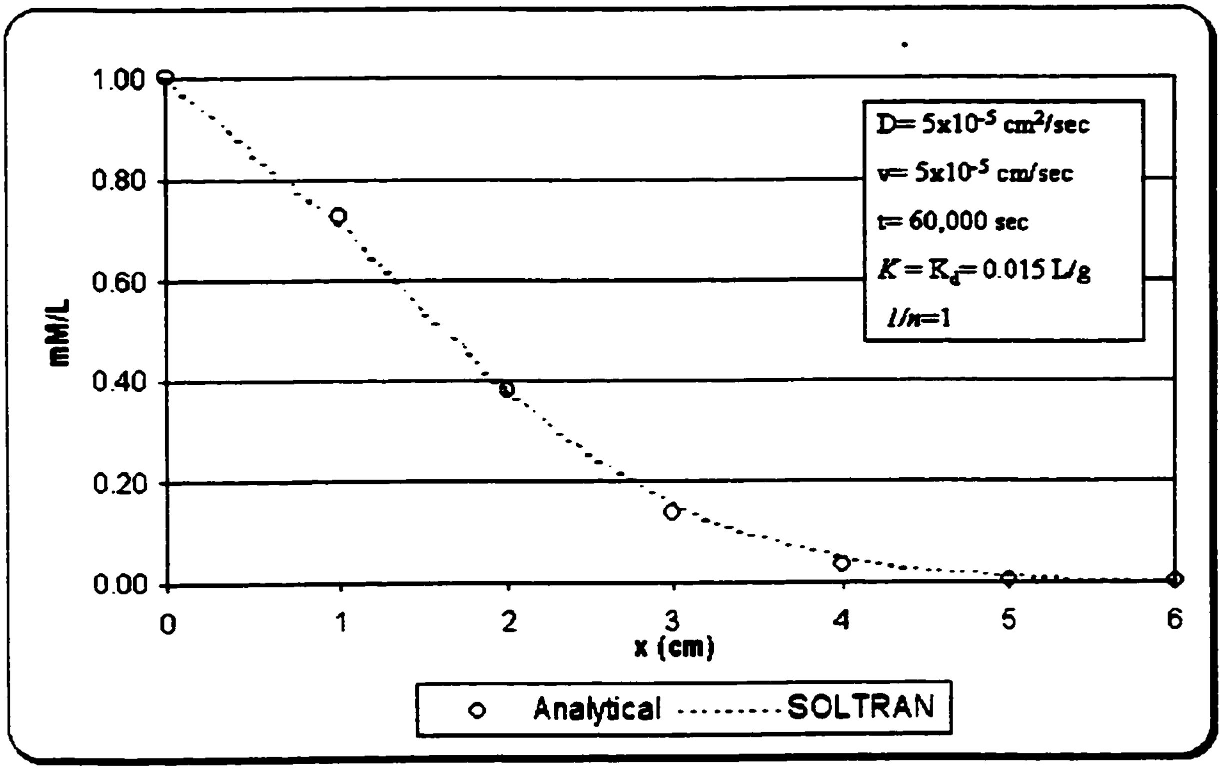


Figure 5-6: Concentration profiles generated by SOLTRAN for Linear and Freundlich adsorption isotherms

5.4. DISCRETIZATION OF DOMAIN

Selection of the time step (dt) and grid size (dx) is an important step in the design of any numerical model for transport of contaminants. Approximation of differential equations produces numerical errors. The numerical errors produce artificial dispersion, also known as numerical dispersion. Ideally, it is desirable to choose small time steps and nodal spacing so that the numerical simulation better approximates the partial differential equations. However, this could result in very large number of time steps and spatial elements, thus increasing computational effort. To minimize errors due to numerical dispersion, the grid size and time steps should be designed so that Peclet number (P_e=v.dx/D) and Courant number (C= v.dt/dx) are equal or less than one. If the values for the parameters dx=1 cm, v= $5\text{x}10^{-5}$ cm/sec, and D=$5\text{x}10^{-5}$ cm^2/sec are substituted in the equation for Pe, one will obtain a Peclet number equal to 1 which satisfies the requirement presented above. Also, if a Courant number equal to one is assumed, then dt=20,000 sec is obtained. However, Anderson and Woessner (1992) suggested making several trial runs of model with different dt values. Then the largest possible dt value that does not significantly change the solution can be used in the production runs.

Figure 5-7 shows the concentration profiles of a conservative solute for dt=1, 60, 600, 6000, and 10,000 seconds. The results obtained by SOLTRAN for a dt value of up to 600 sec are very close and similar. It is only at dt=6000 sec that some deviation is observed. Nevertheless, for all production runs a dt less than 600 sec was used.

5.5. NON-LINEAR ADSORPTION

As mentioned before it is common to use a linear adsorption and incorporate a retardation factor into the model. However, adsorption of contaminants may deviate from this ideal linear adsorption. Approximation of non-linear adsorption with linear adsorption creates some inaccuracy in the results. To illustrate this, a Freundlich isotherm with K=0.0165 and $1/n$=0.6 was assumed. These values were chosen based on the range obtained through laboratory tests of boron adsorption. Then, some data points were generated using the above values for K and $1/n$. A linear adsorption equation was then fitted to the generated points and

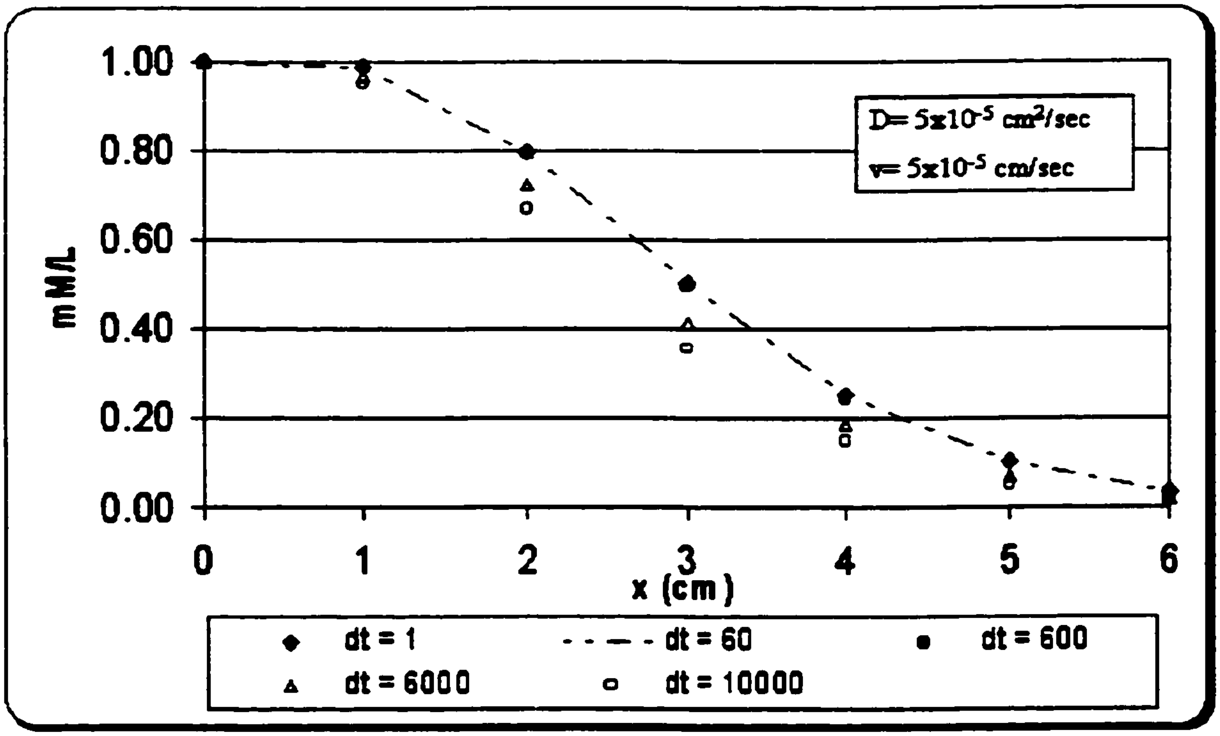


Figure 5-7: The effect of time step on modeling results

the value of K_d, which is the slope of this line, was obtained. Figure 5-8 illustrates data points along with linear and Freundlich adsorption isotherms. Data is not perfectly linear but the relationship is very close to a linear one as the correlation factor was 0.88. K_d was estimated to be 0.0185 L/g.

SOLTRAN was used to simulate the transport of a reactive solute for both linear and Freundlich adsorption isotherms. The BTCs for both cases are presented in Figure 5-9. Although data points of adsorption isotherm follow a nearly linear trend, the BTCs are not the same and show significant differences. Just as an example to show the effect of linear approximation of data, the time of breakthrough at a concentration of 0.8 mM/L was calculated for both Freundlich isotherm and its linear approximation. The time of breakthrough for Freundlich case is 208 hrs, which compares with 245 hrs for linear isotherm case. This implies that the time of breakthrough at this concentration is overestimated by 18%.

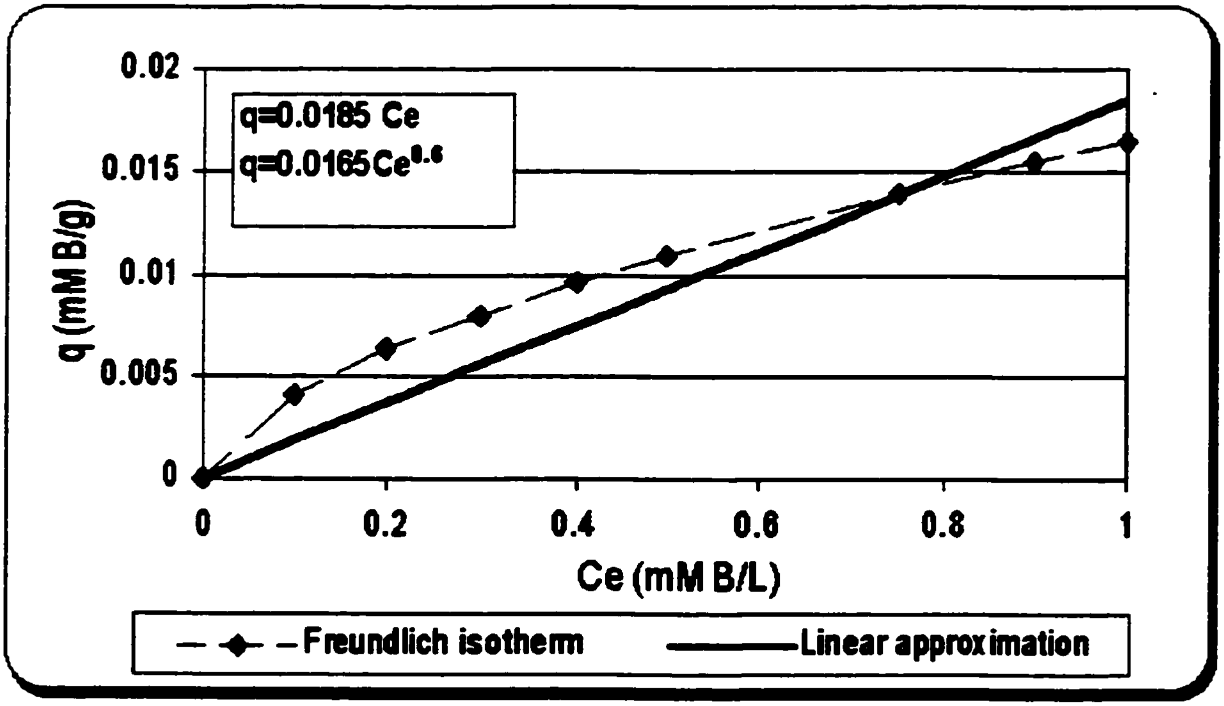


Figure 5-8: Linear approximation of a data set obtained by a Freundlich

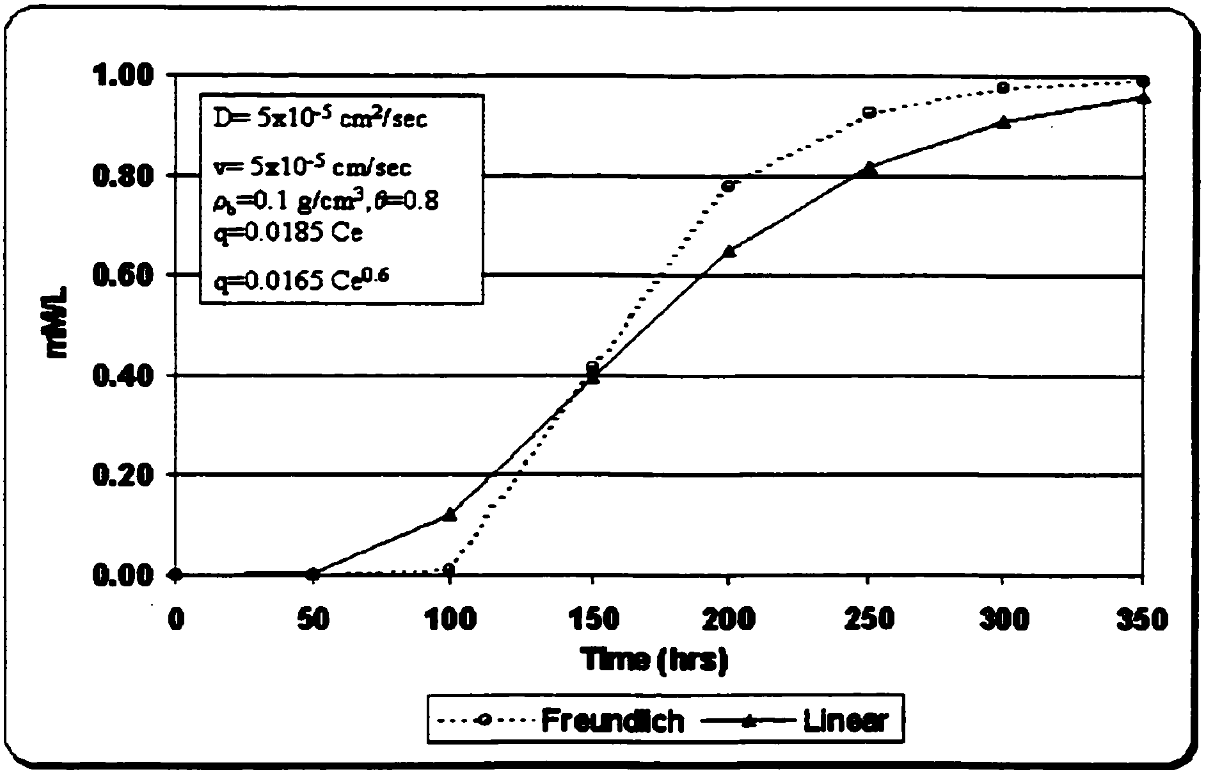


Figure 5-9: Comparison of BTCs obtained by SOLTRAN for Linear and Freundlich isotherm data of Figure 5-8

Deviation between the non-linear and simplified linear curves and the associated error would increase with distance, which could be misinterpreted if linear adsorption is used. The magnitude of error will depend on how well the linear isotherm can describe the actual isotherm.

As another example, the 2nd order adsorption isotherm obtained for adsorption of boron by peat and presented in Chapter 4, at a pH of 9 and a temperature of 22 °C, was approximated with a linear adsorption isotherm (straight line), see Figure 5-10. As it can be seen from this figure data points follow a nearly linear trend with a correlation factor of 0.90. K_d, the slope of the straight line, was calculated as 0.0592 L/g.

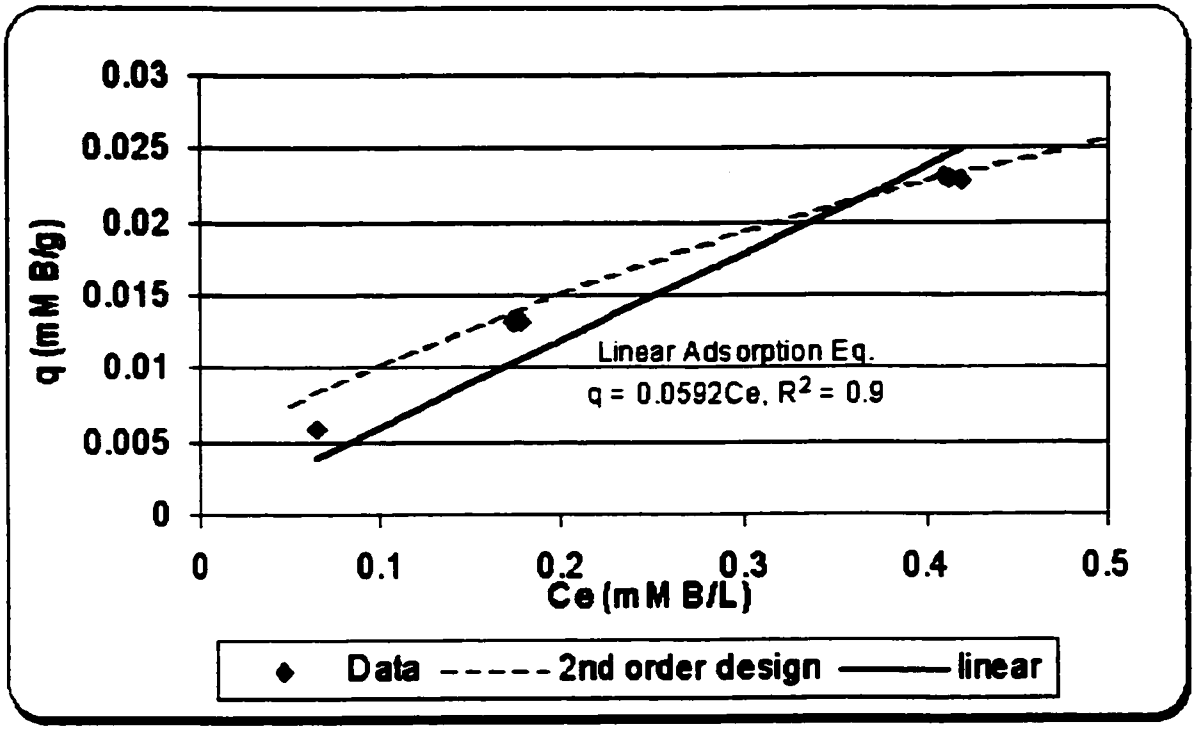


Figure 5-10: Linear approximation of a data set obtained by a 2nd order isotherm equation

The concentration profiles obtained by SOLTRAN are presented in Figure 5-11. As in the case of linear approximation of Freundlich isotherm, although data points of adsorption isotherm follow a nearly linear trend (correlation factor of 0.9), results of 2nd order case show deviation from the linear case, which overestimates the results. The above findings show that small deviations from linear adsorption assumption could result in inaccurate simulation of contaminant transport through the subsurface, which could be misleading, misinterpreted, and result in a poor design. Therefore, it is very important to make sure that when K_d values and retardation factors are used the linear adsorption assumption is satisfied.

