B and Se Transport Modeling in Saturated/Unsaturated Zones

By

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ABSTRACT

There has been renewed interest in the application of models to the transport of non-point source pollutants. However, very little work has been done to evaluate the performance of a functional transient-state model for the transport of a reactive solute over an extensive study period. This research consists of mathematical modeling to simulate water flow, boron and selenium transport through soil in tile-drained croplands.

For Boron part a mathematical model was developed to simulate non-conservative boron transport. The dynamic two-dimensional finite element model simulates water flow and boron transport in saturated-unsaturated soil system, including boron sorption and boron uptake by root-water extraction. Two different models have been employed for the sorption of boron.

Similarly, for selenium part a finite element model is developed to simulate species of selenium transport in two dimensions in saturated/unsaturated zones. The model considers water, selenate, selenite and selenomethionine uptake by plants. It also considers oxidation/reduction, volatilization, and chemical and biological transformations of selenate, selenite, and selenomethionine.

Comparison of boron transport model results with observed data is satisfactory. The model employed with Langmuir isotherm was found to give slightly better simulation results when compared with the model employed with Freundlich. The sensitivity analysis results indicate that the irrigation scheduling and the irrigation water quality are very important parameters for boron accumulation in the soil. Also the adsorption isotherm parameters, which reflect us the soil properties, are found to be important for the boron movement in the soil.

Comparison of selenium transport model with observed data is not quite satisfactory in accuracy when compared with the model for boron transport. This may be the result of the complexity of the mechanisms affecting the selenium transport in soil. There are too many parameters, and due to the errors depending on the parameters, the total error for the estimation of the total selenium increases.

ÖZ

Son zamanlarda noktasal olmayan kaynakların taşınımına yönelik modellerin uygulamasına olan ilgi artmıştır. Ancak reaktif bir kirleticinin, süreksiz zaman için taşınımını kapsamlı bir çalışma süresi için modelleyecek fonksiyonel bir modelin, performansını tespit edecek çalışmaların sayısı çok azdır. Bu çalışma; drenajı yapılmış olan tarım arazilerinde topraktaki su akışının, bor ve selenyum taşınımının matamatik modellemesini kapsamaktadır.

Bor için olan kısımda bor taşınımını modelleyecek bir matematik model geliştirilmiştir. Dinamik iki boyutlu sonlu elemanlar modeli doymuş doymamış toprak sistemlerinde; su akışını ve bor taşınımını sorpsiyon ve bitkilerce kullanımı da dikkate alarak simule etmektedir. Borun sorpsiyonu için iki farklı model kullanılmıştır.

Benzer olarak selenyum için olan kısımda doymuş doymamış bölgelerde selenyum türevlerinin taşınımını modelleyecek iki boyutlu sonlu elemanlar modeli geliştirilmiştir. Model bitkilerce su, selenat, selenit, ve selenometiyonin kullanımını dikkate almaktadır. Aynı zamanda model selenyum türevlerinin oksidasyon/indirgenmesini, gazlaşmasını, kimyasal ve biyolojik dönüşümlerini de dikkate almaktadır.

Bor taşınımı modeli ve buna ait gözlenmiş veriler kıyaslandığında sonuçlar başarılı bulunmuştur. Langmuir izoterminin uygulandığı model sonuçları, Freundlich izotermi ile uygulanan model sonuçlarına nazaran bariz olmayan bir farkla daha iyi netice vermiştir. Hassasiyet çalışmaları da göstermiştir ki, sulama programı ve sulama suyu kalitesi borun topraktaki taşınımını önemli derecede etkileyen parametrelerdir. Aynı zamanda toprağın özelliği hakkında fikir veren adsorpsiyon parametreleri borun toprakta taşınımı açısından önemli bulunmuştur.

Doğruluk dikkate alındığında selenyum taşınımı modelinin gözlenen verilerle uygunluğu bor taşınımı modelininki kadar başarılı sayılamaz. Bu da toprakta selenyum taşınımını etkileyen mekanizmaların kompleksliğinden kaynaklanabilir. Çok sayıda parametrenin bulunması, bu parametrelere ait olan hataların toplamı neticesinde toplam selenyum tahminindeki sapmayı arttırmaktadır.

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CHAPTER 1

INTRODUCTION

Boron(B) is an essential trace element that is required for normal plant growth. The concentration range between deficiency and toxicity is narrow, with yield decrements observed at both insufficient and excessive concentrations. Generally, less than 5% of total soil B is available for crop uptake, which is the reason for the widespread occurrence of B deficiency in the soil. In arid zone soils, B toxicity occurs as a result of high levels of water-soluble B in soils or B additions via irrigation water. As an example about 1/3 of the 0.93 million hectar of irrigated lands in the west side of California's San Joaquin Valley (SJV)(Fig.1.1) contains elevated concentrations of selenium, boron, arsenic and molybdenum (NRC, 1989). The evapoconcentration of drainwaters containing about 300 µg/l of selenium (Se) and its subsequent biomagnifications and bioaccumulation in the aquatic food chain resulted in reduced reproduction, deformity and death of water birds (NRC, 1989).

One of the methods to mitigate the toxicity is to reduce drain-water production. A 6-year investigation of San Joaquin Valley's drainage problem has, among others, recommended improved water management practices to reduce drain-water production. A promising solution to manage the shallow ground water and reduce off-site drain-water disposal is root-water uptake by salt tolerant trees (Bainbridge and Jarrel, 1987). Highly saline waters collected from agricultural subsurface drainage can be reused to irrigate these trees. Such a practice reduces the volume of drain-water that needs to be managed and lowers the saline shallow ground water levels (Tanji and Karajeh, 1993).

Such a agroforestry demonstration site was first monitored in the Murrieta farms SJV, California U.S.A.(Fig.1.1) by a program established by NRCS(Natural Resources Conservation Service) and CDFA(California

Department of Food and Agriculture). Saline subsurface drain-waters from Murrieta Farm's cropland are used to irrigate the Eucalyptus. The drain-waters utilized and that available from the tile drainage system in SJV west side were quite saline, and high in boron, about 10-40 mg/l (Westcot et.al. 1988; Tanji and Dahlgren, 1990).

Symptoms of toxicity in plants are related to high tissue concentrations of B which, in turn, are closely related to concentration of B in the soil. Consequently the management of high B in soils is a must for the health of the plant and crops in agroforestry sites. A model which will simulate the B movement in soil will be very useful for risk assessment and for management purposes. The 1984 discovery of Se toxicosis of birds at the Kesterson National Wildlife Refuge triggered a massive federal/state investigation known as the San Joaquin Valley Drainage Program (SJVDP). One of the objectives of this program was to manage the selenium.

In this study, a 2 dimensional finite element model was developed and used to investigate the B movement in planted and under-drained agroforestry sites. The other objective of this study is to model selenium transformations and transport in two dimensions by Finite Element Method(FEM). By the application of these two models, the eucalyptus plantation, quantitative assessments of the remedial measure of drain water irrigation can be done.

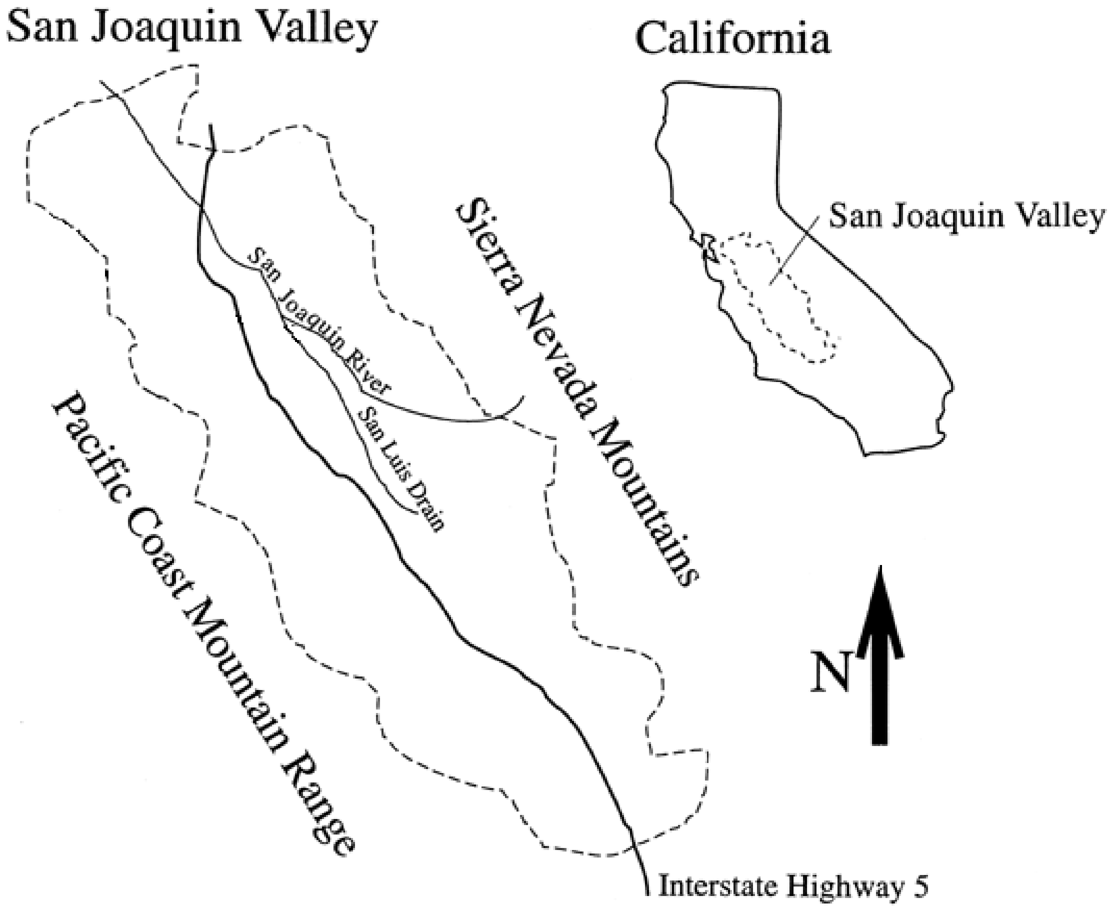

Figure.1.1. The map of San Joaquin Valley

CHAPTER 2

LITERATURE REVIEW

2.1. Background of Boron

2.1.1. Toxicity of Boron:

Availability of quantitative data on element cycles is increasingly recognized as a pre-requisite to assessing potential risks of either inducing long-term deficiency problems or of unacceptable levels of pollutant element accumulation which, in the long-term, could result in toxicity problems to microorganisms and / or higher plants. This is especially true for boron (B), because the acceptable range for water soluble B between deficiency and toxicity is narrow and applications of the element can be toxic to some plants at concentrations only slightly above the optimum for others (Gupta, 1983).

Toxicity of B was first described in barley a long time ago. Symptoms of toxicity, i.e., leaf necrosis, are specific only for barley, but even then may be confused with fungal disease (Jenkin, 1993). Such symptoms are related to high tissue concentrations of B which, in turn, are closely related to soluble B in the soil (Francois, 1992).

Toxicity of B to plants may occur under three main conditions:

-in soils inherently high in B or in which B has naturally accumulated (Severson and Gouch, 1983) ;

-as a result of over fertilization with materials high in B (Gupta et al.,1976) ;

-due to use of irrigation waters with high B concentrations (Branson, 1976.)