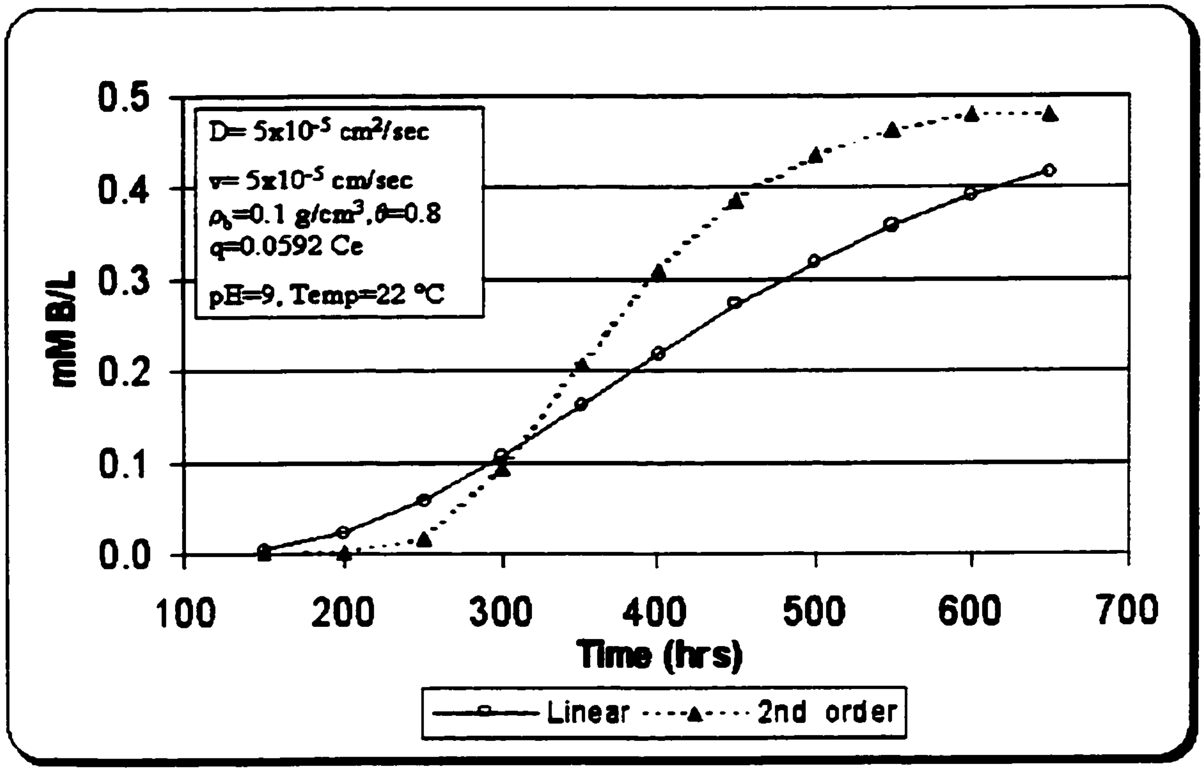


Figure 5-11: BTCs generated by SOLTRAN for Linear and 2nd order adsorption isotherms

5.6. EFFECT OF pH AND TEMPERATURE

One of the features of SOLTRAN is the ability of incorporating the effect of pH and temperature into the model. For this study the 2nd order factorial design equation for adsorption of boron by peat and presented in Chapter 4 was incorporated into the computer code. When dealing with another set of environmental conditions, i.e. different contaminants and/or adsorbing media, a new equation has to be developed based on laboratory experiments to replace the one in the computer code. When using SOLTRAN, the user can specify constant or variable pH and temperature through the domain. This is an important advantage that SOLTRAN has to offer since contrary to the controlled laboratory conditions, environmental conditions could significantly change from point to point in the field. For example, when dealing with vertical movement of contaminant through depth, temperature changes with distance.

To illustrate the effect of pH and temperature on adsorption of boron, two cases were considered. In one case pH and temperature were 7.5 and 22 °C, respectively, while in the second case pH and temperature were 9 and 15 °C, respectively. BTCs for these two cases, shown in Figure 5-12, indicate that the changes in pH and temperature have a strong effect on

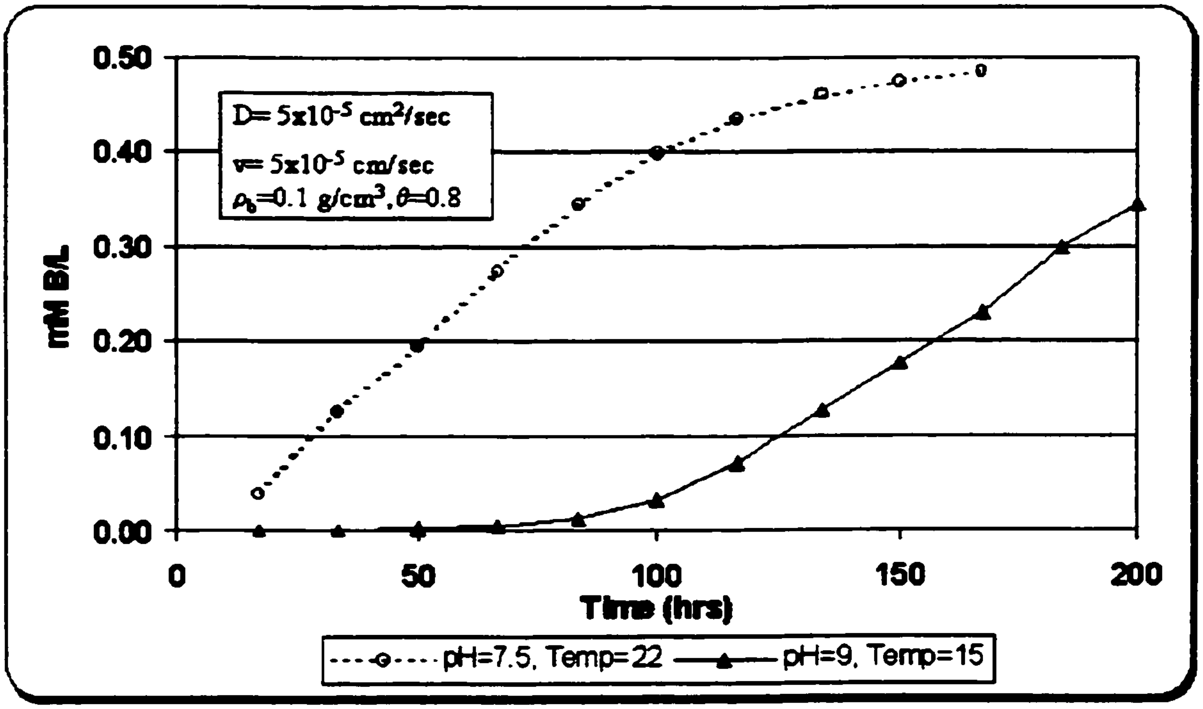


Figure 5-12: The effect of pH and temperature on BTC

transport of boron. It takes about 2.5 times longer for boron to break through under pH=9 and temperature of 15 °C than a pH=7.5 and a temperature of 22 °C. If the laboratory conditions are different from field conditions, or parameters such as pH and temperature vary over time and/or distance, the results obtained by the linear approach (K_d) or other methods that do not consider these changes will not be accurate and could be misleading.

5.7. SUMMARY

The numerical methods for developing a computer code, SOLTRAN, were presented. SOLTRAN uses a finite difference (Crank-Nicolson) method to solve partial differential equations. The adsorption process is incorporated by doing a mass balance at the end of each time step. SOLTRAN handles non-reactive, linear, Freundlich, and 2^{nd} order design isotherms. The code was verified and checked against Ogata-Bank analytical solution. It was demonstrated that neglecting the non-linear characteristics of adsorption by using linear approximation of adsorption isotherm and/or the effect of pH and temperature could produce inaccurate modeling results.

RESULTS OF COLUMN STUDIES

Chapter 6

As indicated in Chapter 3, three sets of peat column tests, Small columns, Medium columns, and Long columns, were carried out. The experimental results for metals, boron, BOD, and COD removals obtained from the column tests are presented and discussed in this chapter. The results of batch adsorption tests presented in Chapter 4 were incorporated in the SOLTRAN model which was developed in Chapter 5 to simulate the transport of boron through peat columns. The simulation results are presented in this chapter as well. Once the simulation results are calibrated and verified with the laboratory column tests, the model can be used to predict the performance of the system in the field.

6.1. SMALL COLUMN TESTS

Five Small columns, 10.2 cm in diameter, 11 cm in height, and packed with dried peat, were prepared according to the procedures explained in Chapter 3. Leachate was applied to all columns except one; the control was permeated with DW. Hydraulic conductivity of the columns were in the order 10^{-3} cm/sec at the beginning and decreased by one order of magnitude (10^{-4} cm/sec) by the end of experiments. Entrapping of solids and/or further settlement of peat over time could be reasons for this decrease observed in hydraulic conductivity. The density of peat within the columns was in the range of 1.06 to 1.09 g/cm^3. The values of hydraulic conductivity and density obtained in the laboratory were in the same range as hydraulic conductivity (10^{-3} to 10^{-4} cm/sec) and density (1 to 1.12 g/cm^3) measured in the field. The dry bulk density of peat in the column was about 0.1 g/cm^3. As mentioned in Chapter 2, a range of 0.12 to 0.15 g/cm^3 is suggested as the maximum dry bulk density for running peat column; above these values columns can get clogged (Rana and Viraraghavan, 1987; McLellan and Rock, 1988).

Prior to permeating the columns they were saturated with DW for approximately 2 days. Leachate was spiked with Fe, Pb, and Zn. In order to dissolve these elements, the pH of the leachate was lowered to 6.0. Influent leachate on average contained 8.5, 4, 3.5, and 14 mg/L of B, Fe, Pb, and Zn, respectively. Based on the Break Through Curve (BTC) of the electrical conductivity of the effluent, one Pore Volume (PV) was estimated at 800 mL. Pore volume (PV) is defined as the total volume available for fluid flow in the column. After the influent to the columns was switched to leachate the electrical conductivity of the effluent was monitored. After passage of 800 mL, electrical conductivity broke through, i.e. reached 50% of influent conductivity. The effective porosity of the peat columns was calculated as 89% (volume of each Small column was 900 mL). The effective porosity is that portion of total porosity that is available to fluid flow. The value of effective porosity obtained in this study is close to the values reported by Mitch and Gosselink (1993). They reported that peat soils generally have at least 80% pore space. Small columns were taken out of service after the passage of different number of pore volumes (3.1, 4.6, 6.4, and 14 PVs).

As an example, the BTCs for the Small column after 14 PVs are presented in Figure 6-1. As it can be seen, peat was very effective in removing Fe, Pb, and Zn. The effluent concentrations of Fe, Pb, and Zn were on average 0.47 mg/L, 0.12 mg/L, and 0.43 mg/L, respectively, which represent removal efficiencies of 88% for Fe, 97% for Pb, and 97% for Zn. In the case of boron, it appeared almost immediately in the treated effluent from the Small columns with an average concentration of 5.8 mg/L. There are two reasons for early break through of boron. First, pH was lowered to spike the solution for Fe, Pb, and Zn. It was shown in Chapter 4 that boron adsorption is pH dependant and lowering pH significantly reduces boron adsorption capacity of peat. The second reason is that peat was oven dried during preparation of Small columns since this set of tests was carried out before it was found that drying could affect boron adsorption capacity of peat. This also reduced adsorption of boron by peat. Combination of the above factors resulted in low adsorption and retardation of boron and consequently an early boron break through. After each column was taken out of service, the peat was taken out of columns, sliced into 4 pieces, and pore water extracted from each slice was analysed for boron and metals. The concentration profiles of B, Fe, Pb, and Zn through the depth are presented in Figure 6-2.

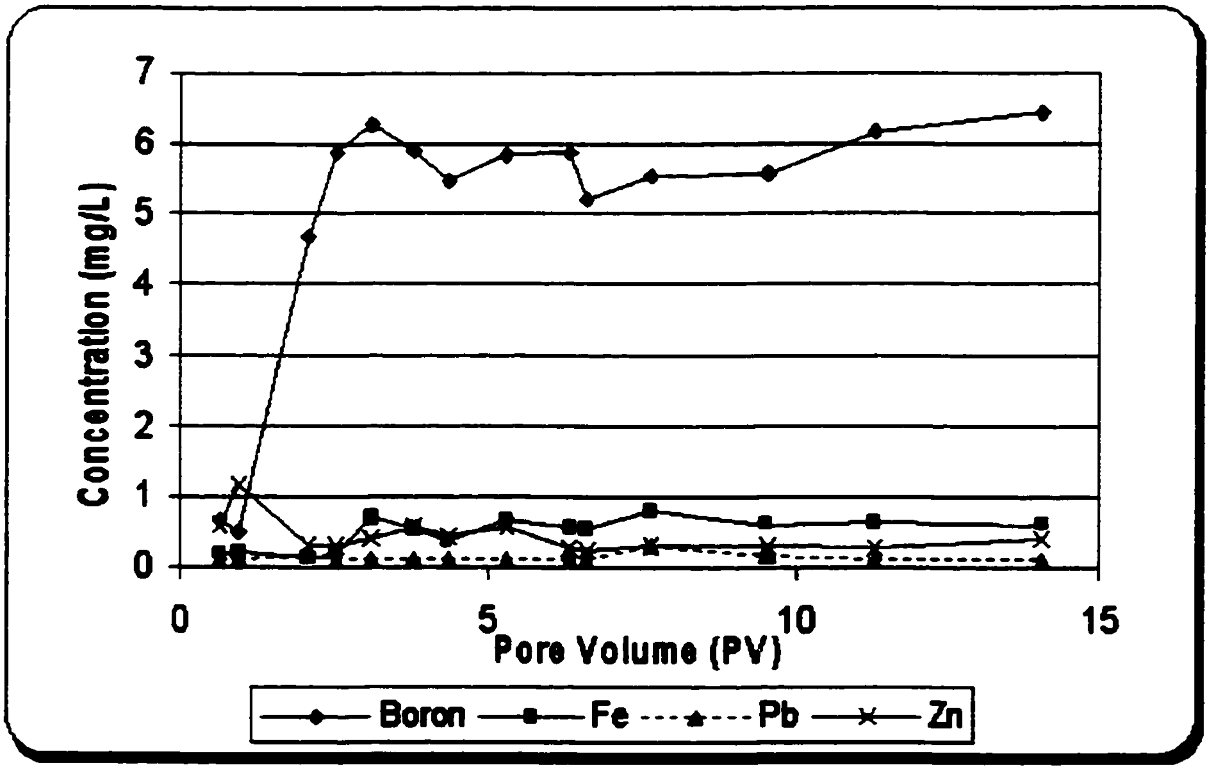


Figure 6-1: BTC for small column after passage of 14 pore volumes

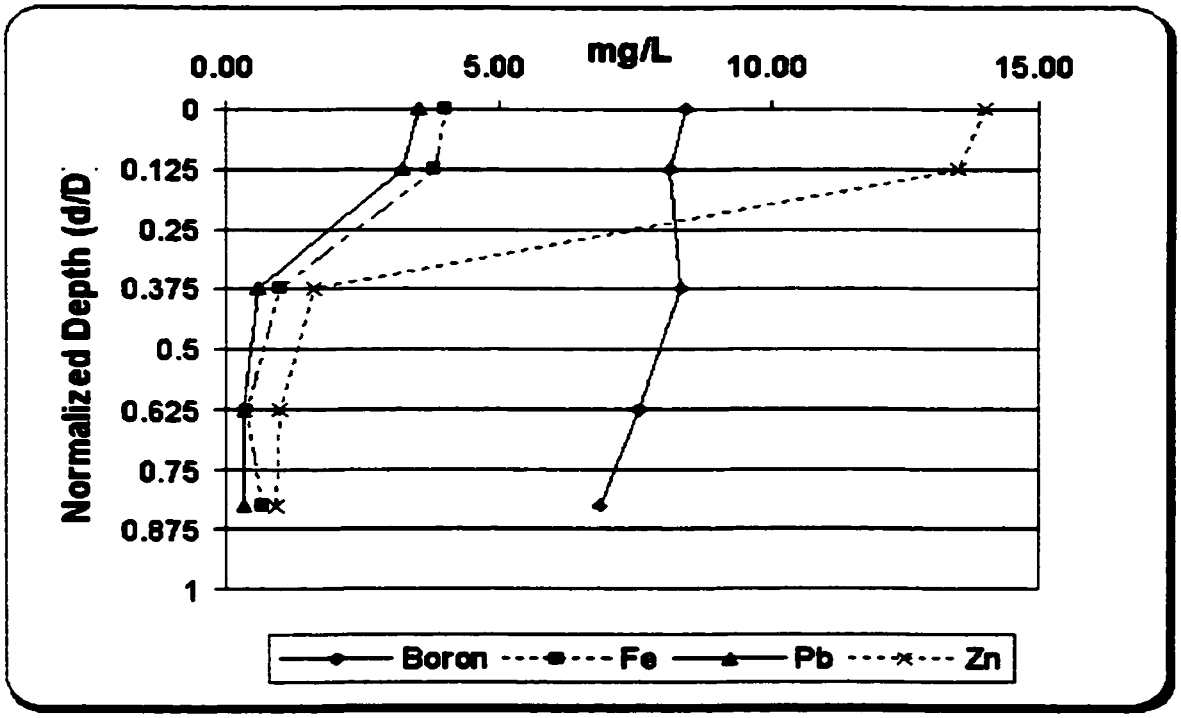


Figure 6-2: Concentration profiles for small column after passage of 14 PVs

Peat columns were very effective in removing metals as Fe, Pb, and Zn were only detected at high concentrations (3.8 mg/L, 3.2 mg/L, and 13.5 mg/L, respectively) within the first 25% length of the Small column. Boron was detected at concentrations between 8.4 mg/L at the top and 6.8 mg/L at the bottom of the small column.

The above findings confirm the results of batch adsorption tests showing that adsorption capacity of peat for metals is significantly higher than that for boron. Based on concentrations profiles through the Small column, it can be concluded that the retardation factor for Fe, Pb, and Zn is at least 56 (R=14/0.25). As mentioned in Chapter 3, the procedure used for Small columns was troublesome and inefficient. Therefore, it was decided to use longer columns using only fresh peat as described in Chapter 3. Also, pumps were eliminated and a leachate holding tank was used to provide a constant head so that leachate flows by gravity.

In the case of the Small columns there were no sampling ports through the depth of the columns. Samples were taken only from the effluent collected from the bottom of each Small column. In these columns near the bottom the velocity increases by a factor of 420 since leachate has to pass through the small hole (5mm dia.) at the bottom compared to the whole cross-sectional area (10.2 cm dia.) available at other locations. Due to variable velocity field no numerical simulation was carried out since SOLTARN assumes a constant and uniform velocity through the porous medium.

BOD_5 and COD of the influent and effluent of the Small columns were measured. Figure 6-3 shows the average of BOD_5 values of influent and effluent for all 5 Small columns. BOD_5 values of the effluent were adjusted by subtracting the amount of BOD_5 measured in the control column (Cell #5) as a result of biodegradable organic matter released by the peat. After this adjustment BOD_5 removals were in the range of 27 to 39%. The same trend was observed for COD, as shown in Figure 6-4. After adjusting the COD values by subtracting peat contribution, COD removals in the range of 14 to 27% were obtained. BOD_5 and COD removal was possibly due to the filtering function of peat columns, adsorption of biodegradable organics by peat and/or biological degradation. It should be noted that the

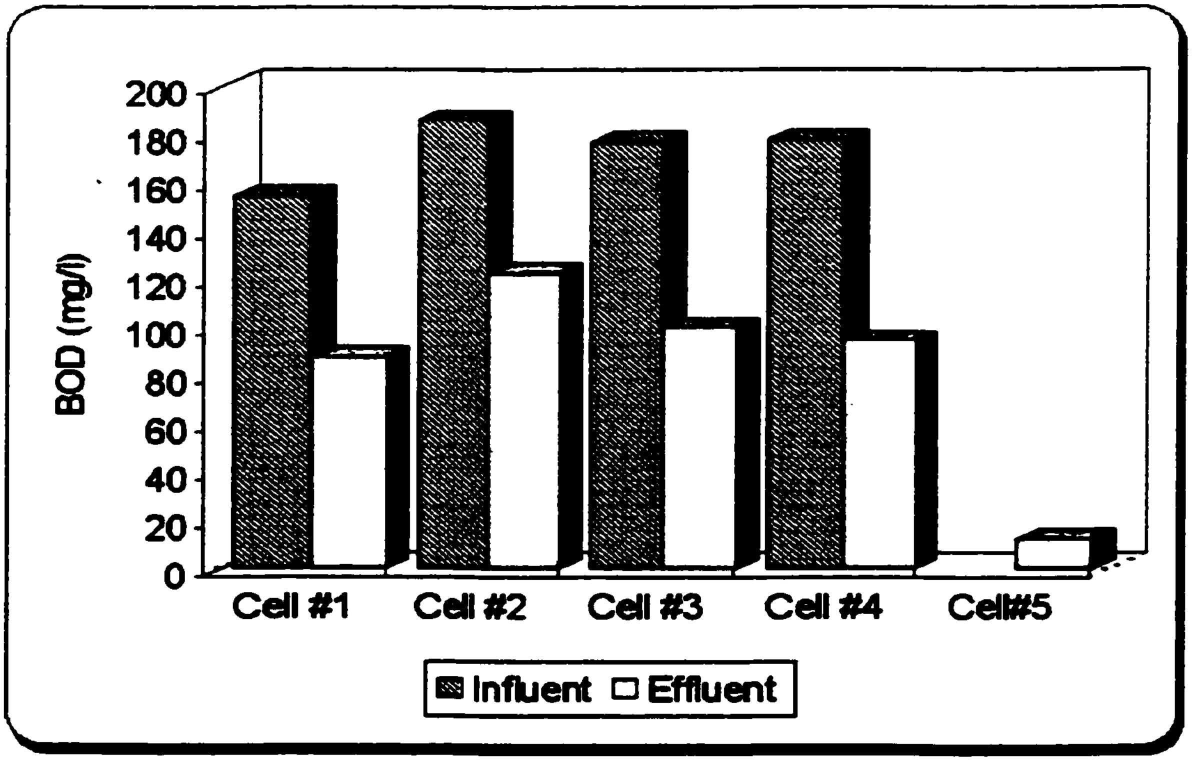


Figure 6-3: BOD removal for small column tests

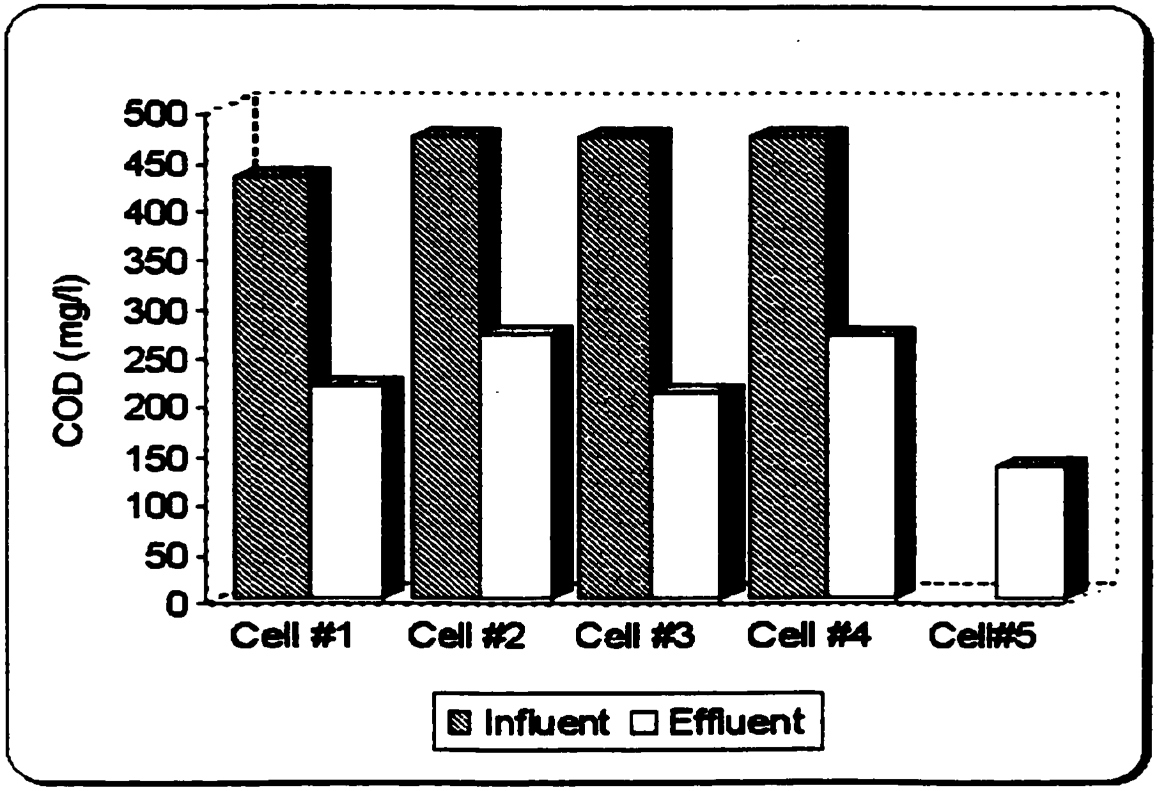


Figure 6-4: COD removal for small column tests

above estimates for BOD_5 and COD removals are based on the initial stages. The amount of organic matter released by peat should eventually decrease as the system reaches a steady state condition. This could result in lower removal efficiency of peat columns over time. On the other hand, it could take some time for bacteria to acclimate to leachate and over time and this could result in higher removals of organic matter. Therefore, it is necessary to monitor such a system over a long period of time and after it has reached a steady state condition. Nevertheless, since leachate came from an industrial waste landfill that does not accept municipal wastes, it is expected that the biodegradability of organic matter in leachate was low and hence not easily reduced through biodegradation and microbial activity.

6.2. MEDIUM COLUMN TESTS

Medium columns were assembled by hand compressing the compost material. For the first trial both CompostH and CompostT were used as received. Dry bulk density of compost material within the Medium column was 0.75 g/cm^3 and hydraulic conductivity was 10^{-2} cm/sec. Such a high hydraulic conductivity did not provide enough contact time for adsorption to occur. In the next step, sieved compost (retained by 3/8" or 9.5 mm) was used and the hydraulic conductivities obtained were in the range of 10^{-3} cm/sec, which were still high. In the third step, compost materials were passed through sieve No.4 (4.76 mm) and further compressed by mechanical devices. The hydraulic conductivity was measured to be 5 x 10^{-4} cm/sec. This was within the range of hydraulic conductivities observed for the peat filter. These columns were used to conduct the subsequent tests. As a result of compressing dry bulk density of compost material in the columns was increased to 1.05 g/cm^3. The above procedure did not result in complete saturation as some air pockets remained within the Medium columns. Also, one column was prepared using fresh peat and the results were compared with compost columns.

Figure 6-5 shows the boron BTCs for peat and CompostH. The results for CompostT was similar to those obtained for CompostH. Comparison of the BTCs from the two columns shows that peat has a higher adsorption (removal) capacity for boron than compost material. About 2.5 times more leachate went through peat column than CompostH column for treated effluent concentration to reach 2 mg B/L. These results are in agreement with adsorption results presented in Chapter 4, which showed that peat had a higher boron adsorption capacity than both compost materials. As mentioned before, this is due to higher organic content of peat compared to compost material.

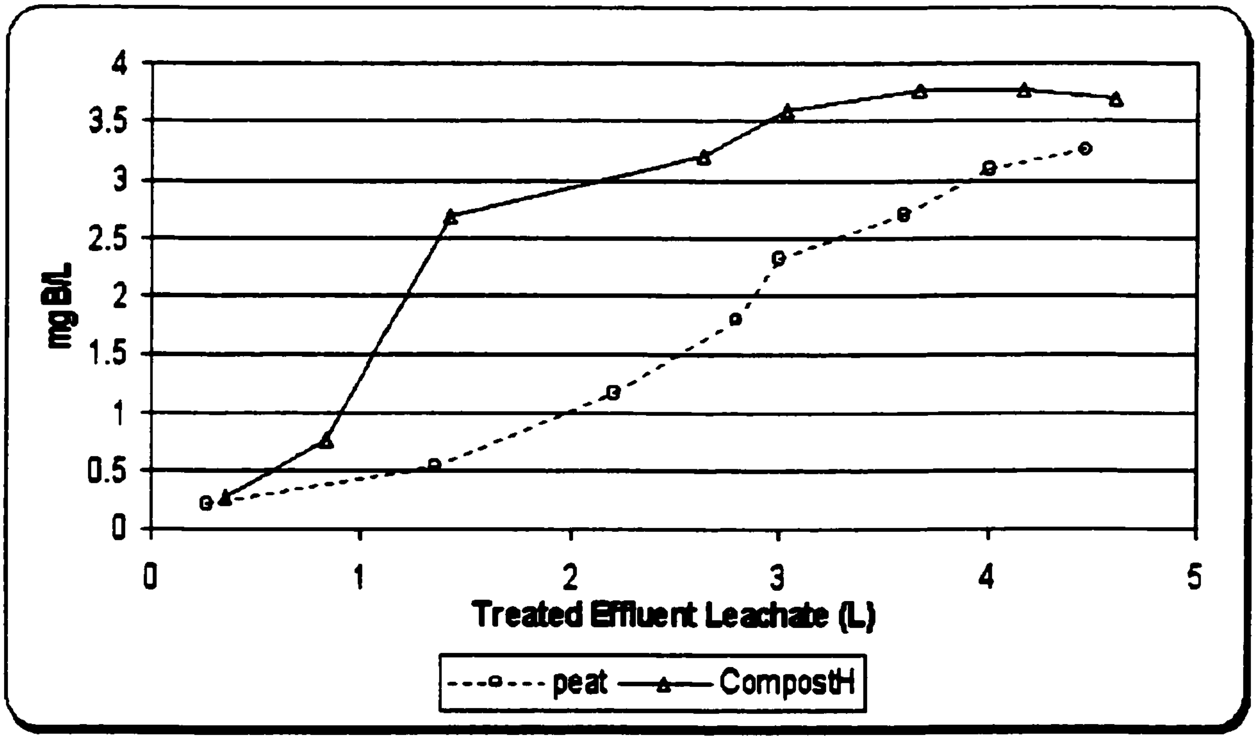


Figure 6-5: Boron BTCs for Peat vs. CompostH from Medium Columns

A set of Medium columns with different lime-to-peat ratios were prepared and monitored over time to evaluate the effect and the feasibility of adding lime to peat columns. A ratio by weight of 1 g lime to 100 g peat (wet weight) resulted in an optimum pH of about 9 for Medium peat columns. It was shown in Chapter 4 that maximum boron adsorption on peat occurs at a pH around 9. At a higher ratio, 3.5 g lime to 100 g peat (wet weight), the pH of the effluent form the Medium columns was about 11. At pH values higher than 9 boron adsorption decreases and consequently peat is less effective in removing boron from the leachate.

Figure 6-6 shows the boron BTCs of two columns, one with fresh peat and the other one with fresh peat mixed with lime (1g lime to 100 g fresh peat ratio). The addition of lime and the increase in pH resulted in higher adsorption of boron and a retarded BTC. About 1.5 times more leachate went through the column containing fresh peat mixed with lime (pH=9) than the one with no lime (pH=7.3) for effluent concentration to reach 2 mg B/L. Therefore, the lime addition approximately increased the removal capacity of peat by 50%. As indicated in Chapter 3, complete saturation of Medium columns was not achieved. Also, there was no sampling port through the depth and for the same reasons explained in the case of Small columns no SOLTRAN simulation was carried out.

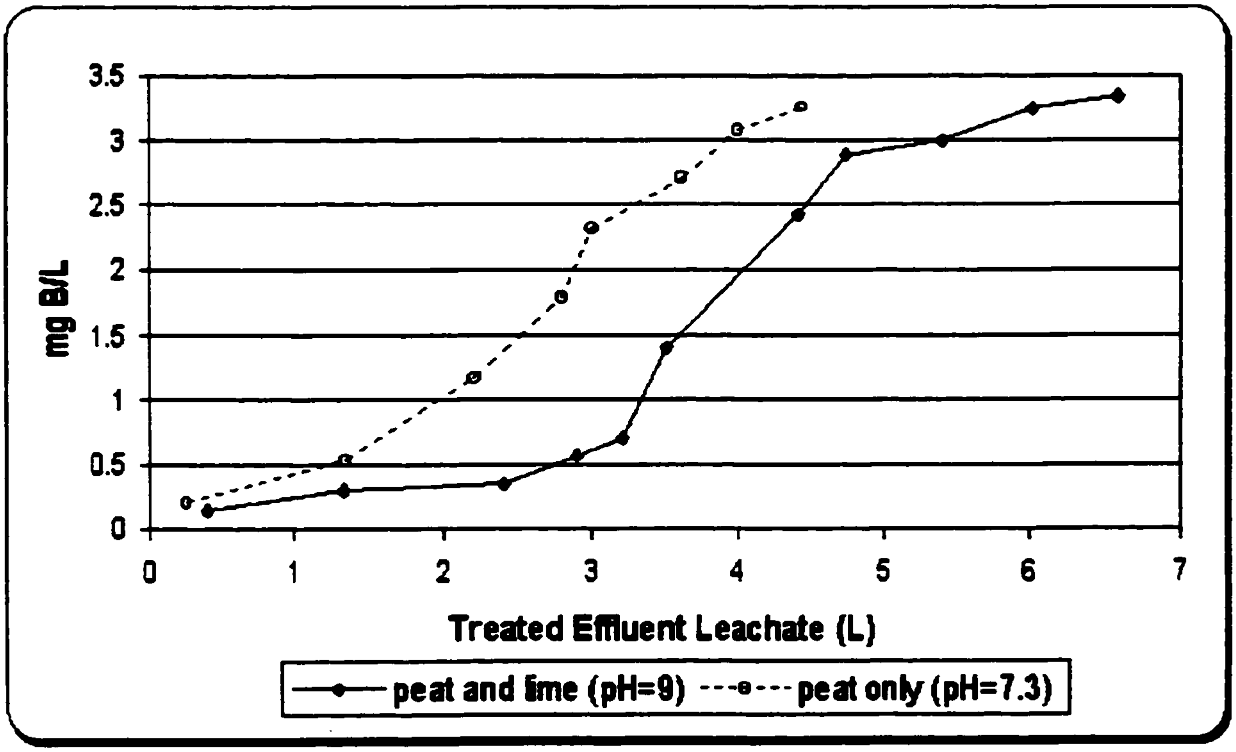


Figure 6-6: The effect of lime addition on boron BTCs for Medium columns

6.3. LONG COLUMN TESTS

Six Long columns, three (columns 1,2, and 3) with only fresh peat and three (columns 4,5, and 6) with fresh peat mixed with lime (1 g lime to 100 g peat ratio) were prepared and monitored over time. As mentioned in Chapter 3, two sampling ports located at 1/3 and 2/3 of the height of the Long columns were used for collecting the samples. The exact location of each sampling port was measured at the end of experiments when the columns were disassembled.