Excessive concentrations of B are found very often in saline soils in areas with little or no drainage. Waters containing more than $3.7x10^{-4}$ mol B l^{-1} are generally toxic for all crops (Keren and Bingham, 1985). This corresponds to a concentration of 4 mg/l, so water draining into rivers and ground waters with this boron concentration would be an indication of toxic soil solution.

2.1.2.Some sources of Boron:

Geologically, boron is found as a constituent of axenite, tourmaline, ulexite, colemenite, and kermite (Evans and Sparks, 1983). Sedimentary rocks contain more boron than igneous rocks (Neal 1997).

Some river waters used for irrigation may contain high concentrations of B at certain times of the year due to the contributing springs draining areas high in Boron. Generally, ground waters emanating from light-textured soils contain higher B concentrations than those from heavy textured soils (Jain and Saxena, 1970).

Fly ash is the residue from the combustion of lignite, which enters the flue gas stream and is captured by emission control devices. The ash is subsequently removed, transported, and deposited in open storage areas where it accumulates in large amounts. The usage of fly ash as a fertilizer is also a source for Boron because of the Boron content of fly ash.

Since treating the soil to remove or reduce excess Boron by leaching (Prather, 1977) is not economically feasible, selecting or breeding crop cultivars with high tolerance resistance to B toxicity is a promising approach.

2.1.3.Boron adsorption on soil:

Boron adsorption and desorption in soils are phenomenon that empirical formulas are developed to explain the behavior of B in soil. The sorption can be defined by sorption isotherms. A sorption isotherm is the relation between the amount of metal sorbed and the equilibrium concentration of the element (Joan E. McLean and Bert Bledsoe, 1992). The sorption highly depends on the soil properties. So the laboratory studies must be done to evaluate the sorption parameters in order to get an accurate isotherm for the specified soil type.

Boron adsorption can be described by the adsorption isotherms listed below:

-the Freundlich adsorption isotherm:

$$X = kC^n - X_0 \qquad (2.1)$$

where X is the amount of B adsorbed per unit mass of soil (mg kg^{-1}); C is the equilibrium solution concentration of B (mg L^{-1}); X_0 is the initial adsorbed B concentration (mg kg^{-1}); k, n are empirically fitted parameters.

-the Langmuir adsorption isotherm:

$$X = \frac{b \cdot K_c}{1 + K_c} - X_0 \qquad (2.2)$$

where K_c and B are empirically fitted parameters.

-the kinetic Freundlich equation (Chardon and Blaauw 1998):

$$X = kt^m C^n + B_1 e^{qt} - A \qquad (2.3)$$

where t is time (days), B_1, q, n , m, k (L kg^{-1}) are all empirically fitted parameters.

-the temperature-dependent Langmuir equation:

$$X = \frac{T \cdot p \cdot b \cdot K \cdot C}{1 + K \cdot C} + B_1 e^{qT} - A \quad (2.4)$$

T is temperature (°C); and, b(mgkg^{-1}), K(Lmg^{-1}), A, p, are all empirically fitted parameters.

2.2. Background of Selenium

2.2.1. Toxicity of Selenium:

Selenium belongs to a group of micro nutrient elements required in very small amounts by animals and humans for the basic functions of life. Toxicity and essentiality of Selenium have been widely discussed by many authors (e.g.Forchhammer &Boeck, 1991; Sager,1994 a,b). The concentration of selenium in plants and animals is strongly correlated with its concentration in soils. Plants and products derived from plants transfer the selenium taken up from the soils to humans (Girling, 1984).

As a natural constituent of soil minerals, selenium, Se, is normally present in soil at low concentrations ranging from 0.01 to 2 mg/kg (Dungan and Frankenberger, 1999). Under the agricultural practice of intense irrigation, the Se in these soils can be leached out and further concentrated at locations where drainage water is disposed (Tanjii et al., 1986, 1992; Fujii et al., 1988; Deverel and Gallanthine, 1989). Since Se contamination in soil and water has caused serious damage to the wildlife, a significant amount of research in the past decade has been directed at the study of Se fate and behavior in soil–water systems (Frankenberger and Benson, 1994; Frankenberger and Engberg, 1998).

2.2.2.Properties of Selenium:

As a metalloid, selenium Se has properties of both metals and nonmetals (McBride, 1994). It can exist not only in inorganic forms with various chemical valences, but also as organic compounds in both gas and nongaseous phases. The behavior of Se in soil is therefore extremely complicated, and difficult to predict. Four types of chemical reactions dominate Se transformations in soil, reduction, oxidation, methylation, and demethylation (Doran and Alexander, 1977a; Tokunaga et al., 1994; Zawislanski and Zavarin, 1996; Zhang and Moore, 1997). The speciation of Se is dependent on numerous soil factors such as the redox potential, pH, biological activity, and the presence or absence of complex ligands (Masscheleyn et al., 1990, 1991; Jayaweera and Biggar, 1996).

The production of methylated Se gases from inorganic Se species is a complex chemical process mediated by soil microorganisms. This process involves a series of reduction reactions that transform Se species in higher oxidation states to lower ones. The methylation step then takes place through assimilatory activities of methylating microorganisms (Dungan and Frankenberger, 1999).

Se exists in soils in a number of different forms including elemental selenium, selenides, selenites, selenates and organic selenium compounds (Berrow &Ure, 1989).On account of the existence of different selenium species in soils, total selenium concentrations does not necessarily reflect the extent to which growing plants take up selenium. Nye and Peterson (1975) found that the water-soluble Se of soils correlated better with the uptake of selenium by plants, and this could therefore be used as a measure of the potentially available soil selenium. However, the significance of soil physical-chemical factors such as redox behavior, pH, or microbiological activity in affecting plant selenium uptake is also considerable, the plant availability of Se increases with increasing pH values(Hart .el &Bahners,1988; Pfannhauser,1992a).

In alkaline soils (pH 7.5 –8.5) selenite may be oxidized to soluble selenate ions which are readily available to plants. Whereas, in acid soils (pH 4.5 –6.5) it is usually bound to iron hydroxides, and thus, is unavailable to plants. Many transfer reactions can be promoted by microbial activities, including volatilization losses.

In most aquatic systems, Se can exist in four oxidation states, +VI, +IV, 0, and -II and in several organic forms (Cutter, 1982; Masscheleyn et al., 1989). The solubility and mobility of the Se species is largely dependent on pH and redox conditions (Masscheleyn et al., 1989; Weres et al., 1989). Thermodynamic calculations indicate that selenate, in the highly soluble form SeO_4^{2-} is the stable form of Se in oxic waters. Selenite SeO_3^{2-} is found in less oxic conditions and can be strongly adsorbed by Fe and Mn oxyhydroxides (Balistrieri and Chao, 1990). The microbial reduction of selenate and selenite to elemental Se could be an important mechanism for the incorporation and retention of Se in soils and sediments since Se(0) occupies a large region of the Eh-pH stability field (Garbisu et al., 1996; Oremland et al., 1990; Zhang and Moore, 1997). Similarly, the microbial oxidation of Se(0) to selenite and selenate can play a significant role in oxic soils (Dowdle and Oremland, 1998).

2.2.3.Se transport in soil:

Selenate is the most oxidised chemical species of Se with a chemical valence of 6+ (Se^{6+}). Selenate can be both chemically and biologically reduced into selenite (Se^{4+}), which is then further reduced to elemental (Se^0) or organic Se (Se^{2-}). Methylation of Se is generally considered to occur on reduced Se species with a chemical valence of ≤ 4+, however, the exact order in which the reaction steps occur is still debated (Z.Dungan and Frankenberger, 1999). These simultaneous and sequential Se reactions can be represented by the following conceptual model:

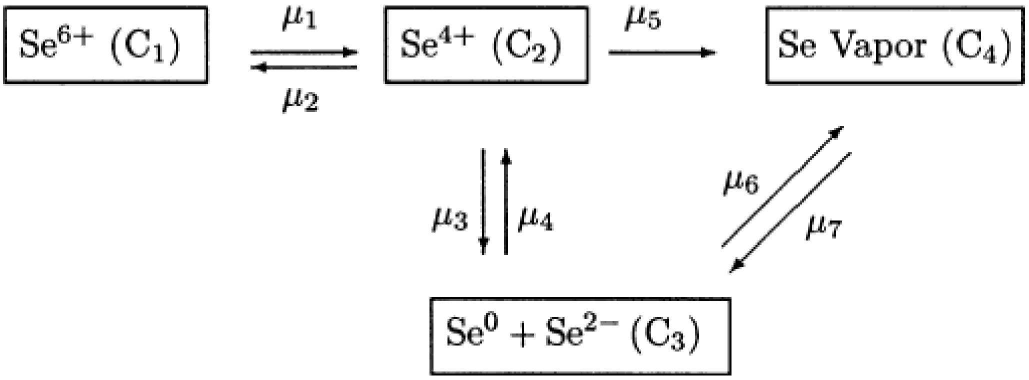

Figure.2.1. Reactions of Selenium in Soil

where μ_i, is the forward or backward reaction rate coefficients among various Se species.

Assuming equilibrium partitioning, no water flow, and that the reactions only occur in solution, the general governing equations depicting the diffusive transport of the four above Se species or fractions in a soil can be written as follows:

$$\frac{\partial C_{1l}}{\partial t}\left(\theta+\rho\cdot K_{d1}\right)=\xi_1\cdot D_1\cdot\frac{\partial^2 C_{1l}}{\partial x^2}+\mu_2\cdot\theta\cdot C_{2l}-\mu_1\cdot\theta\cdot C_{1l} \tag{2.5}$$

$$\begin{aligned}\frac{\partial C_{2l}}{\partial t}\left(\theta+\rho\cdot K_{d2}\right)&=\xi_1\cdot D_1\cdot\frac{\partial^2 C_{2l}}{\partial x^2}+\mu_1\cdot\theta\cdot C_{1l}+\mu_4\cdot\theta\cdot C_{3l}\\&-(\mu_2+\mu_3+\mu_5)\cdot\theta\cdot C_{2l}\end{aligned} \tag{2.6}$$

$$\begin{aligned}\frac{\partial C_{3l}}{\partial t}\left(\theta+\rho\cdot K_{d3}\right)&=\xi_1\cdot D_1\cdot\frac{\partial^2 C_{3l}}{\partial x^2}+\mu 3\cdot\theta\cdot C_{2l}+\mu_7\cdot\theta\cdot C_{4l}\\&-(\mu_4+\mu_6)\cdot\theta\cdot C_{3l}\end{aligned} \tag{2.7}$$

$$\begin{aligned}\frac{\partial C_{4g}}{\partial t}\left(\frac{\theta+\rho\cdot K_{d4}+aK_h}{K_h}\right)&=\frac{\xi_1\cdot D_l}{K_h}\cdot\frac{\partial^2 C_{4g}}{\partial x^2}+\xi_g\cdot D_g\cdot\frac{\partial^2 C_{4g}}{\partial x^2}+\mu_5\cdot\theta\cdot C_{2l}+\\&+\mu_6\cdot\theta\cdot C_{3l}-\mu_7\cdot\theta\cdot\frac{C_{4g}}{K_h}\end{aligned} \tag{2.8}$$

Where the second subscripts l and g refer to the liquid l and gaseous g phases, respectively; x is the distance; t is the time; θ is the volumetric water content; ρ is the bulk density; a is the volumetric air content; K_{dj} is the adsorption coefficient for Se species j; K is the dimensionless Henry's law h constant of Se vapor; D_l and D_g are the dispersion coefficients for the liquid and gaseous phases, respectively; and ξ_l and ξ_g are the tortuosity factors for the liquid and gaseous phases, respectively, which account for the reduced cross-sectional area and increased path length in a soil compared to a pure liquid or gaseous phase.