Initially column tests were started with distilled water. Then the influent was switched to leachate diluted with L-B (boron free leachate). To get an estimate of dispersion coefficient the conductivity of the samples collected from both sampling ports were monitored over time. Conductivity started to increase as leachate replaced DW. The break through curves (BTCs) for conductivity at both sampling ports for one of the Long columns are presented in Figure 6-7. The effective porosity was also estimated at 85%. SOLTRAN

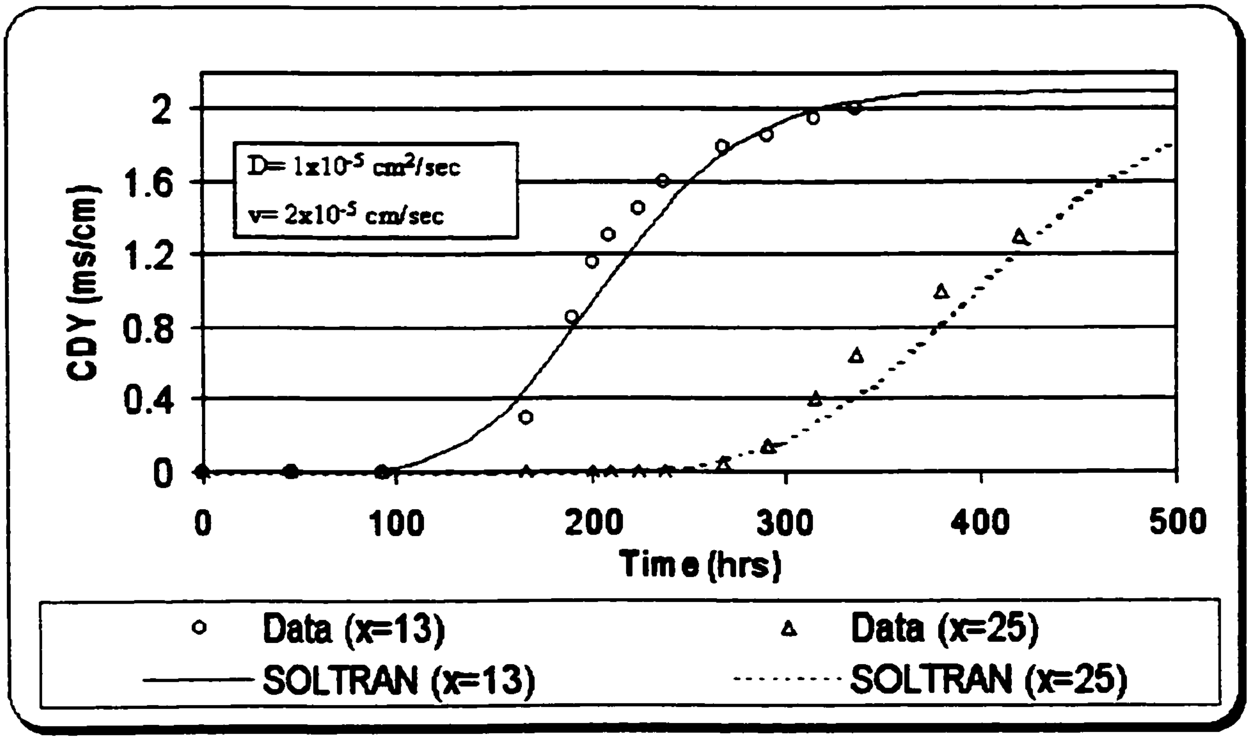


Figure 6-7: BTCs for electrical conductivity at x=13 cm and x=25 cm

program was used to simulate these BTCs. The average linear pore water velocity measured in the laboratory (v= 2 x 10^{-5} cm/sec) was used as the input velocity. Electrical conductivity was assumed to behave as a conservative tracer and the dispersion coefficient was adjusted until a good match at both locations was obtained. The dispersion coefficient was estimated as 1 x 10^{-5} cm^2/sec. For simulations of Long columns this value was used as an initial guess and then adjusted during calibration to match the observed BTCs. For each case the average velocity and dry bulk density measured in the laboratory were used as input parameters for the SOLTRAN program.

Figure 6-8 shows the measured and simulated boron BTCs at both sampling ports for column 1; the average pH of effluent was 7.5. ρ_b and the average linear pore water velocity were measured as 0.12 g/cm^3 and 4.5 x 10^{-5} cm/sec, respectively. A dispersion coefficient of 8 x 10^{-5} cm^2/sec gave the best BTCs for both locations. Simulated results obtained by SOLTRAN were in good agreement with the measured data. The regression coefficient

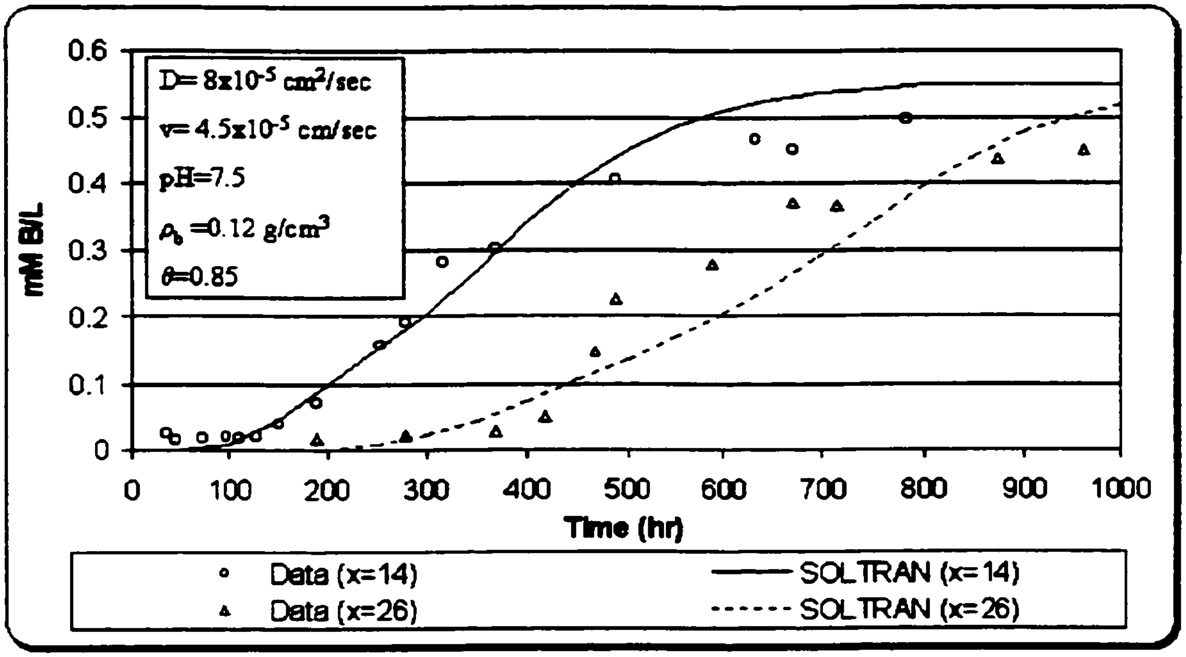


Figure 6-8: Boron BTCs for column 1 at x=14 cm and x=26 cm

between the simulated and observed results at x=14 cm was 0.98. The MARE was calculated as 2.3 x 10^{-2} mM/L, which was small compared to influent concentration of 0.55 mM/L.

Over the time period that the Long columns were sampled and monitored the maximum effluent boron concentration was slightly lower than the average influent boron concentration, 0.5 mM B/L vs. 0.55 mM B/L. This could be due to the so-called tail effect which is observed in the case of two-domain or dual porosity medium. In this case the adsorption for a small portion of porous medium is not instantaneous and rate limited. Non-linearity of isotherm and/or non-reversibility (hysteresis) could also produce the tail effect (Bruseau, 1994).

Figure 6-9 illustrates the simulated and measured BTCs (using non-linear 2nd order equation developed in Chapter 4) for Long column 2. This column was the same as Long column 1 except that the average velocity as measured in the laboratory was 3 x 10^{-5} cm/sec.

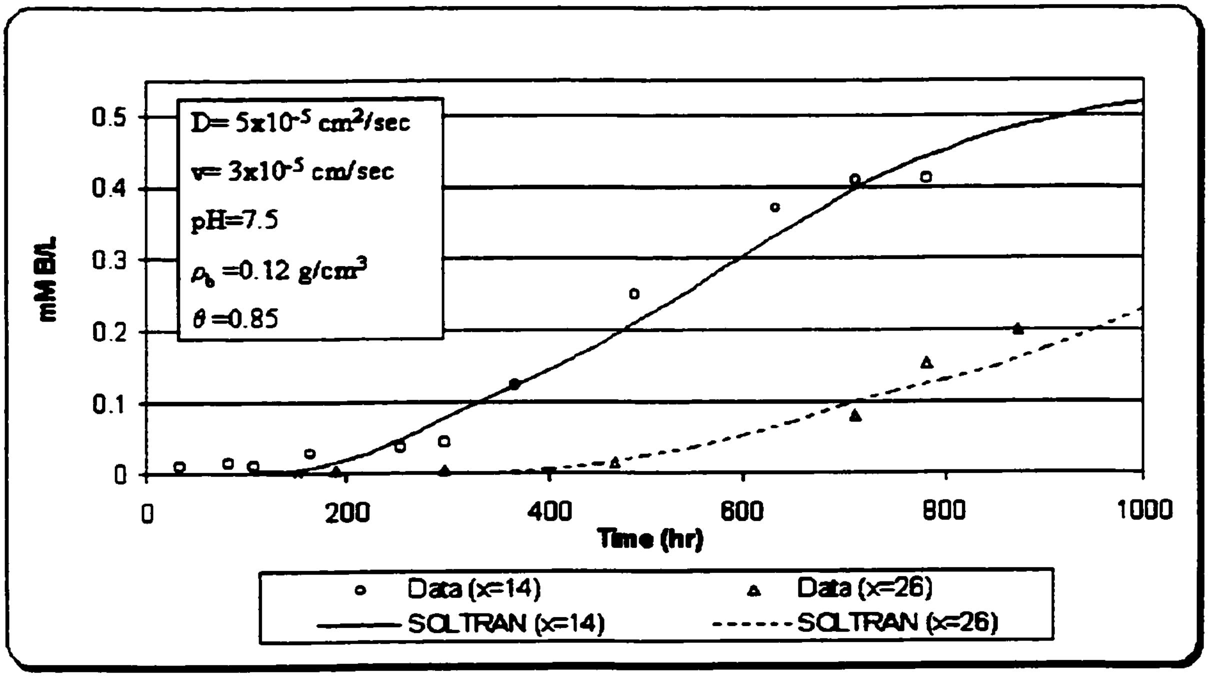


Figure 6-9: Boron BTC for column 2 at x=14 cm and x=26 cm

Dispersion coefficient obtained by numerical simulation was 5 x 10^{-5} cm^2/sec. The results for column 3 were the same as column 2.

To check the reproducibility of the results the BTCs obtained for Long columns 1 and 2 were plotted in Figure 6-10. Since the average velocity was different the BTCs were plotted based on pore volumes not based on time. The figure shows that the reproducibility of the results was high (correlation factor was 0.999). Dispersion coefficient (D) is related to velocity (v) and dispersivity (α_d) according to the following equation (Fetter, 1994).

$$D = \alpha_d \, v + D_d \qquad (6\text{-}1)$$

D_d is the molecular diffusion and is in the order of 10^{-7} cm^2/sec and can be ignored in this case since it is two orders of magnitude less than dispersion coefficient values. If dispersivity, α_d, is calculated for columns 1 and 2, the values of 1.7 cm and 1.8 cm will be obtained

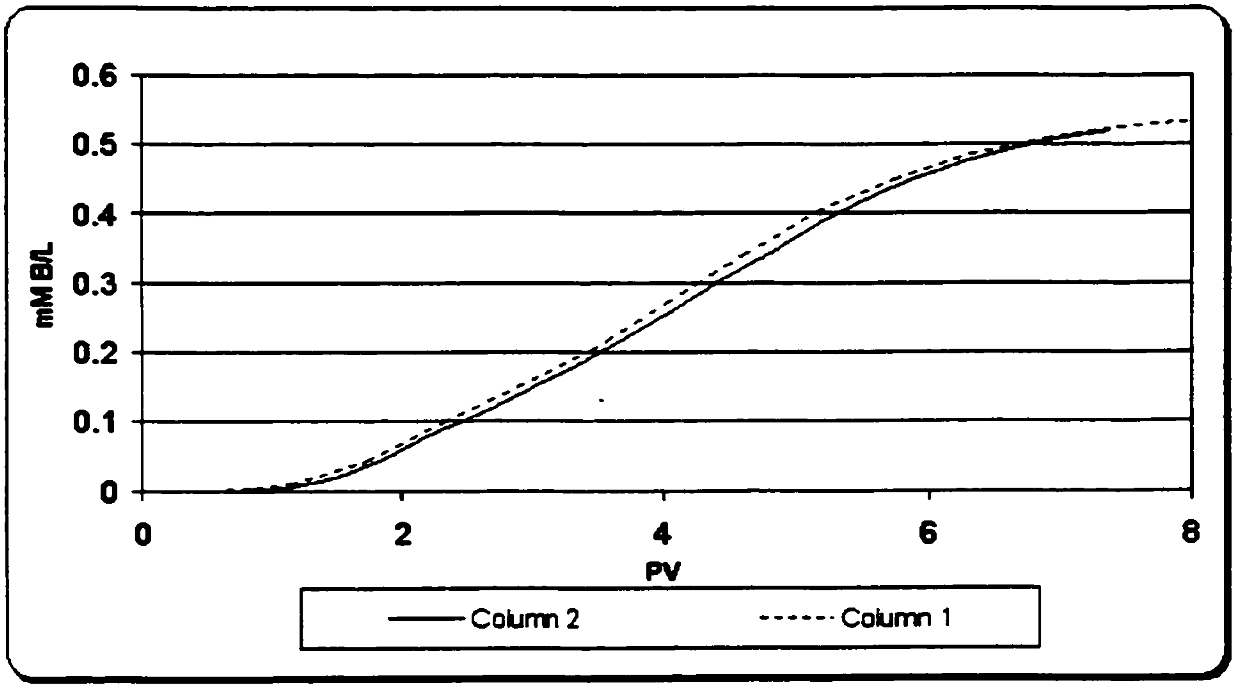


Figure 6-10: Boron BTCs for columns 1 and 2 at x=14 cm

respectively, which are very close. Dispersivity is a property of the material and theoretically if the columns are the same, the dispersivity should be the same. However, variations in packing of peat material within the columns could result in some variations in the magnitude of dispersivity. Nevertheless, as mentioned above the values of dispersivity obtained for different columns were very close (1.7 and 1.8). Also, the dispersivity value obtained was within the range reported in literature. According to Fetter (1994), pore-scale dispersivity measured in the laboratory is on the order of centimetres, whereas macrodispersivity measured in the field is on the order of meters.