The values of ξl and ξg can be calculated by various empirical relationships between gas diffusion and soil porosity and volumetric water content (Penman, 1940; Millington and Quirk, 1960; Troeh et al., 1982; Freijer, 1994). Based on Jin and Jury (1996), ξ_l and ξ_g can be calculated using the following equations (Millington and Quirk, 1960):

$$\xi l = \frac{\theta^{10/3}}{\varphi^2} \tag{2.9}$$

$$\xi g = \frac{a^2}{\varphi^{2/3}} \tag{2.10}$$

where φ is the total soil porosity. Eqs. 2.1–2.4 are applicable for soil systems where soil water content is sufficiently high that the solid phase is not directly exposed to the gaseous phase, thus no partitioning occurs between the solid and gaseous phases. It is also assumed that the air phase in the soil is immobile, i.e., the soil air is at atmospheric pressure, and density gradients are negligible.

2.2.4.Adsorption-Diffusion process of Selenium:

Selenium released from a high-level waste repository in deep under-ground may be transported through the surrounding rocks. Understanding the migration behavior of Selenium in the rocks is important in performance assessment of the geological disposal system.

The rocks are classified as fractured or porous media in terms of migration mechanisms and transport models. Porous media can be described based on the assumption that a continuously and homogeneously distributed pore exists in sedimentary rocks in which fractures are not developed. Selenium migrates in porous media with groundwater in connected pore spaces, and interacts with the surrounding solid phase (sorption, etc.). If groundwater movement is sufficiently slow, Selenium transport will be controlled by diffusion. It is necessary to understand sorption and diffusion behavior of Selenium for prediction of their migration in sedimentary rocks.

In the pH range between 2 and 13 sorption behavior of Selenium is usually evaluated using the distribution coefficient, K, which represents the distribution of Selenium between solid and aqueous d phase. The distribution coefficients are generally acquired by two methods, the batch sorption and diffusion experiments. The distribution coefficients obtained by the diffusion experiments using intact rocks close to in situ condition are more realistic than those by the batch experiments. However, most of the distribution coefficients have been acquired by batch experiments because of experimental simplicity. Only few studies for comparing the distribution coefficients obtained by batch sorption and diffusion experiments have so far been reported (Bradbury and Stephen, 1985; Meier et al., 1988; Berry et al., 1994). These results showed little agreement as to consistency between distribution coefficients obtained by batch sorption and diffusion experiments. For example, Bradbury and Stephen (1985) indicated that the batch experiment using crushed rocks might overestimate sorption by as much as one or two orders of magnitude. Therefore, it is necessary to investigate the consistency and the difference between the distribution coefficients obtained by the batch sorption and diffusion experiments.

2.2.5. Sorption behavior of Selenium:

Sorption of Se on tuff samples and some of its constituent minerals, smectite, clinoptilolite, quartz, biotite, pyrite, K-feldspar, chlorite and lignite can be explained by fraction and distribution coefficient. The fraction of sorbed Se and the distribution coefficient can be determined using the following equation, respectively:

$$R_S = \frac{C_b - C_t}{C_b} \cdot 100 \tag{2.11}$$

$$K_d = \frac{C_b - C_t}{C_t} \cdot \frac{L}{S} \tag{2.12}$$

Where R is the fraction of sorbed Se (%), K_d is the distribution coefficient ($m^3\ kg^{-1}$), C_b is the concentration of Se in the blank solution ($kg\ m^{-3}$), C_t is the concentration of Se in the test solution ($kg\ m^{-3}$), and L / S is the liquid solid ratio ($m^3\ kg^{-1}$).

The sorption behavior of Se on minerals can be explained by their point of zero charge (PZC). The minerals with high PZC, such as Fe-oxyhydroxide sorbs Se strongly and the minerals with low PZC, such as quartz sorbs Se weakly. The pH dependencies of Se sorption are dominated by the surface charge of minerals, which depends on pH of solution.

2.2.6. Diffusion behavior of Selenium:

The changes of the concentration of Se with respect to time is expressed by the use of Fick’s law for one-dimensional diffusion as the following equation (Skagius and Neretnieks, 1984),

$$\frac{\partial C_p}{\partial t} = \frac{D_e}{\alpha} \cdot \frac{\partial^2 C_p}{\partial x^2} \tag{2.13}$$

where C_p is the concentration of Selenium in the porewater (kg m^{-3}), t is the diffusing time (s), D_e is the effective diffusion coefficient (m^2 s^{-1}), α is the rock capacity factor ($\alpha=\varepsilon+\rho Kd$), x is the distance from the source in the diffusing direction (m), ε is the porosity, ρ is the dry density of the medium (kg m^{-3}) and K_d is the distribution coefficient (m^3 kg^{-1}).

To solve Eq.(2.5), initial and boundary conditions are specified as follows:

Initial condition:

Cp (t, x)=0, t=0, 0≤x≤L;

Boundary conditions: Cp (t, x)=Co , t>0, x=0; Cp (t, x)=0, t>0, x=L,

The increase in concentration in the measurement cell is given by the following equation (Crank, 1975),

$$C_t = \frac{A \cdot L \cdot C_o}{V} \left[\frac{D_e}{L^2} t - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \cdot \sum_{n=1}^{\infty} \left\{ \frac{(-1)^2}{n^2} \cdot \exp\left(-\frac{D_e n^2 \pi^2 t}{L^2 \alpha} \right) \right\} \right] \tag{2.14}$$

where Ct is the concentration of Selenium in the cell (kg m^{-3}), C_0 is the concentration of Selenium introduced to the cell (kg m-3), A is the cross-section area of the medium (m^2), L is the thickness of the medium (m) and V is the volume of the solutions in the cell (m^3).

For steady state conditions at increased times Eq.(2.6) can be approximated by:

$$C_t = \frac{A C_o D_e}{VL} \left(t - \frac{L^2 \alpha}{6 D_e} \right) \tag{2.15}$$

The effective diffusion coefficient and the rock capacity factor are obtained by adapting Eq.(2.7) for break-through curve. The slope of the break-through curve gives the effective diffusion coefficient.

2.2.7. Reduction of Selenium:

Addition of selenite in aqueous media results in the formation of dissolved Se(IV) species establishing an equilibrium, the state of which depends on solution acidity and temperature. Specifically, the H_2SeO_3, $HSeO_3^-$ and SeO_3^{2-} species, resulting from reactions of SeO_2 with H_2O and H+ , participate in the following acid–base equilibrium, at 25°C:

$H_2SeO_3 \Leftrightarrow HSeO_3^- + H^+$ (pK= 2.46)
$HSeO_3^- \Leftrightarrow SeO_3^{2-} + H^+$ (pK=7.31)

The electro-reduction of H_2SeO_3 and $HSeO_3^-$ takes place according to the following:

$H_2SeO_3 + 4e^- + 4H^+ \Leftrightarrow Se^0$ (s) + $3H_2O$
($E° = 0.740$ V)
$H_2SeO_3 + 6e^- + 6H^+ \Leftrightarrow H_2Se^{-2}$(aq) + $3H_2O$
($E° = 0.360$ V)
$HSeO_3^- + 4e^- + 5H^+ \Leftrightarrow Se^0$ (s) + $3H_2O$
($E° = 0.778$ V)
$HSeO_3^- + 6e^- + 7\,H^+ \Leftrightarrow H_2Se^{-2}$(aq) + $3H_2O$
($E° = 0.386$ V)

Hydrogen selenide reacts rapidly in acidic and intermediate pH but more slowly in alkaline solutions with Se(IV) to give Se (via reactions of the type:

$HSeO_3^- + 2H_2Se \Rightarrow 3Se(s) + 3H_2O$)

2.2.8. Plant uptake of Selenium:

Plants in Se-contaminated soil and sediment can accumulate very large amounts of Se in their tissues (Mikkelsen et al., 1989; Ohlendorf, 1989; Huang and Wu, 1991; Wu et al., 1993). When these plants die, Se accumulates in soil and sediment. Soil and sediment, a major sink of live and dead rooted plants, are the largest reservoir of Se, accounting for more than 90% of total Se (Weres .et al., 1989; George et al., 1996). Of the total Se in sediment, Se associated with organic materials and elemental Se are two major Se pools, accounting for approximately 80% of the sediment Se (Zhang and Moore, 1996). Because of the low availability of elemental Se, Se associated with organic materials is the most available form of Se to organisms. Zhang and Moore (1998) found that concentrations of root-accumulated Se are three times higher than those of surrounding sediment, and approximately 50% of total Se in sediment was in organic materials. Of the total Se present in the tissues of aquatic food chain organisms, Wrench (1978) found that 91% was in organic form. Studies by Besser et al.(1993), Davis et.al. (1988) and Maier et al. (1988) showed that organic forms of Se generally are more toxic than selenite Se IV and selenate Se VI, and bioaccumulate more rapidly Besser et al., (1993). Therefore, information on the speciation of Se in plant and organic materials in soil and sediment is of great relevance to studying the bioavailability of Se in these environments.

2.3. Mathematical statement of groundwater flow :

A complete statement of a 2-dimensional groundwater flow problem consists of four parts:

-specifying the geometry of the 2 dimensional flow-domain
-determining which dependent variable is to be used.
-stating the continuity equation
-specifying the initial and boundary conditions (J.Bear 1979)

2.3.1. Water flow in unsaturated (vadose) zone:

As with the solution of flow problems in the saturated zone, the solution of the partial differential equations of unsaturated flow requires the specification of initial and boundary conditions. The latter are mathematical statements of the space and time distributions of ψ,p,θ depends on the partial differential equation to be solved.

However, unlike the case of saturated flow, the statement of water content distribution alone is not sufficient because $K(\theta_w)$ or $\psi(\theta_w)$ is subject to hysteresis. It is also necessary to state whether a drying or a wetting process is taking place along the boundary.

Initial conditions include the specification of water content (θ_w),pressure (p_w), along the boundaries.

Boundary conditions may be of several types:

-prescribed water content θ_w or head p_w along the boundary. This is a boundary condition of the first type, dirichlet boundary condition. For example, a ponded water on the soil surface, dictating there is a certain water pressure. In a limited situation, we may have a thin sheet of water over the surface so that practically $p_w=0$. Instead, we can always specify the θ_w at saturation, corresponding to $p_w=0$.

-prescribed flux of water at the boundary. This case occurs, for example, when rainfall or irrigation reaches to ground surface, which serves as a boundary to the unsaturated flow domain, at a known rate. For a vertically downward accretion at a known rate N(x,t) we have

$$N \cdot 1 \cdot \boldsymbol{n} = q \cdot 1 \cdot \boldsymbol{n} \qquad (2.16)$$

where 1n is the unit vector normal to the boundary surface.
For the water flux, q, the equation of motion is

$$q_w = K_w(S_w) \cdot \nabla\psi - K_w(S_w) \cdot 1 \cdot \mathbf{z} \tag{2.17}$$

where K_w is the hydraulic conductivity; S_w is the saturation of the soil; ψ is the capillary pressure head($-p_w/\gamma_w$); and z is the unit vector in z-direction.

When we introduce eq.(2.16) into eq.(2.17) for 1**n**≡1**z** we obtain:

$$K_w(\psi)\frac{\partial\psi}{\partial z} = K_w(\psi) - N \tag{2.18}$$

if the rate of accretion, N, is more than the soil can taken up, we may have ponding. This happens when $N=K_0$ (the K at saturation). At that time, θ_w reaches saturation at the surface, pw=0, $\partial p/\partial z=0$, and the downward flow is equal to K_0. If $N>K_0$, ponding(or surface runoff removing part of N) will take place.
The impervious boundary is a special kind of this type of boundary. On it q.**n**=q.1.**n**=0.
-semi pervious boundary: This situation occurs when a thin layer of reduced permeability is formed at the ground surface. When the flow domain is made up of regions of different homogeneous porous media, we require that along the boundary between two media both the flux and the pressure be continuous:
$p_w1=p_w2$; qn1=qn2
This is a boundary of the third type, or a Cauchy boundary condition.

2.3.2. Variably saturated flow:

Water flow in a two-dimensional, isothermal, variably-saturated, rigid porous medium is described with the following form of the Richards equation (Simunek et.al., 1994):

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial x_i}\left[k(h)\left(K_{ij}{}^{A}\frac{\partial h}{\partial x_j} + K_{ij}{}^{A}\right)\right] - S \qquad (2.19)$$

where θ is the volumetric water content; h is the pressure head; S is the sink term; x_i, x_j (i,j=1,2) are the spatial coordinates, t is time, $K_{ij}{}^{A}$ are components of a dimensionless anisotropy tensor K^A, and K(h) is the hydraulic conductivity function.

Soil hydraulic properties are described using van Genuchten's model (van Genuchten, 1980) for the water retention function:

$$S_c(h) = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \frac{1}{(1+|\alpha \cdot h|^n)^m} \qquad h<0 \qquad (2.20)$$

$$\theta(h) = \theta_s \qquad h\geq 0 \qquad (2.21)$$

and the van Genuchten-Mualem model (Mualem, 1976) for the hydraulic conductivity function:

$$K(h) = K_s S_e{}^{0.5}(1-(1-S_c{}^{1/m})^m)^{-2} \qquad h<0 \qquad (2.22)$$

$$K(h) = K_s \qquad h\geq 0 \qquad (2.23)$$

where α and n are shape parameters, S_e is effective saturation, m=1-1/n, θ_r and θ_s are the residual and saturated water contents respectively, and K_s is the saturated hydraulic conductivity.

2.3.3. Solute transport:

There is a similarity between the flow equation and the transport equation. The similarity of the terms can be seen in Table 2.1.

Table.2.1. Analogy of transport and flow equations

Transport equation	Flow equation
Concentration	Pressure head
Solute content	Water content
Convectional transport	Gravitational flow
Hydrodynamic dispersion	Hydraulic conduction
Decay and production terms	Sink and source terms
Specific solute capacity	Specific water capacity

The classical equilibrium model for one-dimensional solute transport during non-steady state flow in a homogeneous porous medium can be expressed in dimensionless form as (S.K. Kamra, B. Lennartz, M.Th. Van Genuchten, P. Widmoser,2000):

$$R\frac{\partial C}{\partial T} = \frac{1}{p}\frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \tag{2.24}$$

where C is the dimensionless concentration, X is dimensionless distance, T is dimensionless time pore volumes , R is the retardation factor, and P is the column Peclet number, expressed as follows:

$$C = C / C_0 \tag{2.25}$$

$$X = z / L \tag{2.26}$$

$$T = V \cdot t / L = q \cdot t / \theta \cdot L \tag{2.27}$$

$$R = 1 + \rho K_d / \theta \qquad (2.28)$$

$$P = V \cdot L / D \qquad (2.29)$$

where C is the solute concentration as a function of time and space and input concentration, respectively (M L^{-3}) , z and L are distance and column length L , t is time (T), V is the mean pore water velocity (L T^{-1}) , q is Darcy water flux (L T^{-1}), ρ is soil bulk density (M L^{-3}) , K_d is the linear adsorption coefficient (LM^{-3}) , θ is the volumetric water content (L^3 L^{-3}), and D is the dispersion coefficient (L^2 T^{-1}).

Solute transport is described generally by the convection-dispersion equation including source/sink terms for transformation processes that follow first and zero order kinetics (Simunek et.al., 1994):

$$\frac{\partial \theta c}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C}{\partial x_i}\right) - \frac{\partial q_i c}{\partial x_i} + \mu_w \theta c + \mu_s s \rho + \gamma_w \theta + \gamma_s \rho - S c_s \qquad (2.30)$$

where c is the solution concentration, s is the sorbed concentration, q_i is the *ith* component of the volumetric flux, μ_w and μ_s are first-order rate constants for solutes in the liquid and solid phases, respectively, γ_w and γ_s are zero-order rate constants for solutes in the liquid and solid phases, respectively, ρ is the bulk density, S is the sink term, c_s is the concentration of the sink term, and D_{ij} is the dispersion coefficient tensor.

CHAPTER 3

A NUMERICAL MODEL FOR BORON TRANSPORT

3.1. Model Development

The computer program consists of several subroutines. Each subroutine serves for different calculations (Figureure.3.1). The main part of the program reads the input data then the subroutine Prep1 generates the FEM mesh according to these data. Subroutine STIFNS adds all of the sink/source terms (calculated in ROOTDNS, ROOTEF, BNDRYF, SOILCH, ROOT, APPLY subroutines) to the global stiffness matrix for water flow. The subroutine ROOTDNS calculates the root density of the plant along the depth. The subroutine ROOTEF determines macroscopic water extraction of the plant. BNDRYF reads boundary conditions from the input data and introduce them into the global matrix. SOILCH evaluates the soil properties (water content, hydraulic conductivity) with respect to van Genuchten formulas. The subroutine CTIFNS adds the sink/source terms to global matrix for mass transport as in the STIFNS subroutine.

Subroutine BORONAD evaluates the B adsorption in the soil with respect to adsorption isotherms.

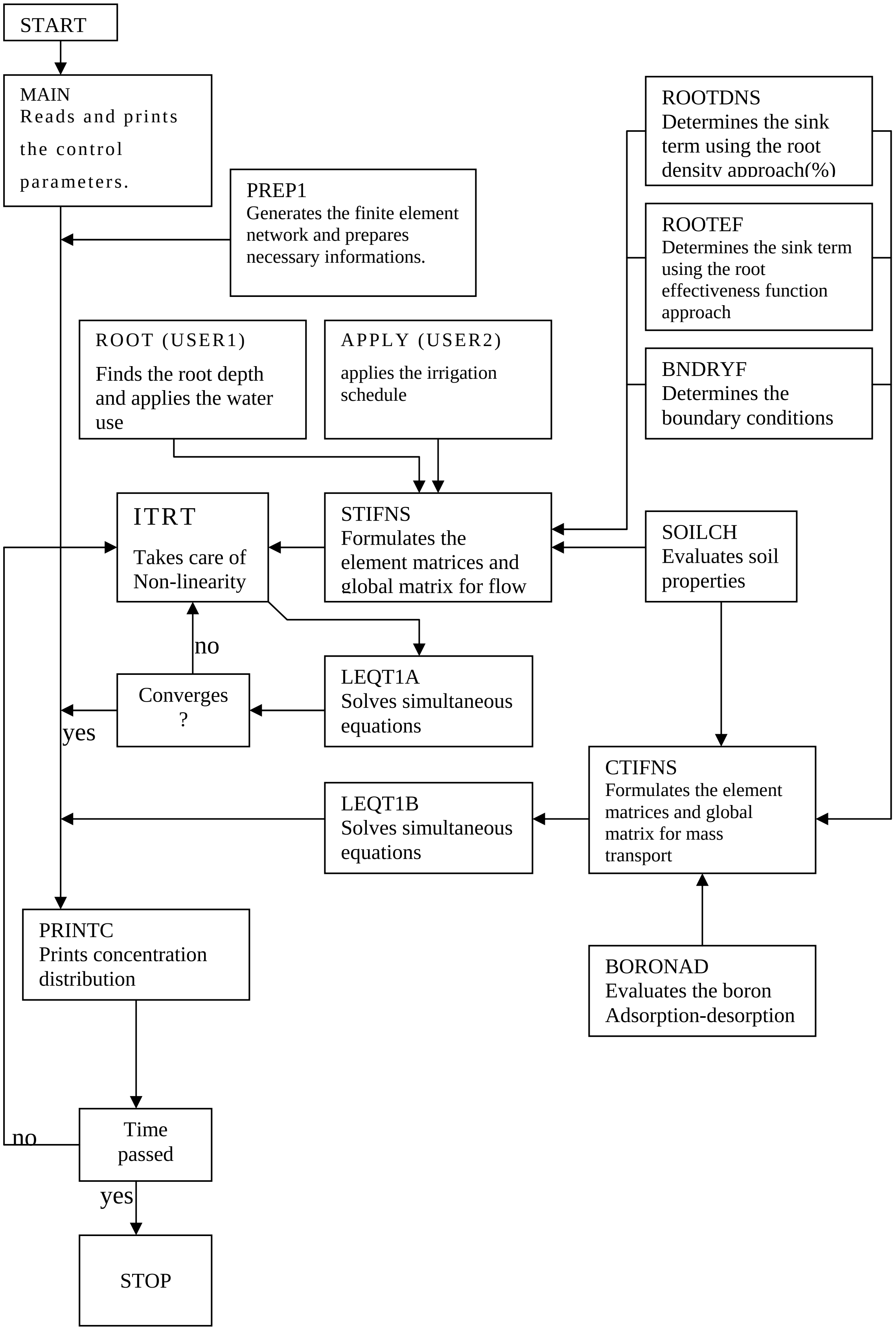

Figure.3.1. Model flow chart for the sequence of computations

3.1.1. Water Flow Submodel

The governing equation describing soil-water flow in two dimensional saturated/unsaturated soil system is given as (Nour el-Din et al., l987a):

$$\left(\lambda \cdot S_s + \frac{\partial \theta}{\partial p}\right) \cdot \frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[K_r \cdot \frac{k_{xx}}{\mu} \cdot \frac{\partial p}{\partial x}\right] + \frac{\partial}{\partial z}\left[K_r \cdot \frac{k_{zz}}{\mu} \cdot \left(\frac{\partial p}{\partial z} - \rho \cdot g\right)\right] \mp Q \quad (3.1)$$

where K_r = relative hydraulic conductivity; k_{xx} = conductivity tensor in x-direction; μ = kinematic viscosity; p = soil-water pressure; k_{zz} = conductivity tensor in z-direction; ρ = fluid density; g = gravitational acceleration; λ = a coefficient (1 = saturated flow; 0 = unsaturated flow); Ss = storage coefficient describing water volume released from storage under a unit decline in hydraulic head; θ = volumetric water content; and Q = the strength of all the sources and sinks in the system such as applied irrigation water rate, water rate extracted by roots and evapotranspiration rate.