Figure 6-11 shows the measured boron concentrations along with simulation results obtained for the two sampling points for Long column 4. This column was prepared by mixture of peat and lime and had an average pH of effluent was 9. ρ_b and the average velocity were measured as 0.12 g/cm^3 and 4.5 x 10^{-5} cm/sec, respectively. Dispersion coefficient value of 1 x 10^{-4} cm^2/sec gave the best results between simulated and actual data. The

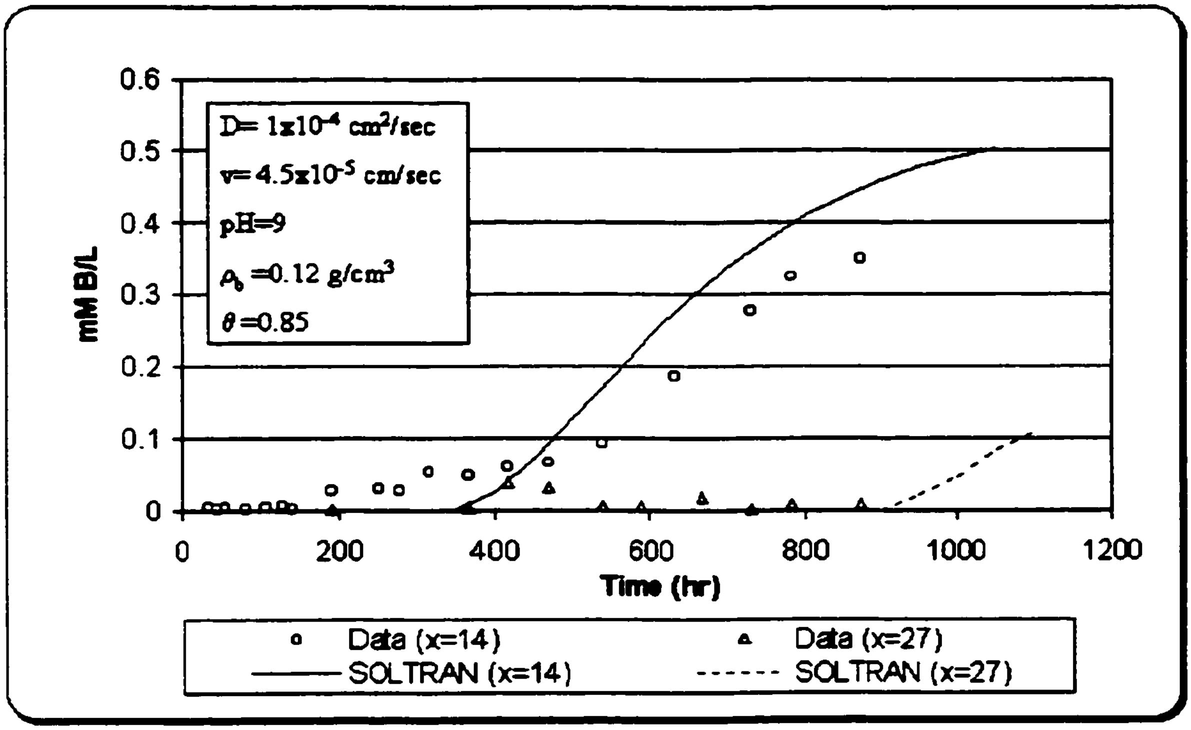


Figure 6-11: Boron BTCs for column 4 at x=14 and x=27

correlation factor between the simulated results and actual data at x=14 cm was 0.98. The MARE (for x=14 cm) was calculated as 3.4 x 10^{-2} mM/L, which is small compared to influent concentration of 0.55 mM/L. Based on the calculated value for dispersion coefficient, dispersivity is estimated to be 2.2 cm, which is very close to values of 1.7 and 1.8 cm obtained for the case where pH = 7.

To show the effect of addition of lime and pH increase the simulated BTCs for Long columns 1 and 4 are plotted in Figure 6-12. Addition of lime and subsequent pH increase significantly enhanced the boron adsorption capacity of peat. This is in agreement with the results presented in Chapter 4. The break through at 0.5 C_o for Long column 4 occurred almost 2 times later than that of Long column 1. In other words, addition of lime increased the capacity of the system by a factor of 2.

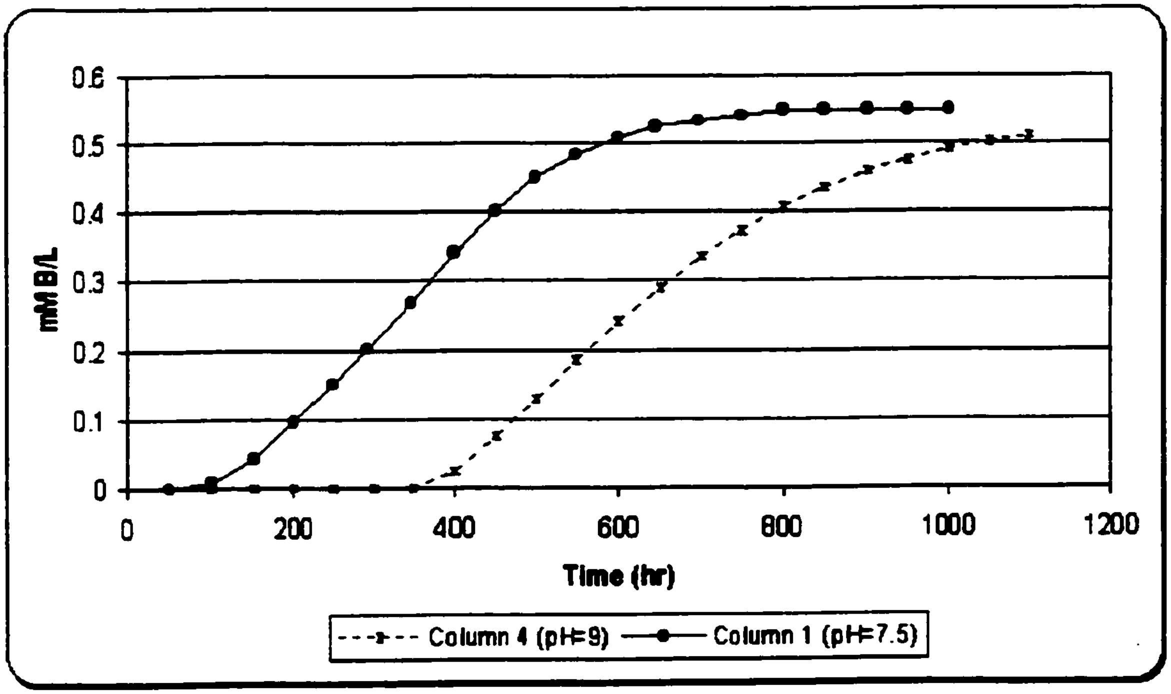


Figure 6-12: Boron BTCs for columns 1 and 4 at x=14

6.4. COLUMN TEST USING AMBERLITE RESIN

As mentioned in Chapter 3, one small column with an area of 1 cm^2 and length of 20 cm was packed with Amberlite resin. Synthetic solution made from boric acid with an intial concentration of 1.7 mM B/L (18.4 mg B/L) was passed through this column using a Peristaltic pump. Boron concentration of the effluent was measured and it is shown in Figure 6-13. Boron broke through after passage of about 270 pore volumes. This compares with 4 pore volumes for the peat with pH =7.5. This implies that the boron removal capacity of Amberlite is about 70 times greater than peat. This is consistent with the results of adsorption tests presented in Chapter 4, which showed that boron adsorption capacity of Amberlitre was 100 times greater than peat. As mentioned before, in practice these columns have to be regenerated once the capacity is exhausted. Nevertheless, it may offer an economically feasible alternative, which is worth investigating.

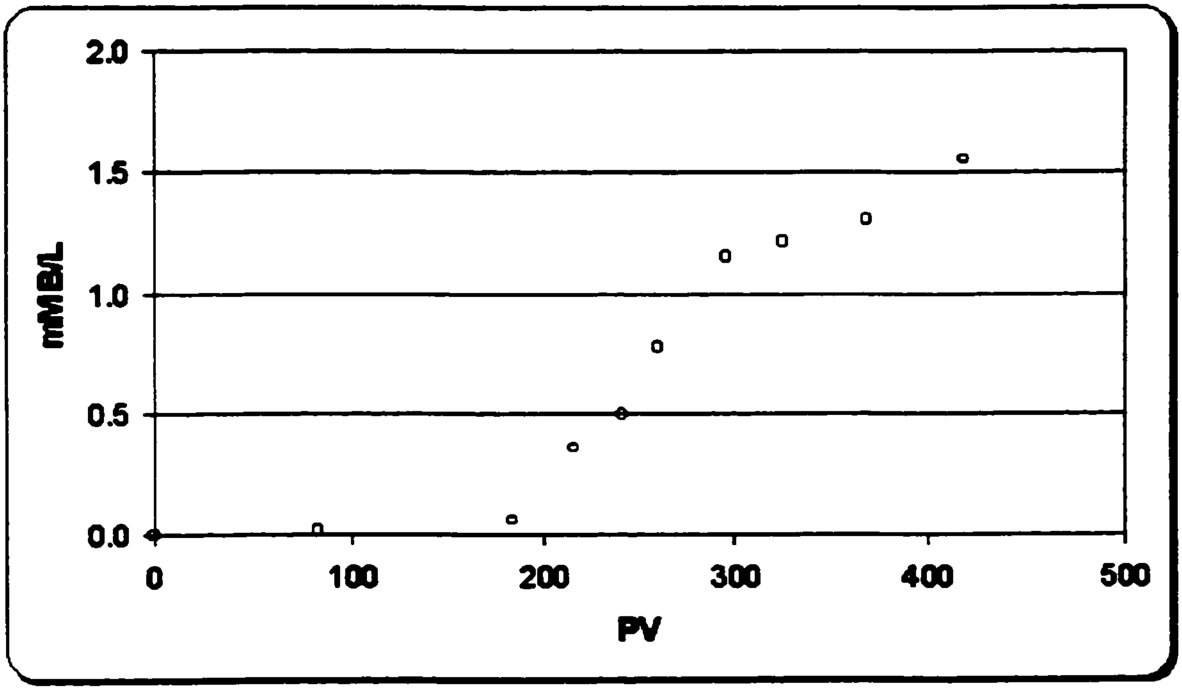


Figure 6-13: Boron BTC for Amberlite column

In summary, laboratory column tests showed that peat columns were very effective in removing metals from leachate. Peat columns also removed 27% to 39% of BOD_5 and 14% to 27% of COD from leachate, but these results are based on the initial stages of column tests not the steady state condition. The SOLTRAN program was utilized to simulate the laboratory column tests results under different pH conditions. The values of dispersion coefficient obtained by simulation of laboratory column tests were in the range of 5×10^{-5} to 1×10^{-4} cm^2/sec, the difference is due to the effect of velocity as dispersion coefficient is related to velocity and dispersivity. The dispersivity, α_d, value obtained for the columns was very close and in the range of 1.7 to 2.2 cm. The effective porosities of columns were between 85% (Long columns) to 89% (Small Columns). The adsorption capacity of peat for boron can be significantly enhanced by the addition of lime and pH increase up to pH=9. The hydraulic conductivity of the columns were in the range 10^{-4} cm/sec, which were within the range of values observed in the field. Amberlite was far more efective than peat and other organic adsorbents in removing boron.

Chapter 7

RESULTS OF FIELD MONITORING

As indicated in Chapter 3, the Engineered Wetland System (EWS) at Huneault Waste Management landfill site consisted of a vertical flow subsurface (VFS) peat filter followed by a free water surface (FWS) wetland. The collected leachate was pumped and distributed over the top of the peat filter. The filtrate was collected through a subsurface drainage system at the base of the peat filter then discharged into the FWS wetland. The results of monitoring of this system over a two-year period (1996-97) are presented and discussed in this chapter. Also, the results of simulation of this system obtained by the computer program SOLTRAN, which was developed in Chapter 5 are presented and compared with data collected in the field.

7.1. MONITORING RESULTS

The monitoring program included the collection of samples and analysis for inductively coupled plasma (ICP) metal scan (heavy metals, calcium, sodium, boron), total carbon (TC), total organic carbon (TOC), biochemical oxygen demand (BOD_5), chloride, ammonia, and total phosphorous (TP). Also, pH, dissolved oxygen (DO), total dissolved solids (TDS), and temperature of the collected samples were measured in the field. Hydraulic conductivity of the peat filter at different depths were measured and monitored over time. In addition, soil samples from the peat filter were collected and analyzed for boron content and heavy metals.

7.1.1. Boron and Metal Analysis

The collected leachate samples were filtered (2 μm Glass Microfibre GF/C filter) and then analyzed by ICP method for boron (B), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb) and zinc (Zn). Concentrations of Cd, Cr, Cu, Mn, Ni and Pb were very low, below detection limit most of the time. Thus, they are not presented and discussed.

Boron concentrations as high as 19 mg/L were measured in the leachate produced at HWM landfill site. This is almost 100 times greater than PWQO criteria for surface discharge. The average boron concentrations measured in the ponds, at different levels within the peat filter (Levels A to D), and in the wetlands surface water are shown in Figure 7-1. The initial concentration of boron in the holding ponds varied from 10 to 19 mg/L, with an average of μ= 14 mg B/L and a standard deviation of σ =2.7. The peat filter consistently showed high boron removal efficiencies. The concentration of boron decreased as the leachate passed through the peat filter reaching an average value of 1.1 mg/L at the bottom of the peat filter (level D at 1.7 m below grade), which indicates a 92% removal efficiency.

As the leachate enters surface water, boron concentration increases to an average value of 5.0 mg B/L. A reason for the observed increase in boron concentration between the bottom of the peat filter and surface water wetland could be the leakage of untreated leachate through channeling or short-circuiting within the peat filter. The average concentrations recorded

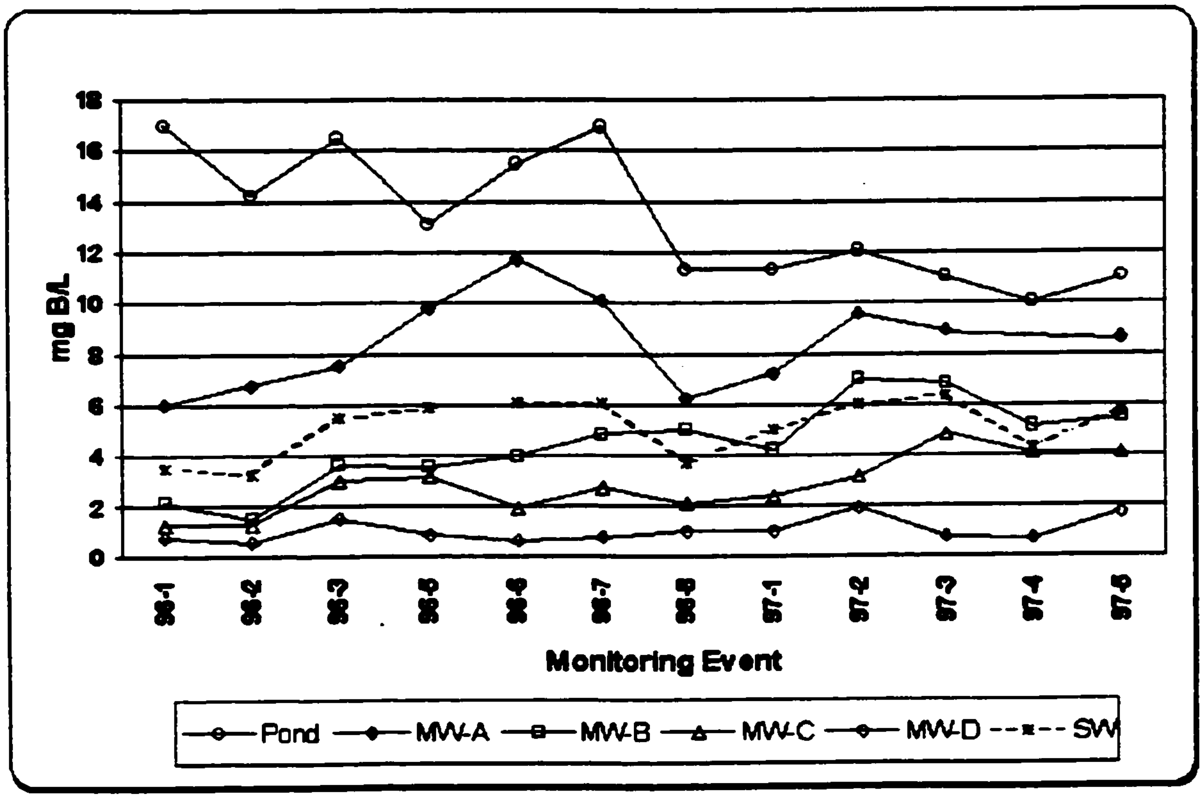


Figure 7-1: Boron concentration through the EWS

suggest that as much as 30% of the untreated leachate may be reaching FWS wetlands untreated. Even by considering the effect of leakage the EWT system is providing an overall removal efficiency of 64% for boron removal.

One possible location for leakage through the system was a well installed for monitoring the water level at the northern edge of the peat filter. This location was confirmed to be a source of leakage since a sample taken during the sampling event 96-6, indicated a concentration of 13.7 mg B/L for boron at the bottom of the peat filter at this location. This location was closed using bentonite. However, the same trend continued to exist which shows there were other sources of leakage or short-circuiting. It is apparent that some leachate entered the collection system within the sand layer without receiving any treatment from the peat filter, thus causing the boron concentration to rise in the surface water wetlands. This was further confirmed by comparing boron concentrations at the two manholes, MHW and MHE within the peat filter. These two manholes are connected through a header pipe and water flows towards MHE. Boron concentration at MHE was on average 5.6 mg B/L compared to 2.2 mg B/L at MHW, a clear indication that some untreated leachate entered the header pipe between these two manholes. Due to frequent repairs of the irrigation systems and changes in the leachate distribution system as well as the effects of freeze and thaw and desiccation to the top portion of the peat layer, the upper 0.3 m of the peat filter was severely cracked and fissured. These conditions were visible during the fieldwork and should have contributed to the leachate leakage through the system.

FWS wetland was ineffective in reducing boron concentrations. It was expected that plants and vegetation in EWS wetland would adsorb some boron, however, the statistical comparison of boron concentrations measured through FWS wetland show no significant differences. The background concentration of boron in the groundwater within the constructed wetland was on average 1.0 mg B/ L as measured at W-1 and W-2. This shows that groundwater has not been contaminated or impacted by the operation of the EWS.

Distribution of iron and zinc within the peat filter and surface water wetland did not show any specific trend. Iron concentrations varied from values as low as <0.01 up to 2.3

mg/L with most (around 98%) measurements being below 1.0 mg/L. Iron concentrations as high as 8.1 mg/L had been measured during 1990-95. However, based on the results for 1996-97 iron concentration is low and according to the surface water discharge criteria it is not a concern. Zinc concentrations were within the range of <0.06 to 0.6 mg/L with just one incidence of 2.1 mg/L. Initial concentration of calcium in the ponds was between 250 and 300 mg/L which was reduced to values in the range of 30-140 mg/L in 1996 and below 50 mg/L in 1997 within the peat filter and the surface water wetlands. Sodium concentrations were in the range of 50-450 mg/L without any specific trend within the peat filter. Sodium concentrations within the surface water were in the range 150-300 mg/L. Although Ca and Na within the measured range are not of environmental concern, the results indicate that the EWS was efficient in removing cations in general.

7.1.2. BOD_5, TOC, Cl, NH_3, TP, TDS, conductivity, pH and DO

The leachate produced at the Huneault Landfill site is weak in terms of biodegradable organic matter concentrations. The average BOD_5 of the leachate collected at this landfill is about 100 times lower than the average BOD_5 of other landfills in Ontario (Table 2-1). This is due to the fact that no municipal waste is received at this landfill. The initial dissolved BOD_5 of the leachate in the ponds was in the range of <5-18 mg/L with an average of 9.1 mg/L, which was reduced to values between <5 to 6 mg/L when the leachate percolated through the peat filter and <5 mg/L within the surface water wetlands. The detection limit for BOD_5 was 5 mg/L. A minimum reduction of 45% for BOD_5 is obtained. According to Kadlec (1999), wetlands possess irreducible background concentrations of some substances, about 5 mg/L in the case of BOD_5.

The initial concentration of total organic carbon (TOC) in the pond varied from 80 to 150 mg/L, with an average of 113 mg/L, which was reduced to an average value of 74 mg/L at the top of peat filter (level A) and to 39 mg/L at the bottom of the peat filter (level D). As in the case of boron, the concentration of TOC increased as the leachate entered the surface water wetlands and reached an average value of 49 mg/L. This increase again shows that there was leakage or short-circuiting through the peat filter as explained for boron. The TOC removal efficiency of the peat filter was 65%. Even with considering the effect of leakage, the system is showing an overall efficiency of 57%. Figure 7-2 shows the variation of the average concentration of TOC within the system. It has the same trend as boron.

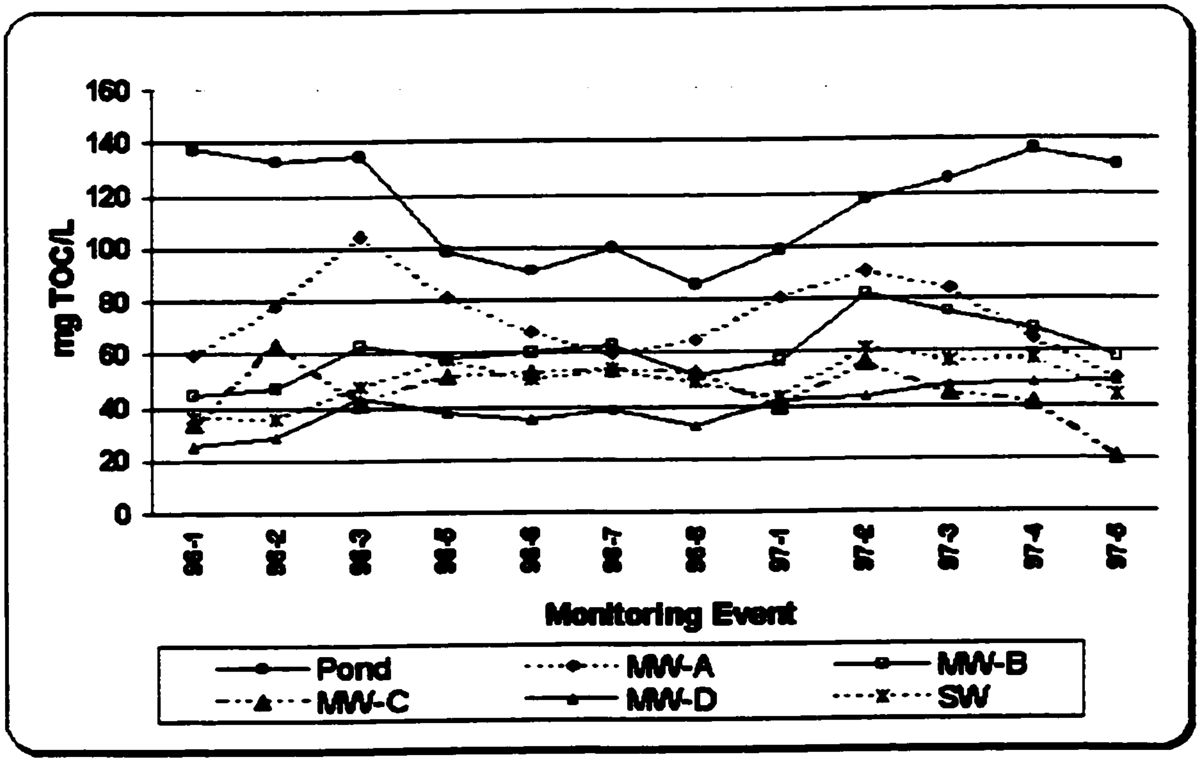


Figure 7-2: TOC concentration through the EWS

Chloride is not a pollutant, it acts as a conservative element. Initial chloride concentration was 300-450 mg/L in the pond. Chloride concentration within the surface water wetlands was in the range of 200-400 mg/L.

The peat filter was very effective in removing ammonia. The average concentration of ammonia at different locations of the system is shown in Figure 7-3. The range of initial ammonia concentration was quite wide with concentrations as low as 4.5 mg/L and as high as 33 mg/L, with an average value of 20.5 mg/L. The ammonia concentration was reduced to an

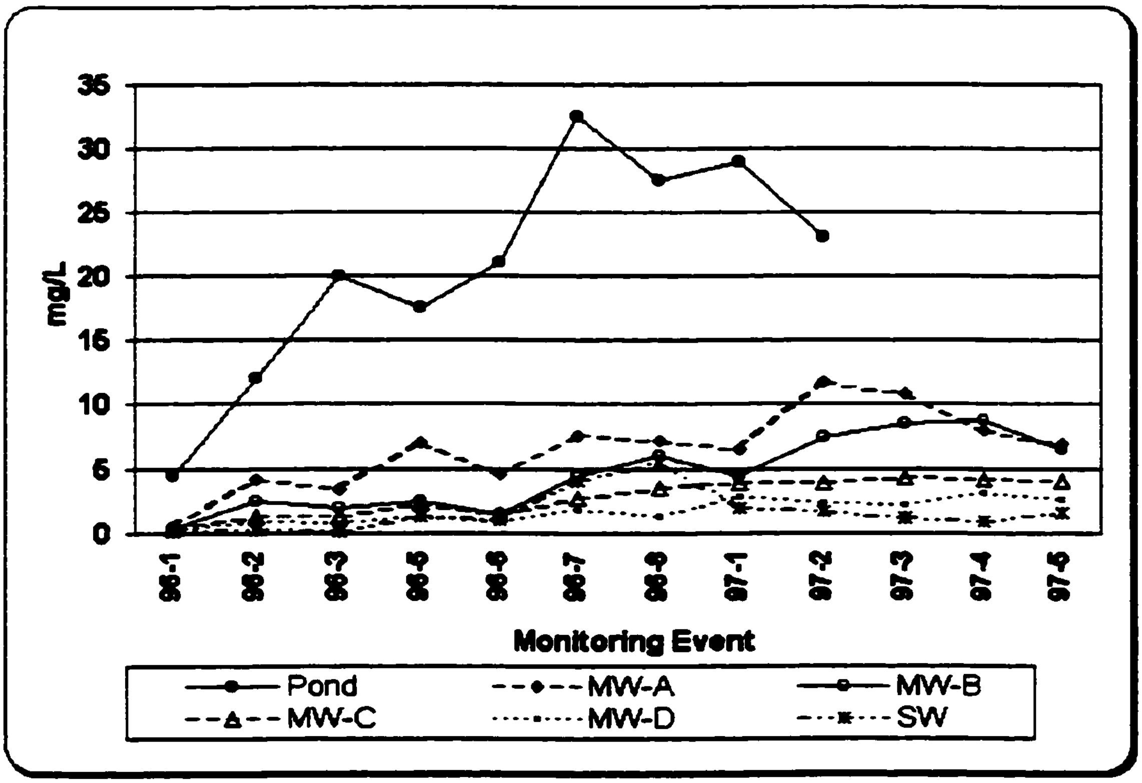


Figure 7-3: Ammonia concentration through the EWS

average value of 6.4 mg/L at the top of peat filter (level A) and to 1.7 mg/L at the bottom of peat filter (level D). Comparison of ammonia concentration measured at MHW and MHE shows that the ammonia concentration at MHE has increased to an average value of 4.9 mg/L due to leakage of untreated leachate. FWS wetland was effective in removing ammonia as it decreased through surface water wetland. This can be attributed to an increase in pH within the surface water which caused ammonia to volatilize. The removal efficiency of the peat filter for ammonia was 92%. There was not a significant amount of phosphorous present in the raw leachate, and most of the measurements were close or below the detection limit of 0.05 mg/L.

Total dissolved solids (TDS) were reduced from an initial average value of 2100 mg/L to an average value of 910 mg/L at the bottom of the peat filter. This implies a 57% removal. TDS increased to an average value of 1100 mg/L as the leachate entered the surface water wetland. As expected, conductivity had the same trend as TDS. pH was in the range of 6.5 to 7.6 within the pond and peat filter and then increased to values between 7 and 9 as the leachate entered into surface water wetlands. Dissolved oxygen was initially between 0.1 to 2.5 mg/L, then it slightly increased to values in the range of 2-3.5 mg/L within the peat filter. Surface water wetlands had an oxygen level of 8-11 mg/L.

The monitoring of the Engineered Wetland System has demonstrated that the EWS was quite effective for contaminant removal from landfill leachate. Although FWS wetland was effective in reducing the concentration of ammonia, however most of the treatment efficiency, especially in the case of boron, was accomplished through the VFS peat filter system. On average, the peat filter removed 92% of boron, 65% of TOC, 57% of TDS, 92% of ammonia and at least 45% of BOD_5. As expected, the concentrations of contaminants were reduced through the depth of engineered peat filter as the leachate moves towards the bottom of the filter. Adsorption and filtration are most probably the main mechanisms for contaminants removal. Increases in concentrations of contaminants were observed as the leachate reaches the surface water wetland. Leakage of untreated leachate through the peat filter was suspected of causing the increase in concentrations in FWS wetland.

7.1.3. Hydraulic Conductivity

Hydraulic conductivity of the peat filter was measured by conducting slug test in the field at the beginning (26 June) and at the end (25 November) of 1996 as well as the middle (10 July) of 1997. The program SUPERSLUG was used to calculate hydraulic conductivity of peat at each monitoring well. The hydraulic conductivity of the peat filter was in the range of 10^{-3} to 10^{-5} cm/sec. The hydraulic conductivity showed a decreasing trend towards the bottom of the peat filter as the hydraulic conductivities measured at level C were an order of magnitude lower than the ones measured at level A (top of peat filter). This is due to the fact that the materials at the bottom were more compressed thus restricting the flow. Hydraulic conductivity of the sand layer (level D) was in the range of 10^{-4} cm/sec, one order of magnitude higher than the bottom layer of the peat filter (level C) and close to the values measured in the top layer (level A) of the peat filter. No specific change was observed over the time period indicating that flow was not restricted.

7.2. SIMULATION RESULTS

SOLTRAN program was used to simulate the performance of the VSF filter component of the EWS. The first step is to choose the time and spatial step. Anderson and Woessner (1992) suggest that for transport modeling dx should be less than $4\alpha_d$. If the value of 1.8 cm obtained for dispersivity in Chapter 4 is used, dx should be less than 7.2 cm. A dx= 5 cm was used. To satisfy the requirement for Courant number, dt has to be less than 2.5 days. A time step of one day was used for simulation results.

The leachate generation rate was estimated at 57, 000 m^3/yr (Castonguay, 1997). About one-third of the leachate was treated through EWS and the rest was recirculated into the landfill. Considering the surface area of the landfill and operation period of six months, the average velocity (loading rate) through peat filter is estimated at 0.02 m/day. Also, in July 1997 the retention ponds were emptied due to odor problems and all of the leachate was hauled to a municipal wastewater treatment plant in Ottawa. Based on the total volume of hauled leachate, another estimate of average velocity at 0.01 m/day was obtained. Therefore, it was decided to use an average velocity of 0.015 m/day. The same bulk density (0.12 g/ cm^3) and effective porosity (85%) obtained during column tests were used as input parameters. The variable boron concentrations as measured in the field (ponds) was used as influent concentration. As mentioned before, SOLTRAN does an interpolation to estimate the concentration for each time step.

Figure 7-4 shows the results of simulation obtained by SOLTRAN as well as collected data in the field. The collected data at level B (0.9 m below surface) and C (1.2 m below surface) are more spread than the simulated results. There are a number of reasons for this. As mentioned before, there were frequent repairs of the irrigation systems and changes in the leachate distribution system, which resulted in cracks and fissures at peat surface, the upper 0.3 m. Therefore, untreated leachate could have passed through these channels. This could

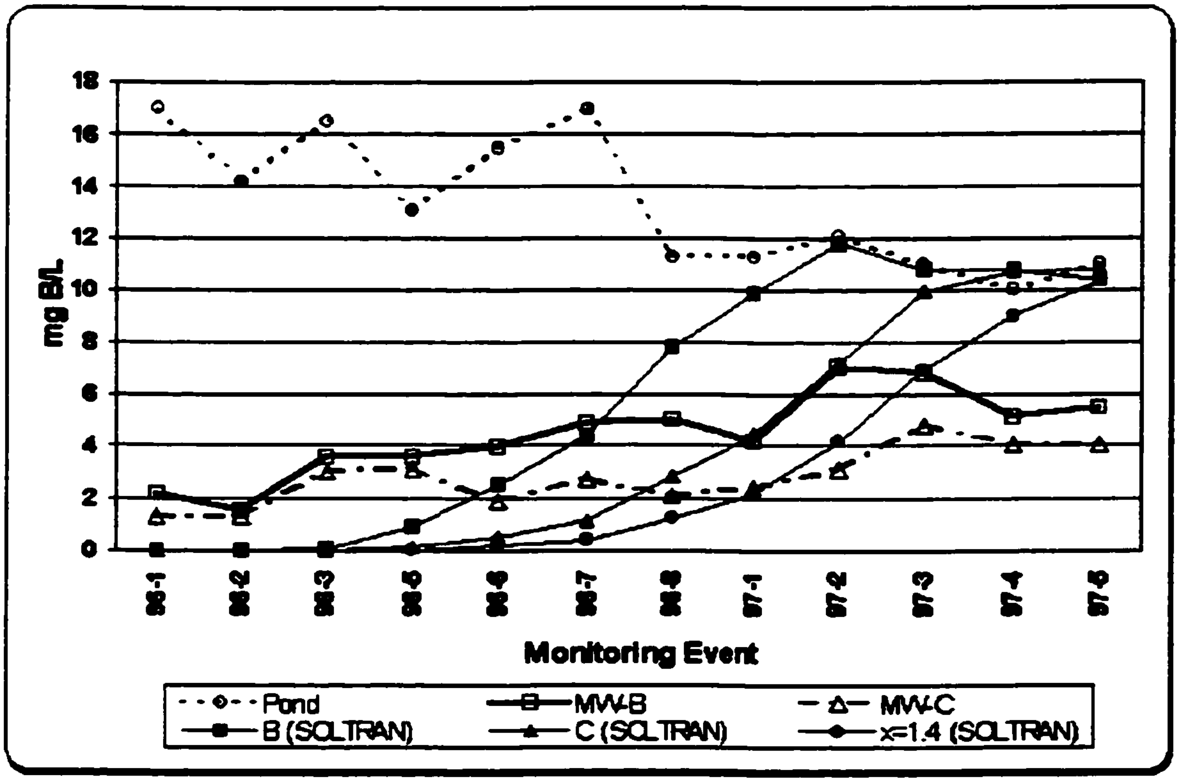


Figure 7-4: Comparison of collected data with simulation results obtained by SOLTRAN (at pH = 7)

result in elevated concentrations observed at early stages of monitoring. Also, the system was not working on a continuous basis, which could result in further spreading of concentration. In addition, during sampling it was observed that some bentonite was present in the collected leachate. Adsorption of boron by bentonite could have reduced boron concentration in the collected samples. It was confirmed in the laboratory that boron adsorbs on to bentonite (0.1 mg/g at equilibrium concentration of 8 mg/L). Combination of the above factors resulted in deviations and spreading of concentrations observed in the field. Nevertheless, the simulated results at x=1.4 m (bottom of peat layer) shows that boron should break through at the end of the second year of monitoring. In fact, this was the case and the next sampling at the beginning of 1998 proved that the adsorption capacity of peat filter was exhausted, as effluent concentration from the peat filter was the same as influent concentration. This showed that the peat filter had to be replaced.

As indicated in Chapter 6, the addition of lime could enhance the adsorption capacity of the peat. Figure 7-5 shows the results of simulations obtained by SOLTRAN at pH=9 for the same conditions as used in the previous step. Comparison of the results obtained at levels A and B at two pH levels shows that the addition of lime and increase in pH could significantly increase the adsorption capacity of the peat filter and extend the design period by about another year. This is in agreement with the results obtained earlier, which showed the adsorption capacity of peat was improved by 50 to 100%.