Equation (3.1) assumes that air flow is neglected and water is the only fluid in the porous media and Darcy's law is applicable. It also assumes that the soil-water pressure and hydraulic conductivity are continuous functions of soil water content. Equation (3.1) is nonlinear since the hydraulic conductivity and the soil water content are functions of the unknown soil-water pressure. Hence, an iterative procedure is used for solving equation (3.1). The solution of equation (3.1) requires initial and boundary conditions and these are expressed as:

$p(x,z,0) = p_0(x, z)$ for $t=0$ in R (3.2a)

$p(x,z,0) = p_0(x, z)$ for $t>0$ on T_1 (3.2b)

$$-\left[K_r \cdot \frac{k_{ij}}{\mu} \cdot \left(\frac{\partial p}{\partial z} - \rho \cdot g\right)\right] = q_n(t) \qquad \text{for } t>0 \text{ on } T_2, \quad i,j=1,2,3 \qquad (3.2c)$$

where R denotes the entire flow domain and T_1 and T_2 represent the portions of the boundary of the domain. n is the unit normal vector perpendicular to the boundary surface, and q_n is the flux normal to the boundary. Equation (3.2a) describes the initial condition in terms of known soil-water pressure. Equations (3.2b) and (3.2c) are Dirichlet-type, and Neuman-type boundary conditions, respectively. The details of water flow part including initial and boundary conditions, root water-extraction, and soil hydraulic properties can be obtained from Nour el-Din et. al.(1987a), and Karajeh et al. (1991)

3.1.2. Boron Transport Submodel

D-HYSAM which treats dissolved mineral salts as a conservative parameter was extended to consider boron adsorption/desorption process which acts as a source/sink and boron uptake by root-water extraction process which acts as a sink for the boron concentration in the solution phase.

Reactive solutes are considered in this submodel. The transport of solute species is assumed to be in an isotropic porous medium, which is homogeneous with respect to the relevant transport and flow parameters. It is assumed that the solute species do not interact with the medium.

When the conservation law for solute mass is applied for a representative elementary volume of a porous media, the advection-dispersion equation with sink and source terms for boron transport is expressed as:

$$\frac{\partial}{\partial t}\left(\theta \cdot C+\rho_b \cdot K_d \cdot C\right)=\frac{\partial}{\partial x}\left(\theta \cdot D_{xx} \cdot \frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial z}\left(\theta \cdot D_{zz} \cdot \frac{\partial C}{\partial z}\right)-\frac{\partial}{\partial x}\left(q_x \cdot C\right)$$

$$-\frac{\partial}{\partial z}\left(q_z \cdot C\right) \mp C_{sorp} + Q \cdot C_{irr} \mp U_{br} \qquad (3.3)$$

where ρ= bulk density of the porous media; K_d = distribution coefficient; C = boron concentration; D_{xx} = total diffusion coefficient (molecular diffusion plus hydrodynamic dispersion) in the x-direction; D_{zz} = total diffusion coefficient (molecular diffusion plus hydrodynamic dispersion) in the z-direction; q_x = unit flux in x-direction; q_z = unit flux in z-direction; C_{irr} = boron concentration in irrigation water; C_{sorp} = boron content by boron adsorption and desorption in the soil; and U_{br} = boron uptake by root water extraction.

Numerical solution of equation (3.3) requires initial and boundary conditions. As an initial condition boron concentration along the soil profile, is specified when time is equal to zero. The boundary conditions (eq.3.2a, 3.2b, 3.2c) can be specified as Dirichlet-type, Neuman type, and Cauchy type for specified concentration, zero flux, and prescribed flux, respectively.

3.1.3. Boron Sorption Submodels

Two different sorption isotherms were adapted to boron sorption.

3.1.3.1. Langmuir isotherm:

Boron in soils exists partly in the solution and partly in the sorbed phase, and boron fixation in soils may range from temporary to nearly permanent. The more permanently fixed boron is released at a slow rate, and at low concentrations. In this study, readily leaking boron, which includes soluble boron and that part of fixed boron that desorbs easily, was considered. For the prediction of adsorption and desorption of boron, the Langmuir adsorption isotherm (Tanji, 1970) was considered. The Langmuir adsorption isotherm is commonly employed in the practice for modeling boron sorption process. For example: Shani et.al. (1992)

considered a number of sorption models for movement of boron in Utah soils. In their transient solute transport model, they chose to use the Langmuir adsorption isotherm over others because input data for field soils were not readily available for the more sophisticated sorption models.

The Langmuir adsorption isotherm is expressed as (Tanji, 1970):

$$q = \frac{\left(K_{ad} \cdot Q_{adc} \cdot C\right)}{\left(1 + K_{ad} \cdot C\right)} \tag{3.4}$$

where q = boron in the sorbed phase (mg/kg); C = boron in the solution phase (mg/kg); K_{ad} = adsorption equilibrium constant (L/kg), Q_{adc} = maximum adsorptive capacity of the soil for boron (mg/kg).

Boron concentration in the solution phase and boron in the sorbed phase are computed depending upon their initial values, the amount of boron desorbed, and soil water content variable. This can be expresses as (Tanji, 1970):

$$C = C_0 + WY \tag{3.5}$$

$$q = q_0 - Y \tag{3.6}$$

where C_0 = initial boron concentration in the solution phase (mg/L); q_0 = initial boron in the sorbed phase (mg/kg); W = soil water content variable (kg/l); and Y = amount of desorbed boron (mg/kg).

When equations (5) and (6) are substituted into equation (4) the following equation is obtained for the computation of the amount of desorbed boron in any soil column:

$$Y = q_0 - \frac{\left[K_{ad} \cdot Q_{adc} \cdot (C_0 + W \cdot Y)\right]}{\left[1 + K_{ad}\left(C_0 + W \cdot Y\right)\right]} \tag{3.7}$$

Since adsorption and desorption may take place simultaneously at different depths in a soil column, Y has a positive value for desorption and negative value for adsorption. Desorption and adsorption of boron respectively acts as a source and sinks for the boron concentration in the solution phase in a soil column. In the computational procedure, Y is first estimated from equation (7) with K_{ad}, Q_{adc} for that particular element. Then, *C* and q are computed through equations (5) and (6) by substituting *Y* into these equations. For the next time step, *C* and q found from equations (5) and (6) are substituted back into equation (7) as C_0 and q_0, respectively. This procedure is continued for each time step until the end of simulation period.

3.1.3.2. Freundlich isotherm:

The Freundlich adsorption isotherm is expressed as:

$$q = K \cdot C^{1/N} \tag{3.8}$$

where q = boron in the sorbed phase (mg/kg); C = boron in the solution phase (mg/kg); K(l/kg), N = Freundlich parameters which are empirically fitted from experimental data.

When equations (5) and (6) are substituted into equation (8) the following equation is obtained for N=1 for computing the amount of desorbed boron in any soil column:

$$Y = \frac{K \cdot C_0 - q_0}{1 - K \cdot W} \tag{3.9}$$

3.1.4. Boron Uptake Submodels

3.1.4.1. Rootdns submodel:

In this submodel the root density of the plant is evaluated. Plant roots are assumed to have full depth of penetration equal to the root zone depth down to the surface of the water table. The root extraction pattern is variable with depth (Figure.3.3.) Field root analysis for eucalyptus has been also used to represent the root distribution of eucalyptus trees in an agroforestry system. Root water uptake is considered as a series of sinks distributed among the nodal points in the root zone, and the extend of the extraction is proportionally calculated according to the water requirements at that time. This extraction patterns varies with the root density distribution.

3.1.4.2. Rootef submodel:

In this submodel, a macroscopic root extraction approach is described as an analogy of Ohm's law in which the flux (q) is proportional to a potential difference ($\Delta\phi$) and inversely proportional to resistance (R_s):

$$q = -\frac{\Delta\phi}{R_S} \qquad (3.10)$$

The unit flow rate of water from the soil to the root at any point in space and time is equal to the soil-water and root-water pressure difference divide by a combined root and soil- water flow resistivity:

$$Q = \frac{P - P_r}{R_S} \qquad (3.11)$$

Molz (1976) has considered the effect of the soil-water salinity on the water extraction by

$$Q = \frac{P - P_r + P_0}{R_S} \tag{3.12}$$

in which P is the soil water pressure, P_r is the root water pressure and P_0 is the osmotic pressure, and R_s can be approximated as:

$$R_S = \frac{1}{K_r \cdot K_{Sij} \cdot b} \tag{3.13}$$

where K_r is relative hydraulic conductivity, K_{Sij} is the hydraulic conductivity tensor and b is the root effectiveness function.

Substituting equation (13) in (12), the root extraction sink term becomes:

$$Q = K_r \cdot K_{Sij} \cdot \left(P_s - P_r + P_0\right) \cdot b \tag{3.14}$$

The root effectiveness term is a shape function which accounts for the physics of the root uptake and it is evaluated and defined in many different ways in the literature (Gardner, 1964; Whisler et al., 1968; Nimah and Ranks, l973a; and Karajeh et al., 1994). In this study the formulation of Karajeh et.al. (1994) was employed. Karajeh et.al. (1994) experimentally evaluated the root effectiveness function for Eucalyptus trees by taking the ratio between the root length increments in the soil profile to the bulk volume of the root zone per tree (Figure.3.2.) The resulting expression for the root effectiveness function obtained by Karajeh et al. (1994) for Eucalyptus is a third degree polynomial:

$$b = 57.41 - 0.88 \cdot d + 5.32E - 3 \cdot d^2 - 1.15 \cdot d^3 \qquad (3.15)$$

where d is the soil depth(cm); b is the root effectiveness function.

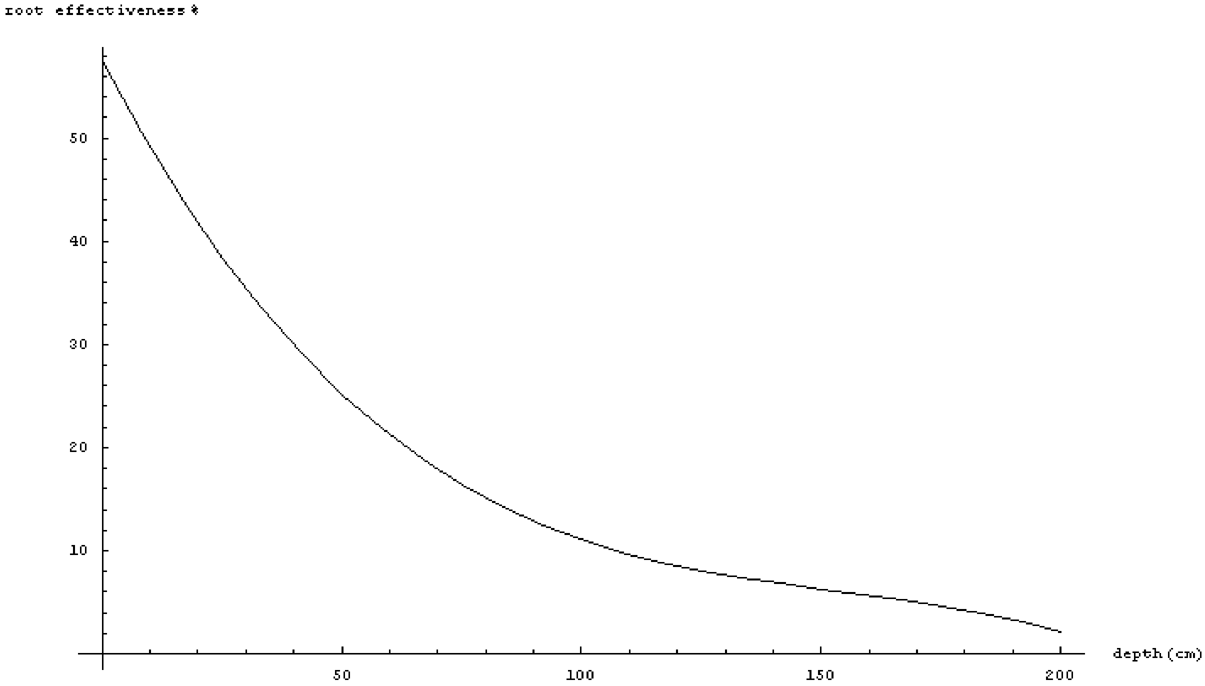

Figure 3.2. Root effectiveness function

Osmotic pressure is obtained from:

$$P_0(atm) = -4.5E - 4 \cdot C(mg/l) \qquad (3.16)$$

Because the change in concentration is very small between successive time steps, C is taken as the concentration at the previous time step.