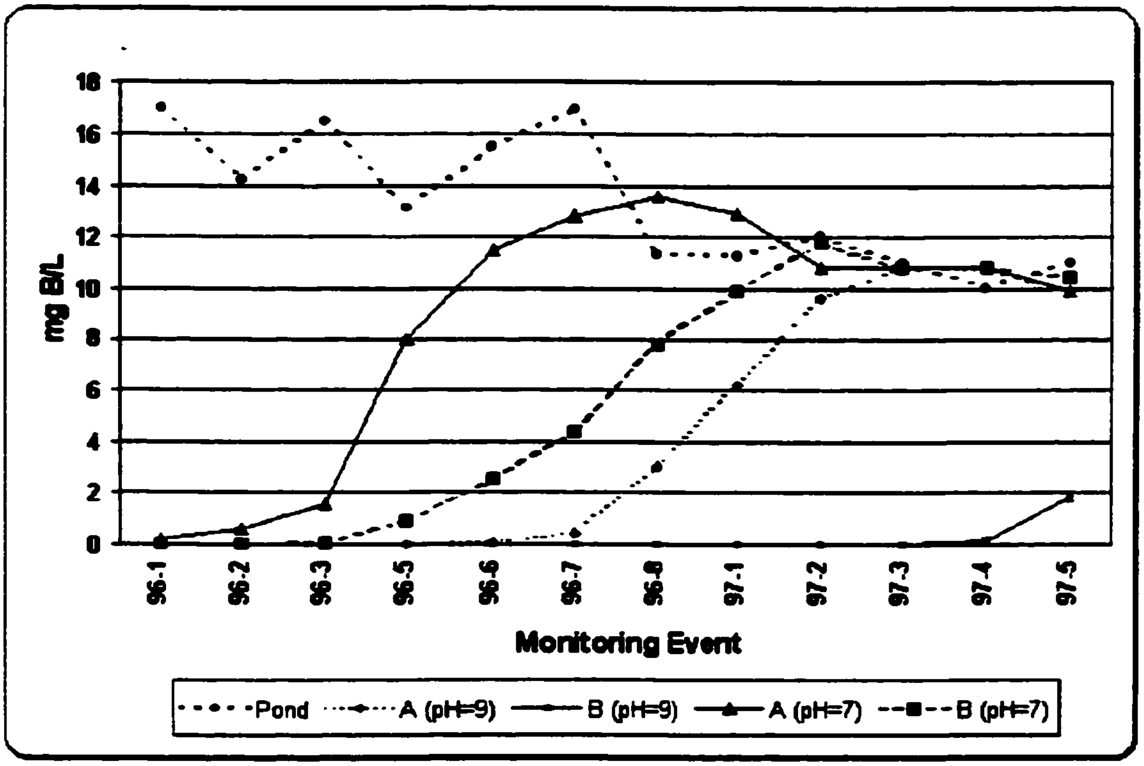


Figure 7-5: Simulation results obtained by SOLTRAN at pH = 7 and pH=9

7.3. SOIL SAMPLE ANALYSIS

To measure the retention of contaminants by peat soil, some soil samples from different depths of the peat filter were collected, digested with acid and analyzed by ICP. Soil samples were collected in May 1997 and November 1997. The boron concentrations within peat soil are presented in Table 7-1. The results show an increase or accumulation of boron over time and through the depth of the peat filter.

Table 7-1: Boron concentrations at different levels within the peat filter (mg/Kg)

Distance below grade	May 1997			November 1997			
	#1	**#2**	**Ave**	**#1**	**#2**	**#3**	**Ave**
40-50 cm (top)	42	77	**60**	85	115	69	**90**
75-85 cm (middle)	96	49	**73**	--	73	92	**83**
100-110 cm (bottom)	36	36	**30**	57	--	84	**70**

CONCLUSIONS AND RECOMMENDATIONS

Chapter 8

8.1. CONCLUSIONS

Leachate from most landfills in Ontario does not meet the surface water discharge criteria for boron and as a result leachate has to be treated before discharge into the environment. An engineered wetland system was used to treat the landfill leachate produced at Huneault Waste Management landfill. Treatment and transport modeling of boron and other contaminants in landfill leachate in the engineered wetland system were investigated through laboratory tests, field monitoring, and mathematical modeling. The main parameter of concern was boron.

It was concluded that boron is mainly present in inorganic form, i.e. borate ion or boric acid, in landfill leachate.

Statistical analysis of batch adsorption tests showed that drying peat, even at room temperature, significantly reduces its adsorption capacity for boron. Therefore, it is recommended to use fresh peat to conduct batch adsorption or column tests.

Adsorption of boron by peat was not affected by shaking the containers at a speed of up to 200 rpm and solution-to-soil ratios up to 0.4. Adsorption of boron by peat was a fast process as kinetics tests showed that adsorption was virtually complete within 2.5 hours.

Adsorption of boron was very dependent on pH, with the maximum adsorption occurring around the pH of 9-9.5. It was concluded that boron adsorption by peat occurs through ion exchange with hydroxyl ions. It was shown that this pH dependency of boron adsorption by peat could be used to enhance the adsorption capacity through the addition of lime to peat. The optimum ratio was 1 g lime to a 100 g wet peat, which resulted in increasing the pH to 9. As a result, boron adsorption capacity of peat was increased by 50-100%.

The ionic strength or composition of leachate had a significant effect on the adsorption of boron by peat. However, the presence of other anions such as SO_4^-, Cl^- or combination of both in synthetic solutions made from boric acid had no significant effect on boron adsorption by peat. Therefore, either peat favors the adsorption of boron over these other anions or the adsorption sites are very specific to boron. Adsorption of boron decreased with temperature increase. The effect of temperature on boron adsorption by peat was confirmed by two-level factorial design experiments. Boron desorption showed hysteresis as only 24% to 45% of adsorbed boron was released.

The examination of the assumptions and procedures in conducting batch adsorption tests revealed that the linear and non-linear regression of batch adsorption data, in the case of regressing q vs. C_e, are not statistically correct. Two types of error were recognized. One due to violation of assumption during linear transformation of the equations and the second one due to definition of dependent and independent variables. A new code, NLPEFM, was developed that does not produce any of these two errors. The magnitude of these errors depends on the nature and characteristics of the data, and could be very significant.

Second-order design model offers some advantages over Freundlich adsorption model. Second-order model can describe boron adsorption at any pH and temperature while Freundlich adsorption models are to be used for a specific set of environmental conditions under which they were developed. Development of second-order design model also can be achieved with less laboratory effort than the Freundlich model.

Boron adsorption capacity is directly related to organic matter content of peat and compost materials and shows a positive effect, i.e. boron adsorption increases with organic matter content. Amberlite resin was far superior to peat and other organic material in adsorbing and removing (70 to 100 times) boron from leachate. The draw back is the setup and maintenance of columns that need to be regenerated with acid and basic solutions.

Peat also proved to be effective in removing metals such as iron, lead, and zinc from landfill leachate. Peat can also remove organic matter to some extent (27-39% removal for

BOD_5 in column tests during initial stages of the test and 45% BOD_5 removal in the field; 65% removal for TOC in the field).

A new transport code, SOLTRAN, was developed and verified against an analytical solution. SOLTRAN has the capability of handling non-linear adsorption case. It was shown that the use of distribution coefficient (k_d) and linear approximation of adsorption isotherms by using retardation factor produces inaccurate results. SOLTRAN also has the capability of incorporating pH and temperature into transport model. The other advantage of this model is that it needs very few parameters, in the case of column tests only dispersion coefficient. SOLTRAN was used to predict the results of column tests and to predict the performance of the peat filter.

Monitoring of the engineered wetland system at Huneault Waste Management landfill demonstrated that peat filter can effectively treat landfill leachate. However, such a system has to be maintained well. Problems with leakage of untreated leachate observed in the case Huneault Waste Management system reduced the efficiency of the system. Free water surface component of the engineered wetland system proved to be ineffective in reducing boron concentration. Although the treated leachate through peat filter did not meet the discharge requirement, as much as 92% of boron was removed by this system. The other shortcoming of peat filter was that it functioned only for two years and peat had to be replaced. However, by mixing peat with lime the life expectancy of this system can be increased by 50 to 100%.

8.2. RECOMMENDATIONS

As indicated in the case of Small and Medium columns, SOLTRAN assumes uniform and constant velocity field. To improve its capability a separate code or a previously developed code for fluid flow can be incorporated into SOLTRAN in order to make it more versatile. The fluid flow code computes the velocity at each node and then this information can be used by SOLTRAN to calculate the transport modelling of contaminants.

Another modification of SOLTRAN could be the provision of a regression procedure for finding the best estimates of calibrated parameters. For this thesis this was done by trial and error until a satisfactory match between the data and simulated results were obtained.

To improve the efficiency of the peat filter and better benefit from the contaminant removal capacity of the peat at Huneault Waste Management landfill, it is suggested that part of surface water wetland be converted to a second peat filter in which the leachate flows horizontally. The second peat filter would work in series with the first one and provide additional treatment capacity. This second filter is much less susceptible to leakage since leachate has to move through a length of 10-20 m distance through the peat compared to the 1.4 m thickness in the first peat filter. It should also be noted that the surface water wetland is not contributing towards removal of boron, a key target contaminant at this site, and by converting part of the wetland to a second peat filter the available space could used more efficiently. In doing so, the life expectancy of the Engineered Wetland System is also increased. It is also suggested that the system be operated on a continuous mode. In addition, it is suggested that the option of mixing peat with lime and increasing the pH in full scale be explored. As mentioned above, this could significantly increase the treatment capacity of the system.

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AMBERLITE -743

Appendix A

(The following information is extracted from the document provided by Rohm & Haas Company)

Amberlite – 743 ion exchange resin, a product of Rohm and Haas Company, is a unique ion exchange resin specifically used to remove borate and boric acid under a variety of conditions. The presence of such compounds, even in very small concentrations, is frequently a major concern in the use of certain water supplies or in chemical processes. The media in which the boron occurs usually have a high concentration of cations and other anions, so that total ion removal is impractical and a specific boron removing operation is essential. The characteristics of Amberlite – 743 are presented in Table A-1.

Table A-1. Characteristics of Amberlite - 743

Moisture Content	58% (approximate)
Density	640 to 720 g/L
Theoretical Boron Capacity	5.7 mg B/mL
Operating Boron Capacity (Figure A-1)	Rate Dependant 3 mg B/mL at 8 L/hr/L 1 mg B/mL at 32 L/hr/L

Amberlite – 743 resin has been shown to be nearly universal in its high selectivity for boron. Salts, including bases, do not interfere significantly. The concentration of boric acid or salt background in water also has little effect upon the selectivity. Even though Amberlite will be used in a column operation, a batch technique is applicable.

Regeneration

Sulfuric acid (10%) at a level of 48 g/L gives good regeneration of Amberlite –743. Following the elution of the borate with sulfuric acid, the sulphate is removed by treatment with 4% NaOH at a level of 64 g/L of resin.

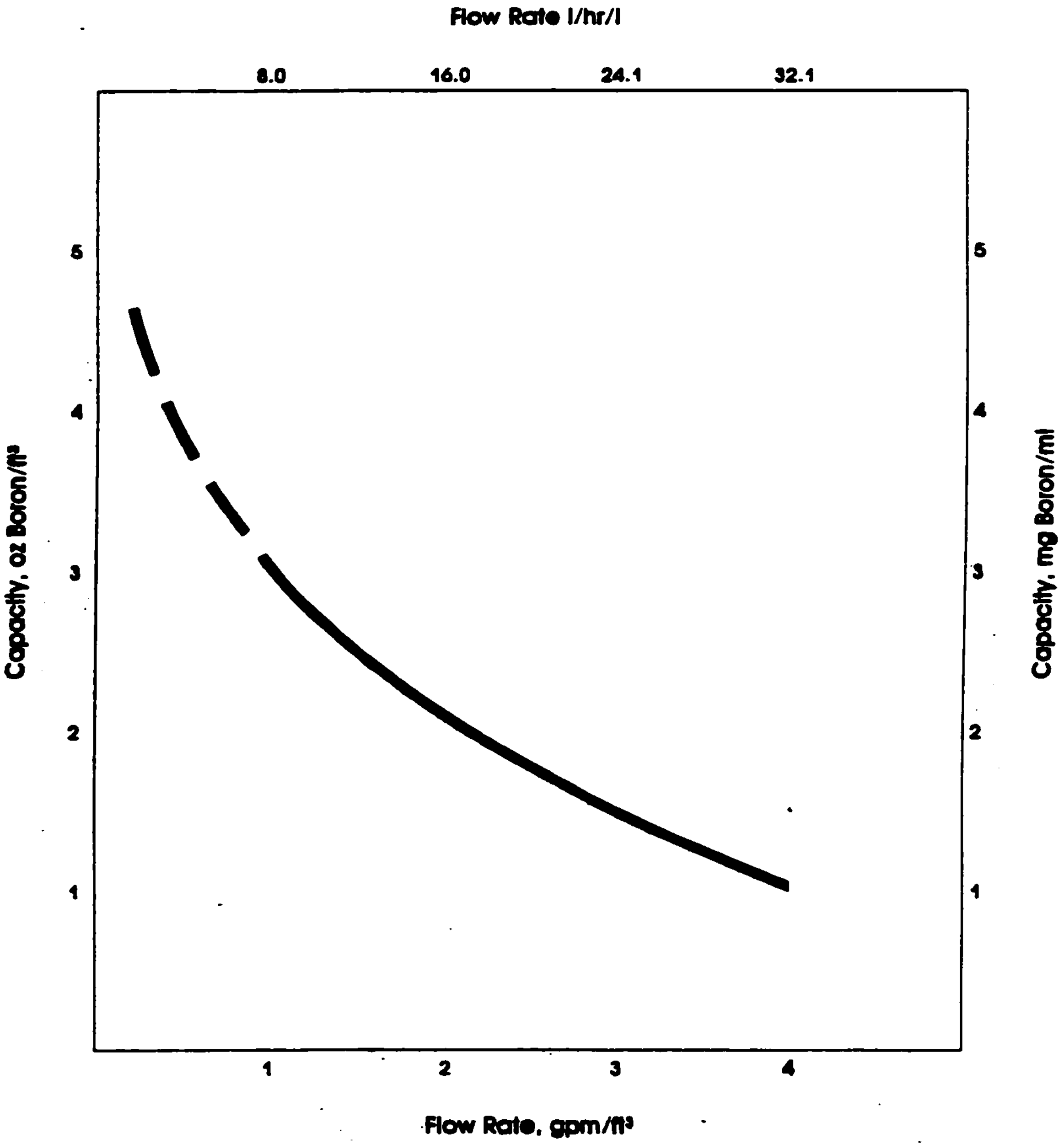

Figure A-1: Flow Rate Dependence of Amberlite 743 Capacity

KINETICS DATA

Appendix B

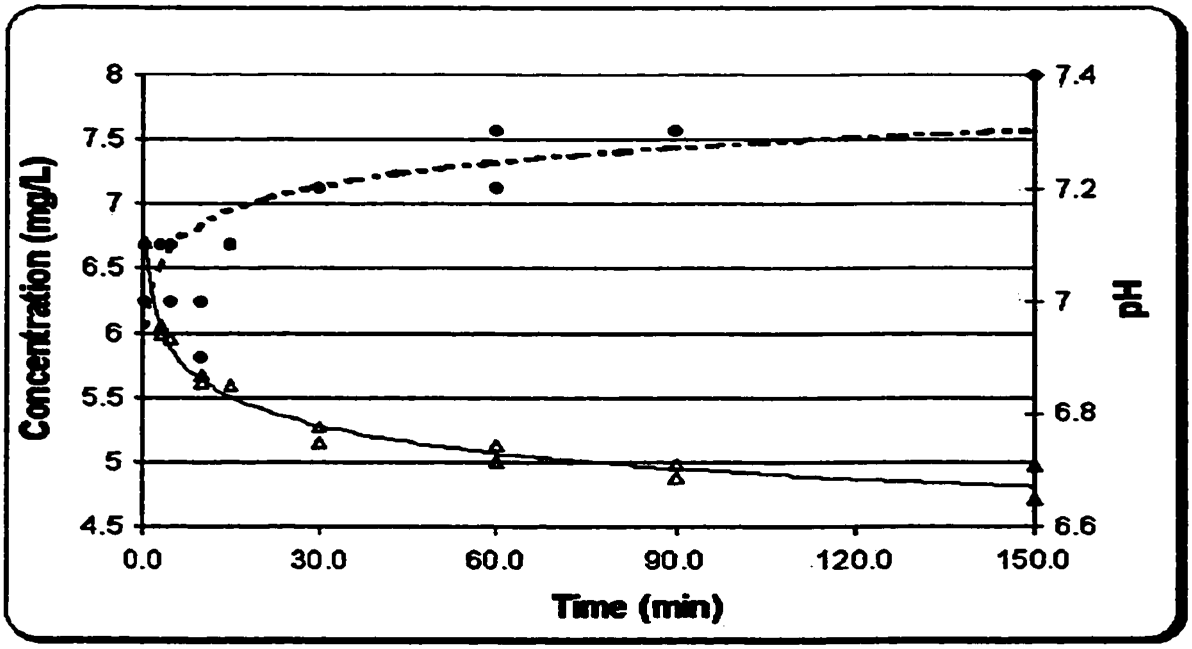

Figure B-1: Kinetics of boron adsorption by peat for second set of data

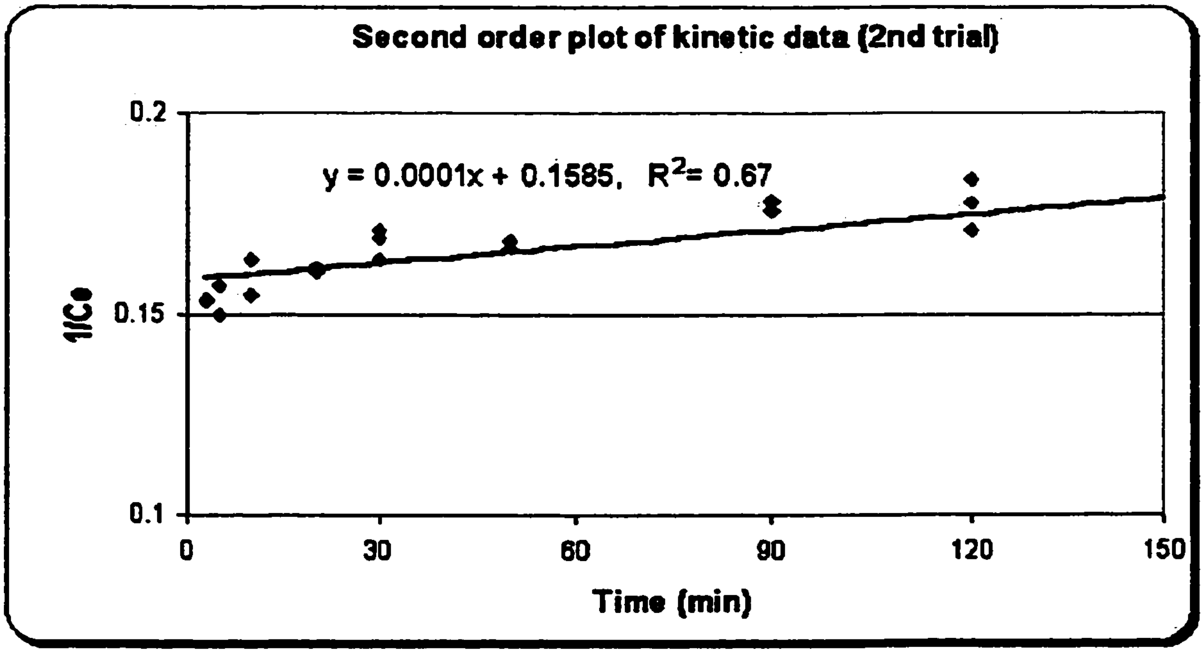

Figure B-2: Second order plot of kinetics for second set of data

LISTINGS OF COMPUTER PROGRAMS

```
!   ***************************************************************
!   *                          SOLTRAN                            *
!   *                                                             *
!   *     A ONE-DIMENSIONAL SOLUTE TRANSPORT MODEL                *
!   *  FOR TRANSPORT OF ADSORBING CONTAMINANTS THROUGH            *
!   *     A PEAT FILTER (FINITE DIFFERENCE METHOD)                *
!   *                                                             *
!   *                          Majid Sartaj                       *
!   *                                                             *
!   *              DEPARTMENT OF CIVIL ENGINEERING                *
!   *               OTTAWA UNIVERSITY,                            *
!   *              OTTAWA, CANADA K1N 6N5                         *
!   *              Email: msartaj@yahoo.com                       *
!   *                                                             *
!   *                          May 2000                           *
!   ***************************************************************
PROGRAM MSSoltran
USE module1
external Input, Trid, TridF, TridG, TridL
call Input
if (isorption.eq.1) then
Call Trid
else
End if
if (isorption.eq.2) then
Write (*,*) 'please enter Kd.'
read (*,*) Kd
call TridL
else
End if
if (isorption.eq.3) then
Write (*,*) 'please enter K and 1/n.'
read (*,*) K , n
Call TridF
else
End if
if (isorption.eq.4) then
Call TridG
else
end if
STOP
END

module module1
IMPLICIT INTEGER (i-j)
public i,j,isorption
character(20) inputfile, outputfile
REAL, public:: a,b,d,alpha(100),P(100),Q(100),Alphac(100),C(100,100000),S(100,100000) &
```

```
 ,pH(100), Tem(100),delx, delt, v, Dis, Rho, theta, ph_cons, Tem_cons,Ci_cons,beta1, &
 beta2,beta, Kd, K, n, R, C_Temp , bl, br, db, bmid, f
end module

subroutine Input
use module1
write (*,*) 'If using a previous set of data, enter 1 otherwise enter 2'
read (*,*) i1
if (i1.eq.1) then
                write (*,*) 'Please enter the filename.'
                read (*,*) inputfile
                open (3, file=inputfile,status='old')
                read (3,*) i, j, delx, delt
                read (3,*) Dis, Rho, theta, v
else
        write (*,*)'Please enter # of elements (i) and # of time steps (j).'
        read (*,*) i, j
        write (*,*) 'Please enter delx (in cm) and delt (in seconds).'
        read (*,*) delx, delt
  write (*,*) 'Please enter Dis (Disperssion), Rho (Bulk density), theta, and Velocity (v).'
        Write (*,*) 'Dis (cm^2/sec)= ?'
        read (*,*) Dis
        Write (*,*) 'Rho (g/cm^3)= ?'
        read (*,*) Rho
        Write (*,*) 'theta = ?'
        read (*,*) theta
        Write (*,*) 'v (cm/sec) = ?'
        read (*,*) v
        write (*,*) 'Please enter a name for Input file.'
        read (*,*) inputfile
        open (3, file=inputfile,status='replace')
        write (3,'(i3,2f15.3)') i, j, delx, delt
        write (3,'(3f15.3)') Dis, Rho, theta, v
                do i2=1,i+1
                C(i2,1)=0.0
                S(i2,1)=0.0
                end do
        write (*,*) 'For constant influent concentartion enter 1 otherwise 2'
        read (*,*) i3
         if (i3.eq.1) then
                write (*,*) 'Please enter constant influent concentration.'
                read (*,*) Ci_cons
                do j5=1,j+1
                C(1,j5)= Ci_cons
                !write (3, '(i5,f15.3)') i4, C(1,i4)
                end do
         else
        100     write (*,*) 'please enter time step and its corresponding concentration'
                read (*,*) i6, Ci_cons
         if (i6.eq.1) then
                i5=i6
                C(1,i5)=Ci_cons
         else
                j1=i6
                do j2=i5+1,j1
                beta1=j2-i5
```

```
                beta2=i6-i5
                beta=beta1/beta2
                C(1,j2)=C(1,i5)+beta*(Ci_cons-C(1,i5))
                end do
                i5=j1
                C(1,i5)=Ci_cons
                if (j1.eq.j) then
                go to 200
                else
                endif
           endif
                go to 100
        200 do i7=1,j
                write (3, '(i5,f15.3)') i7, C(1,i7)
                end do
         endif
endif
write (*,*) 'For non-reactive enter 1, for linear adsorption enter 2, &
for Freundlich enter 3, and for general case enter 4.'
read (*,*) isorption
if (isorption.eq.4) then
write (*,*) 'For constant pH enter 1 otherwise 2'! Variable pH
        read (*,*) i3
          if (i3.eq.1) then
                write (*,*) 'Please enter constant pH.'
                read (*,*) pH_cons
                do j5=1,i+1
                pH(j5)= pH_cons
                !write (3, '(i5,f15.3)') i4, C(1,i4)
                end do
          else
        400     write (*,*) 'please enter node # its corresponding pH'
                read (*,*) i6, pH_cons
          if (i6.eq.1) then
                i5=i6
                pH(1)=pH_cons
          else
                j1=i6
                do j2=i5+1,j1
                beta1=j2-i5
                beta2=i6-i5
                beta=beta1/beta2
                pH(j2)=pH(i5)+beta*(pH_cons-pH(i5))
                end do
                i5=j1
                pH(i5)=pH_cons
                if (j1.eq.i) then
                go to 500
                else
                endif
           endif
                go to 400
        end if
 500 write (*,*) 'For constant temperature enter 1 otherwise 2'
        read (*,*) i3
          if (i3.eq.1) then
```

```
                write (*,*) 'Please enter constant temperature.'
                read (*,*) tem_cons
                do j5=1,i+1
                Tem(j5)= Tem_cons
                end do
          else
         600    write (*,*) 'please enter node # its corresponding temperature'
                read (*,*) i6, Tem_cons
          if (i6.eq.1) then
                i5=i6
                Tem(1)=Tem_cons
          else
                j1=i6
                do j2=i5+1,j1
                beta1=j2-i5
          .     beta2=i6-i5
                beta=beta1/beta2
                Tem(j2)=Tem(i5)+beta*(Tem_cons-Tem(i5))
                end do
                i5=j1
                Tem(i5)=Tem_cons
                if (j1.eq.i) then
                go to 700
                else
                endif
           endif
                go to 600
         700 do i7=1,i
                write (3, '(i5,f15.3)') i7, Tem(i7)
                end do
         end if
else
end if
end subroutine



subroutine Trid
use module1
a=1+Dis*delt/(delx**2)
b=(0.5*Dis*delt/(delx**2))+(v*delt/(4*delx))
d=(0.5*Dis*delt/(delx**2))-(v*delt/(4*delx))
Do j3=2,j+1
alpha(2)=(2-a)*C(2,j3-1)+b*C(1,j3-1)+d*C(3,j3-1)
P(2)=d/a
Q(2)=(alpha(2)+b*C(1,j3))/a
Do i8=3,i+1
Alpha(i8)=(2-a)*C(i8,j3-1)+b*C(i8-1,j3-1)+d*C(i8+1,j3-1)
P(i8)=d/(a-b*P(i8-1))
Q(i8)=(Alpha(i8)+b*Q(i8-1))/(a-b*P(i8-1))
End do
C(i8,j3)=Q(i8)
Do i9=i,2,-1
C(i9,j3)=P(i9)*C(i9+1,j3)+Q(i9)
End do
End do
```

```
300 write (*,*) 'For BTC enter 1 otherwise 2'
Read (*,*) i20
If (i20.eq.1) Then
Write (*,*) 'Please enter distance (x) for BTC and time'
Read (*,*) i25, j20
Do i30=1,j20
j25=60*i30
Write (*,*) i25,j25, C(i25,j25)
Read (*,*)
End Do
Else
write (*,*) 'Please enter a time step to see the results.'
Read (*,*) j4
Do i11=1,i
Write (*,*) i11,j4,C(i11,j4)
read (*,*)
End do
Endif
Go to 300
end subroutine

subroutine TridL
use module1
a=1+Dis*delt/(delx**2)
b=(0.5*Dis*delt/(delx**2))+(v*delt/(4*delx))
d=(0.5*Dis*delt/(delx**2))-(v*delt/(4*delx))
Do j3=2,j+1
          Do i13=2,i
          S(i13,j3)=S(i13,j3-1)
          End do
alpha(2)=(2-a)*C(2,j3-1)+b*C(1,j3-1)+d*C(3,j3-1)-((Rho/theta)*(S(2,j3)-S(2,j3-1)))
P(2)=d/a
Q(2)=(alpha(2)+b*C(1,j3))/a
Do i8=3,i+1
Alpha(i8)=(2-a)*C(i8,j3-1)+b*C(i8-1,j3-1)+d*C(i8+1,j3-1)-((Rho/theta)*(S(i8,j3)-S(i8,j3-1)))
P(i8)=d/(a-b*P(i8-1))
Q(i8)=(Alpha(i8)+b*Q(i8-1))/(a-b*P(i8-1))
End do
C(i8,j3)=Q(i8)
Do i9=i,2,-1
C(i9,j3)=P(i9)*C(i9+1,j3)+Q(i9)
End do
Do i10=2,i
C_Temp=C(i10,j3)
C(i10,j3)=(theta*C_Temp+Rho*S(i10,j3-1))/(theta+Rho*Kd)
S(i10,j3)=Kd*C(i10,j3)
End do
End do
300 write (*,*) 'For BTC enter 1 otherwise 2'
Read (*,*) i20
If (i20.eq.1) Then
Write (*,*) 'Please enter distance (x) for BTC and time'
Read (*,*) i25, j20
Do i30=1,j20
j25=60*i30
Write (*,*) i25,j25, C(i25,j25)
```

```
Read (*,*)
End Do
Else
write (*,*) 'Please enter a time step to see the results.'
Read (*,*) j4
Do i11=1,i
Write (*,*) i11,j4,C(i11,j4)
read (*,*)
End do
Endif
Go to 300
end subroutine


subroutine TridF
use module1
a=1+Dis*delt/(delx**2)
b=(0.5*Dis*delt/(delx**2))+(v*delt/(4*delx))
d=(0.5*Dis*delt/(delx**2))-(v*delt/(4*delx))
Do j3=2,j+1
alpha(2)=(2-a)*C(2,j3-1)+b*C(1,j3-1)+d*C(3,j3-1)
P(2)=d/a
Q(2)=(alpha(2)+b*C(1,j3))/a
Do i8=3,i+1
Alpha(i8)=(2-a)*C(i8,j3-1)+b*C(i8-1,j3-1)+d*C(i8+1,j3-1)
P(i8)=d/(a-b*P(i8-1))
Q(i8)=(Alpha(i8)+b*Q(i8-1))/(a-b*P(i8-1))
End do
C(i8,j3)=Q(i8)
Do i9=i,2,-1
C(i9,j3)=P(i9)*C(i9+1,j3)+Q(i9)
End do
Do i10=2,i
C_Temp=C(i10,j3)
        f=theta*C_temp+Rho*S(i10,j3-1)
        bl=0.0
        br=C_Temp
760     db=br-bl
        bmid=bl+0.5*db
        f2=theta*bmid+Rho*K*(bmid**n)
              if (f2.gt.f) then
              br=bmid
              else
              bl=bmid
              endif
        if (db.lt.0.001) then
        Go to 750
        else
        GO to 760
        endif
       !End do
750 Continue
!write (*,*) f,f2,db, bmid
!read (*,*)
C(i10,j3)=bmid
S(i10,j3)=K*(C(i10,j3)**n)
```

```
End do
End do
300 write (*,*) 'For BTC enter 1 otherwise 2'
Read (*,*) i20
If (i20.eq.1) Then
Write (*,*) 'Please enter distance (x) for BTC and time'
Read (*,*) i25, j20
Do i30=1,j20
j25=60*i30
Write (*,*) i25,j25, C(i25,j25), S(i25,j25)
Read (*,*)
End Do
Else
write (*,*) 'Please enter a time step to see the results.'
Read (*,*) j4
Do i11=1,i
Write (*,*) i11,j4,C(i11,j4)
read (*,*)
End do
Endif
Go to 300
end subroutine


subroutine TridG
use module1
a=1+Dis*delt/(delx**2)
b=(0.5*Dis*delt/(delx**2))+(v*delt/(4*delx))
d=(0.5*Dis*delt/(delx**2))-(v*delt/(4*delx))
Do j3=2,j+1
alpha(2)=(2-a)*C(2,j3-1)+b*C(1,j3-1)+d*C(3,j3-1)
P(2)=d/a
Q(2)=(alpha(2)+b*C(1,j3))/a
Do i8=3,i+1
Alpha(i8)=(2-a)*C(i8,j3-1)+b*C(i8-1,j3-1)+d*C(i8+1,j3-1)
P(i8)=d/(a-b*P(i8-1))
Q(i8)=(Alpha(i8)+b*Q(i8-1))/(a-b*P(i8-1))
End do
C(i8,j3)=Q(i8)
Do i9=i,2,-1
C(i9,j3)=P(i9)*C(i9+1,j3)+Q(i9)
End do
Do i10=2,i
C_Temp=C(i10,j3)
          f=theta*C_Temp+Rho*S(i10,j3-1)
          bl=0.0
          br=C_Temp
760       db=br-bl
          bmid=bl+0.5*db
         f2=theta*bmid+Rho*(-0.255167+0.065608*pH(i10)-0.002952*Tem(i10)-0.208308*bmid-&
0.004055*(pH(i10)**2)-0.0346705*(bmid**2)+0.000309*pH(i10)*Tem(i10)+0.03062*pH(i10)*bmid+&
0.0099167*Tem(i10)*bmid-0.001144*pH(i10)*Tem(i10)*bmid)
                  if (f2.gt.f) then
                  br=bmid
                  else
                  bl=bmid
```

```
                endif
        if (db.lt.0.001) then
        Go to 750
        else
        GO to 760
        endif
750 Continue
C(i10,j3)=bmid
S(i10,j3)=-0.255167+0.065608*pH(i10)-0.002952*Tem(i10)-0.208308*C(i10,j3)-0.004055*(pH(i10)**2)&
-0.0346705*(C(i10,j3)**2)+0.000309*pH(i10)*Tem(i10)+0.03062*pH(i10)*C(i10,j3)+&
0.0099167*Tem(i10)*C(i10,j3)-0.001144*pH(i10)*Tem(i10)*C(i10,j3)
End do
End do
300 write (*,*) 'For BTC enter 1 otherwise 2'
Read (*,*) i20
If (i20.eq.1) Then
Write (*,*) 'Please enter distance (x) for BTC and time'
Read (*,*) i25, j20
Do i30=1,j20
j25=60*i30
Write (*,*) i25,j25, C(i25,j25), S(i25,j25)
Read (*,*)
End Do
Else
write (*,*) 'Please enter a time step to see the results.'
Read (*,*) j4
Do i11=1,i
Write (*,*) i11,j4,C(i11,j4), S(i11,j4)
read (*,*)
End do
Endif
Go to 300
end subroutine
```