Boron uptake by root water extraction can be formulated as analogous to nitrate uptake by plants described by Tanji and Mehran (1979):

$$U_{br} = \lambda_{ad} \cdot C \cdot Q_r / \theta \qquad (3.17)$$

where ,λad = root absorption coefficient, which can be set unity if boron uptake is assumed to be proportional to root water extraction; Q_r = rate of root water extraction; and θ = soil water content.

The rate of root water extraction Q_r is expressed in many different ways in the literature (Nimah and Hanks, 1973; Molz and Remson, 1970; Gupta et al., 1978b; and Karajeh et al., 1994). In this study, the method of Karajeh et al. (1994) is employed and expressed as:

$$Q_r = K_r \cdot K_{s_{ij}} \left(p - p_r + p_0\right) \cdot b \tag{3.18}$$

where Kr = relative hydraulic conductivity; K_{sij} = saturated hydraulic conductivity tensor; p = soil water pressure; p_r = root water pressure; p_o = osmotic pressure; and b = root effectiveness function.

In equation (11), all the diagonal components of the saturated hydraulic conductivity tensor are implicitly assumed to be zero (Davis and Neuman, 1983). The root water pressure p_r is equal to the soil wilting point pressure head of -150m of water (Davis and Neuman, 1983). The osmotic pressure p_0 (atm) is equal to -4.5E-4 C_s. (C_s is in mg/L which is the salt concentration in the solution phase in the crop root-zone) (Tanji, 1990).

Equation (12) and (Figure.3.3) indicate that water extraction by roots is higher at the top part of the soil depth. About 40% of the water extraction occurs at the top 25% of the root depth; about 70% of the water extraction occurs at the top 50% of the root depth, etc.

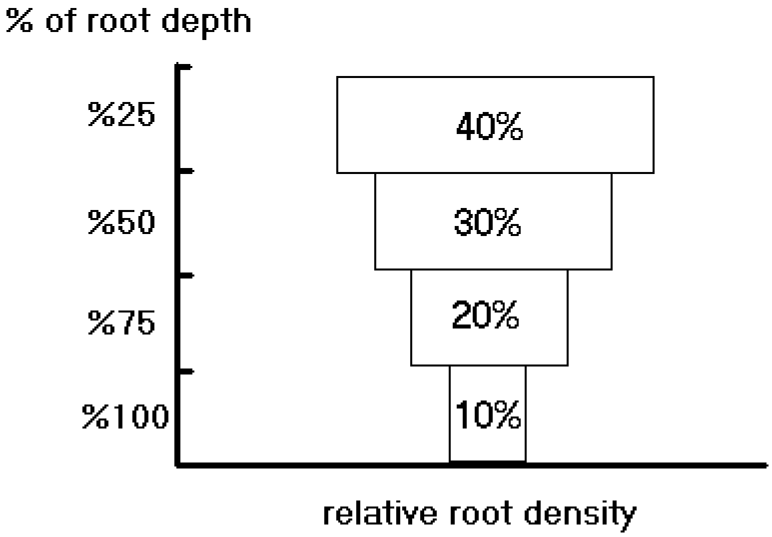

Figure.3.3. The relative root water extraction of eucalyptus tree

Equations (1) and (3) describing water flow and boron transport in a soil column (crop root zone) are solved numerically by employing finite element method (FEM). The existing FEM code developed by Nour el-Din et.al(1987a) was extended in this study by coding and incorporating subroutines related to boron sorption and boron uptake by root water extraction processes into the main program.

3.1.5. Soil Hydraulic properties submodel:

The soil has been assumed to have uniform and homogeneous soil hydraulic properties throughout the depth. The soil pressure head was measured with a tensiometer assuming solute equilibrium between the soil solution and porous cup. In order to relate saturation to relative conductivity, van Genuchten's formulas have been utilized:

$$\theta = \theta_r + \frac{\theta_s + \theta_r}{\left[1 + \alpha \cdot P^n\right]^m} \tag{3.19}$$

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r} \tag{3.20}$$

$$K_r = K_s \sqrt{S_e}\left\{1-\left(1-S_e^{\frac{1}{m}}\right)^m\right\}^2 \tag{3.21}$$

where θ_s, θ_r are the saturated and residual field volumetric water contents, respectively; K_s is the saturated hydraulic conductivity; n and m are statistical parameters, and S_e is the reduced water content.

3.2. Numerical Approach:

Equations 1 and 3 together with their appropriate initial and boundary conditions are solved by the Galerkin method in conjunction with a finite element discretization scheme. Using the Finite Element Method (FEM), the region is subdivided into a network of rectangular elements. The corners at these elements are designated as nodal points and the trial solution for the governing equation is assumed at each node. The errors or residuals resulting from this approximation are minimized by integrating over the entire domain, which giving us the better results.

Let Π(x,z,t) be the trial pressure solution for the variably-saturated flow governing equation (note that the same procedure applies also to the transport equation):

$$\Pi(x,z,t) = \sum_{i=1}^{NPT} \Pi_i(t) \cdot N_i(x,z) \tag{3.22}$$

where Πi(t) is a set of trial pressure parameters at a given time t to nodal points(NPT). Ni(x,z) is a set of shape (basis) function. The shape functions are polynomials with a value of unity at node (i) and zero for all other nodes.

They are, by choice, continuous over the element boundaries, and are to be able to satisfy the boundary conditions at each element. In this case, four point rectangular elements are used along with linear interpolation. Substituting the trial solution Π in the governing equation (3.1), the residual, r, may be defined as:

$$r=\frac{\partial}{\partial x}\left(K_r\cdot\frac{k_{xx}}{\mu}\cdot\frac{\partial\pi}{\partial x}\right)+\frac{\partial}{\partial x}\left(K_r\cdot\frac{k_{zz}}{\mu}\cdot\frac{\partial\pi}{\partial z}\right)-K_r\cdot\frac{k_{zz}}{\mu}\cdot\rho\cdot g-\left(\lambda\cdot S_s+\frac{\partial\theta}{\partial P}\right)\cdot\frac{\partial\pi}{\partial t}$$

$$+\left(K_rK_{s11}\left(\pi-p_r+p_0\right)b'\right) \tag{3.23}$$

The residual due to a basis function N_i is defined by integrating over the area of the element:

$$R_{im}=\sum_{m=1}^{NE}\iint A_m\cdot(r)\cdot dx\cdot dz \quad \text{, i=1,2,...NPT} \tag{3.24}$$

where A_m is the area of the element m.

By introducing the Ni(x,z),the shape functions, into Π(x,z,t) (Davis et.al., 1983; Nour el-din, 1986; and Tracy, 1989), a set of element equations is arrived at with

$$[A]\cdot\{P(t)\}+[B]\cdot\left\{\frac{\partial P(t)}{\partial t}\right\}-\{S\}+\{F\}=0 \tag{3.25}$$

in which [A] and [B] are NPT*NPT square matrices, and {S} and {F} are vectors of length NPT. The definition of each matrix may be stated as:

$$A_{ij}=\sum_{m=1}^{NE}\iint A_m\cdot\left\{-K_r\frac{k_{xx}}{\mu}\left(\sum_{j=1}^{NPT}\frac{\partial N_j}{\partial x}\right)\frac{\partial N_i}{\partial x}+K_r\frac{k_{zz}}{\mu}\left(\sum_{j=1}^{NPT}\frac{\partial N_j}{\partial z}\right)\frac{\partial N_i}{\partial z}\right\}dxdz \tag{3.26}$$

where [A] is called element conductivity matrix,

$$B_{ij}=\sum_{m=1}^{NE}\iint A_m\left\{\left(\lambda\cdot S_s+\frac{\partial\theta}{\partial P}\right)\cdot N_i\right\}dxdz, \qquad \text{if i=j} \tag{3.27a}$$

$$B_{ij} = 0, \qquad \text{if } i \neq j \tag{3.27b}$$

where [B] is the element capacitance storage matrix,

$$S_i = \sum_{m=1}^{NE} \iint A_m \left\{ K_r \frac{k_{zz}}{\mu} \rho \cdot g \right\} \frac{\partial N_i}{\partial z} dxdz \tag{3.28}$$

$$F_i = \sum_{m=1}^{NE} \left(\sum_{all} Q_i \cdot N_i - \sum_{l=1}^{Nl} \int_{l_b} N_i \cdot q_n \cdot d\tau \right) \tag{3.29}$$

where q_n is the value of Neuman-type boundary conditions and q_n is equal to zero at interior nodes or at the impervious boundaries. The summation of S_i and F_i produces the element load vector. The integration included in these matrices are evaluated numerically. Following the evaluation of matrices's coefficients for all elements, a global matrix is formed and solved for each time step.

3.2.1. Time derivative:

In general, there are three ways to approximate the time derivative of the water flow governing equation: forward difference, central difference, or backward difference. Of these three, the backward difference method has proven to be unconditionally stable (Neuman, 1983). This scheme may be represented as follows:

$$\frac{\partial P}{\partial t} = \frac{1}{\Delta t} \left(P_{(t+\alpha\Delta t)} - P_t \right) \tag{3.30}$$

where Δt is the time step, and α is a factor indicating scheme type with 1 for implicit backward and 0.5 for central difference. The pressure is defined at any point as:

$$P_{(t+\alpha\Delta t)} = \alpha P_{(t+\Delta t)} + (1+\alpha) P_{(t)} \tag{3.31}$$

This scheme assumes that the pressure change linearly within a time step. Moreover, a better approximation results if the pressure is allowed to change somewhat within the time increment. In this case a linear variation is utilized.

3.3. Model Application:

3.3.1. Background:

Mendota I

The Mendota site (Murrieta farms) was the first monitored agroforestry demonstration program established by NRC (National Research Council) and CDFA (California Department of Food and Agriculture). Several lines of Eucalyptus camendulensis were planted in 1985 and 1986. The trees were surface irrigated with drainage waters collected from croplands about two years after planting. The under drainage system was installed in 1987. The trees performed remarkably well until they suffered a killing frost damage in December 1990.

Mendota II

Following the killing frost of 1990 at the Mendota site and subsequent harvest of the trees, several lines of frost-tolerant, salinity-tolerant eucalyptus trees were planted in 1992. The experimental site was redesigned, automated for water flows and the soils were also leached. Detailed monitoring was initiated in June 1994.

3.3.2. Site description:

The agroforestry site (7 m in horizontal direction and 3 m in vertical direction) which contains Eucalyptus trees was constructed. The site was assumed to have tile drainage at a depth of 210 cm. The assumed irrigation application and evapotranspiration rates and irrigation schedule are given in Table.3. and Table.4. The irrigation water was applied for 24 hours every 10days. The cumulative applied irrigation during the 220-day period was 121 cm with an estimated irrigation efficiency of 75%. The boron concentration in the applied irrigation water is assumed to be 12 mg/l. The 6-year old eucalyptus had a maximum root penetration of 2.1m. The evapotranspiration rates during this period is presented in Table.3

The soil profile consists of silty clay to clay textures with bulk density of 1.385g/c^3. For the 0-60 cm layer and 60-210 cm soil layer respectively are referred as soil layer 1 and 2. The profile is underlain by impermeable clay layers of very low hydraulic conductivities at a depth of 3 meters. Table.5. gives the parameters used to generate the relationship for the two soil layers included in the study.

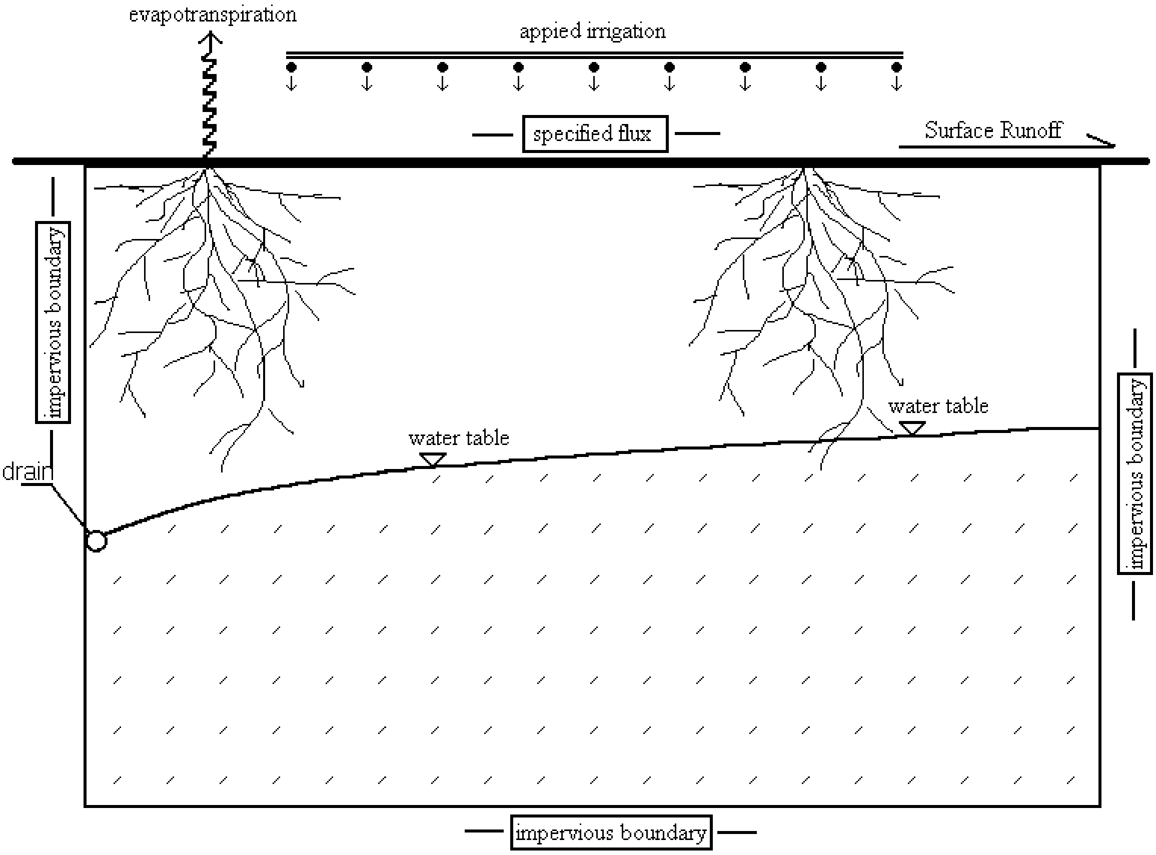

Figure 3.4. Cross section of the agroforestry site

3.3.3. Finite element discretization and initial conditions:

The finite element network (Figure.3.5.) consists of 616 elements and 669 nodes. The vertical and the horizontal dimensions are made small in the vicinity of the drain where large hydraulic gradients are expected to occur, and large at the bottom of the saturated zone where these gradients are expected to be relatively small. The boundary condition at the upper surface is treated as a Cauchy-type boundary where the applied irrigation is considered to be constant for all irrigation events. At the vertical drain side, the upper half adjacent to the drain tube has a Dirichlet type boundary (specified head). The bottom and remaining vertical sides are assumed to have impervious boundaries.(Figure.3.4.)

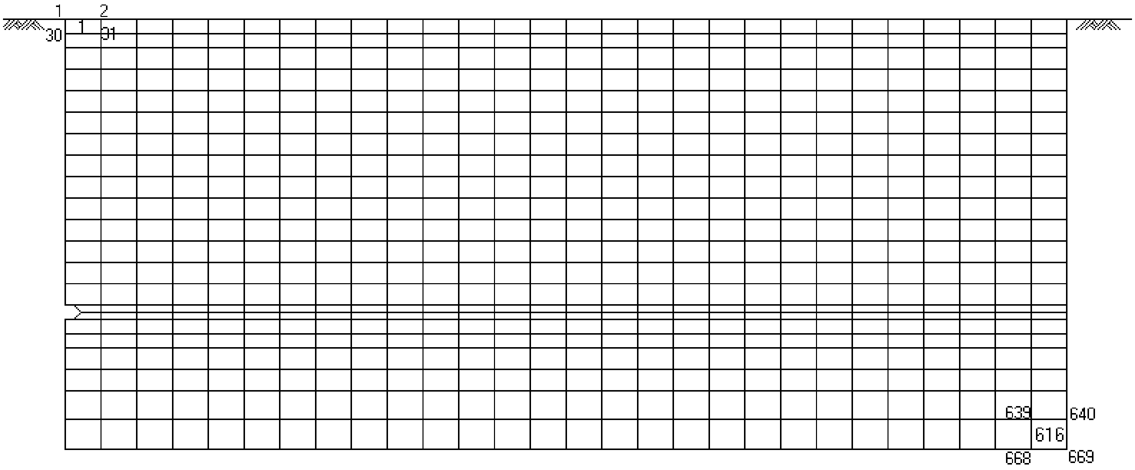

Figure 3.5. The finite element mesh with 616 elements and 669 nodes

3.3.4. Some parameters and input data used in the model:

Tanji (1970) performed laboratory studies on boron equilibrium in different soils by adding solution boron at rates of 2 to 50 mg/L. He determined Langmuir constants K_{ad} and Q_{adc} for each soil by the procedure described by Hatcher and Bower (1958) and Freundlich parameters by soil column experiments.

Table 3.1. Langmuir constants of different soil types (Tanji, 1970)

Soil type	K_{ad}	Q_{adc}
Sandy loam	0.046	10.8
Silt loam	0.038	20.1
Clay loam	0.088	6.7

Table 3.2. Freundlich constants of different soil types (Tanji, 1970)

Soil type	**K**	**1/n**
Sandy loam	0.66	0.6
Silt loam	0.50	0.8
Clay loam	0.56	0.9

Table 3.3. Irrigation rates

Time (day)	Irrigation rate (cm/day)	Time (day)	Irrigation rate (cm/day)
0.2-1.2	3.13	54.2-55.2	5.33
10.2-11.2	3.13	65.2-66.2	7.96
21.2-22.2	3.13	76.2-77.2	7.96
32.2-33.2	5.33	87.2-88.2	8.04
43.2-44.2	5.33		

Table 3.4. Evaporation rates

Time (day)	Evaporation rate (cm/day)
0-30	0.461
30-61	0.537
61-91	0.64
91-121	0.61

Table 3.5. Soil hydraulic parameters

Soil type	θ_r	θ_s	α	n	S_s	K_s	ρ_b
1	0.02530	0.425	0.0250	1.65	0.0002	13.3	1.385
2	0.02525	0.425	0.0129	1.98	0.0002	13.3	1.385

3.4. Sensitivity Analysis:

The purpose of sensitivity analysis is to identify those input factors that most strongly affect the model's response and to determine a good precision of inputs and constants used in the model.

In the sensitivity analysis the effects of some model parameters on boron distribution in the system have been investigated. For this purpose a small mesh consisting of 96 elements and 121 nodes was prepared. Here, the parameters included in the sensitivity test are:

- simulation time
- langmuir parameters
- freundlich parameters
- concentration of irrigation water
- λ, the root absorption coefficient
- number of irrigations

3.4.1. Simulation time:

In the sensitivity analyses for time, the simulation time was chosen as 75 days and the Boron concentration of the irrigation water was 8.4 mg/l. Figure.3.6 shows that the most important thing effecting the Boron distribution is the applied number of irrigation rather than the simulation time.

There is an irrigation in every 10 days resulting a peak in the Boron concentration.

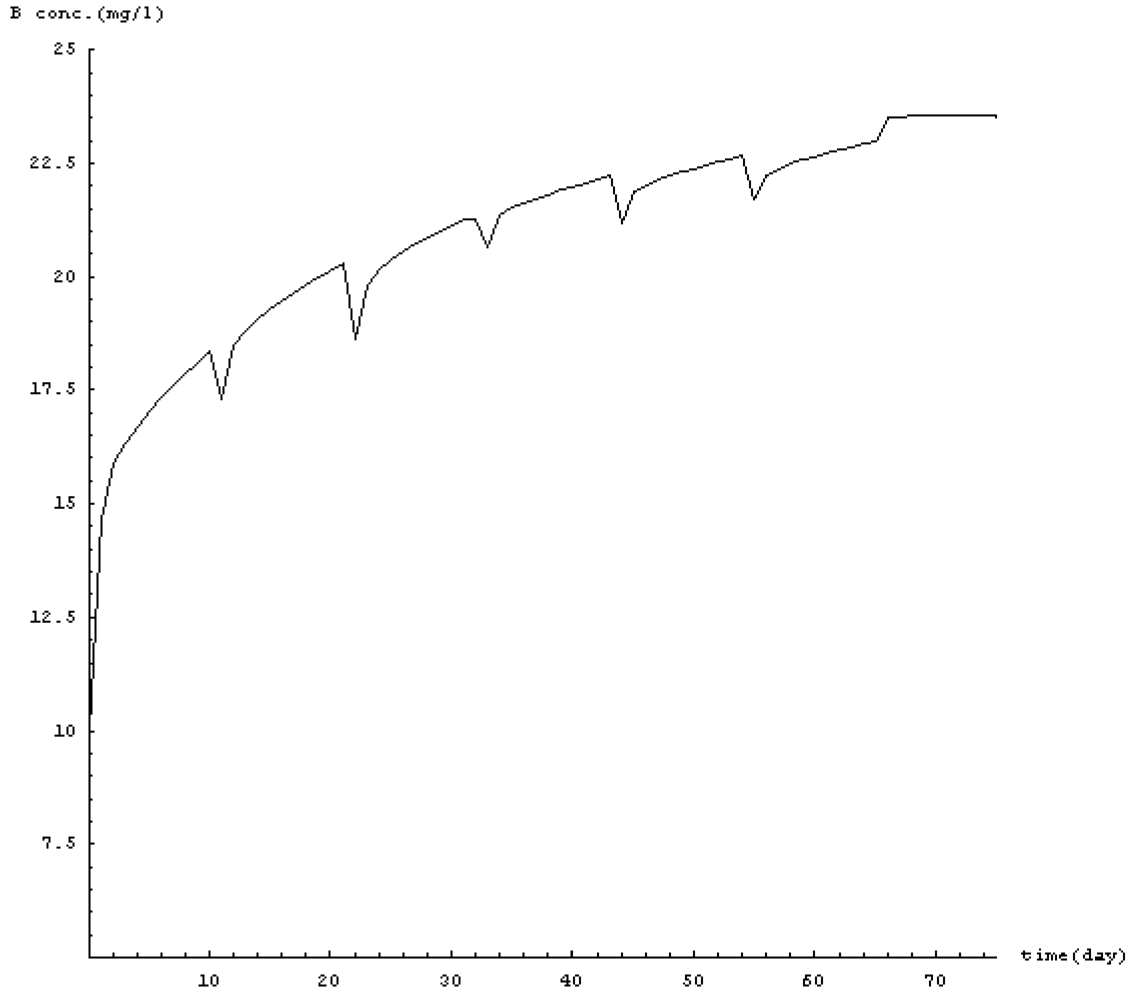

Figure 3.6. Boron concentration along the simulation time

3.4.2. Langmuir parameters:

K_{ad} and Q_{adc} are defining the soil properties of Langmuir isotherm for the Boron sorption-desorption process.

3.4.2.1. Adsorption equilibrium constant,(K_{ad}):

For the K_{ad} analysis the simulation period was chosen as 20 days. The Boron concentration irrigation water was 8.4(mg/l). The effect of K_{ad} on the sorption of Boron on the soil media was found to be very important. As it can be seen from (Figure.3.7) the increase of K_{ad} results in lower concentration distribution in soil phase especially for the unsaturated (vadose) zone.

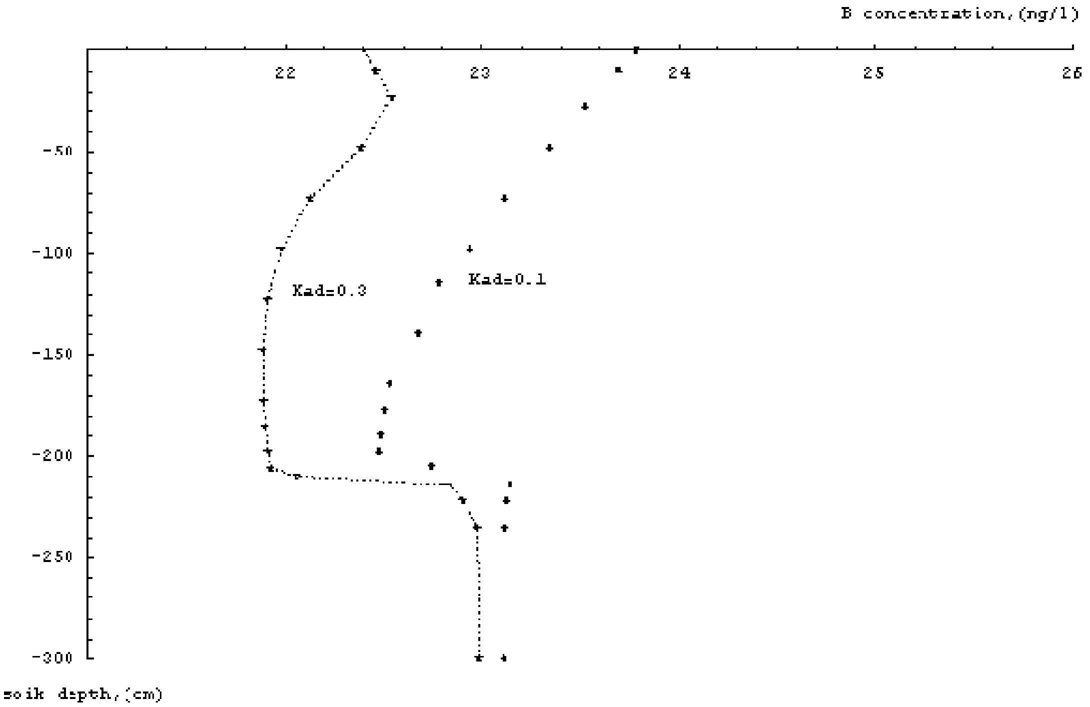

Figure 3.7. The effect of K_{ad} on Boron concentration distribution

3.4.2.2. Maximum adsorptive capacity,(Q_{adc}):

For the Q_{adc} analysis the simulation period was chosen as 60 days. The Boron concentration of the irrigation water was 8.4(mg/l). Q_{adc} is also important for determining the ratio of sorbed Boron concentration in soil media. Figure.3.8 shows that the increase of maximum adsorptive capacity results in lower concentration distribution in soil.

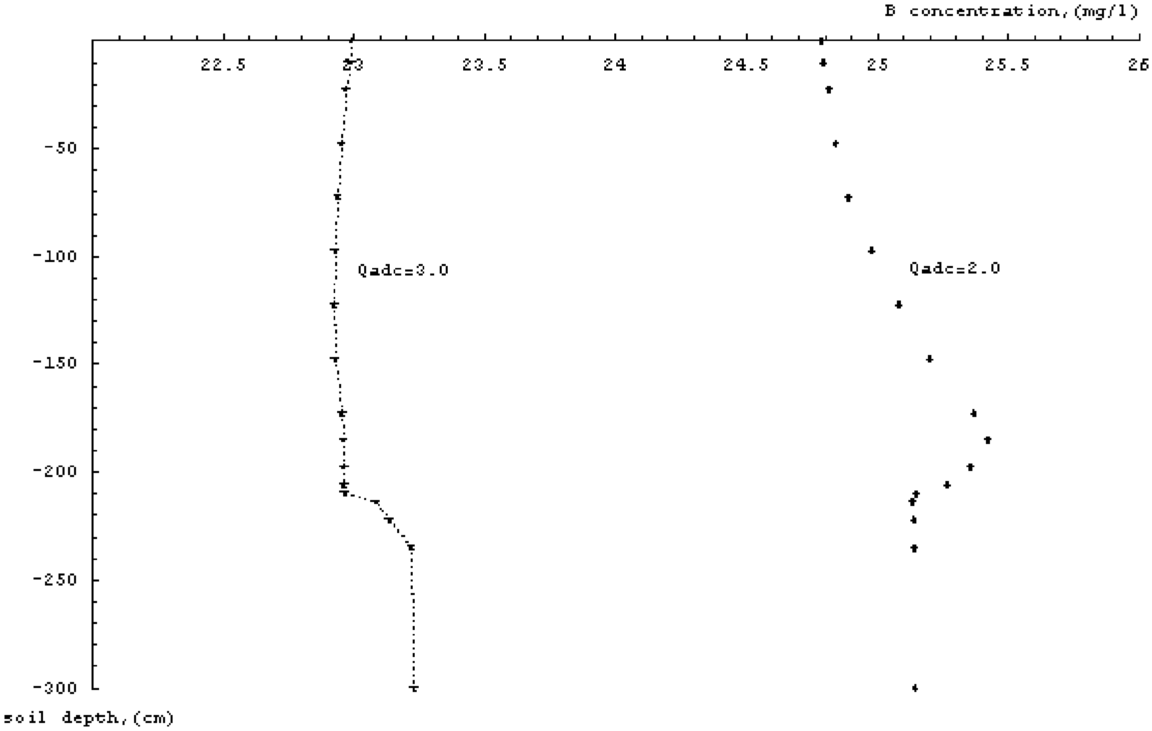

Figure 3.8. The effect of Q_{adc} on Boron concentration distribution

3.4.3. Freundlich parameter,K:

For the freundlich parameters the simulation period was chosen as 20 days and the boron concentration of irrigation water was 8.4 mg/l. Since the freundlich equation is already linearized, in sensitivity analyses only the effect of parameter K, was investigated.

The decrease of parameter K has shown a higher B concentration accumulation along the soil depth, which can be seen in Figure.3.9.

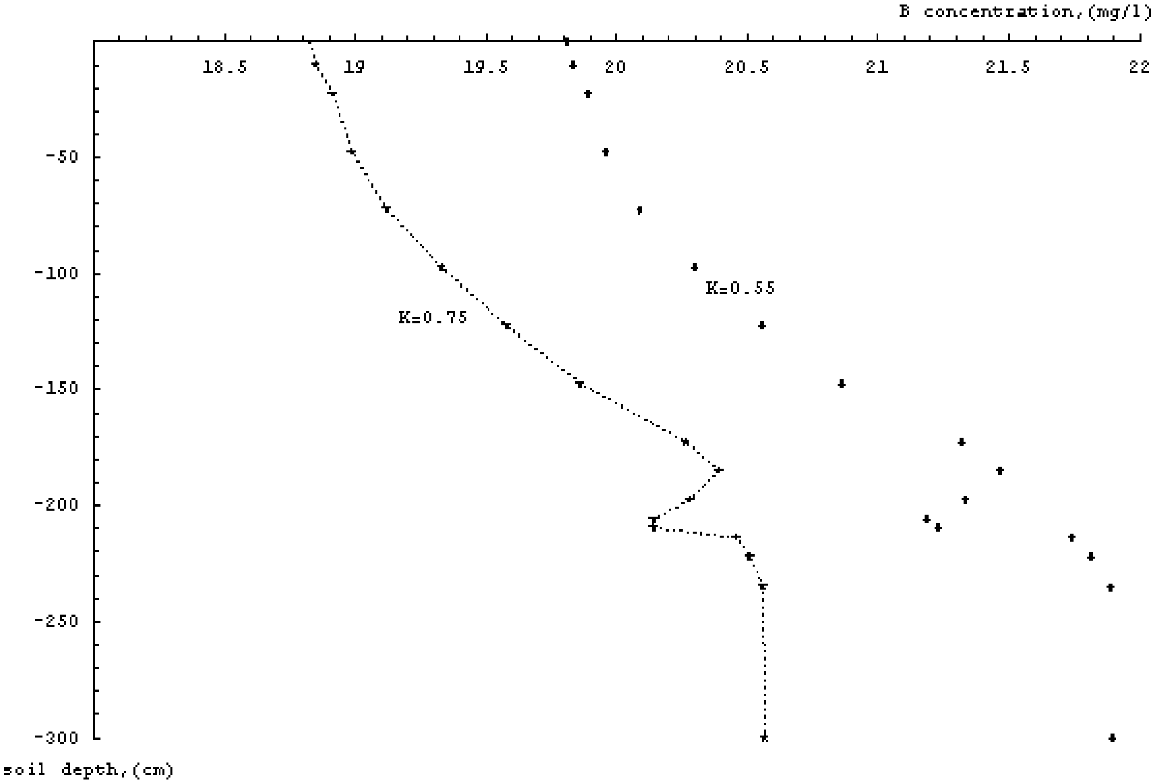

Figure.3.9. The effect of parameter K on Boron concentration distribution

3.4.4. Concentration of irrigation water,(C_{irr}):

For the C_{irr} analysis, the simulation period was chosen as 20 days. The Boron concentration of the irrigation water was 8.4(mg/l). Surely the concentration of irrigation water will affect the accumulation of Boron in soil.

As seen in Figure.3.10, 2 mg/l increase in Boron concentration in applied water results in a small increase in boron distribution of sorbed phase.

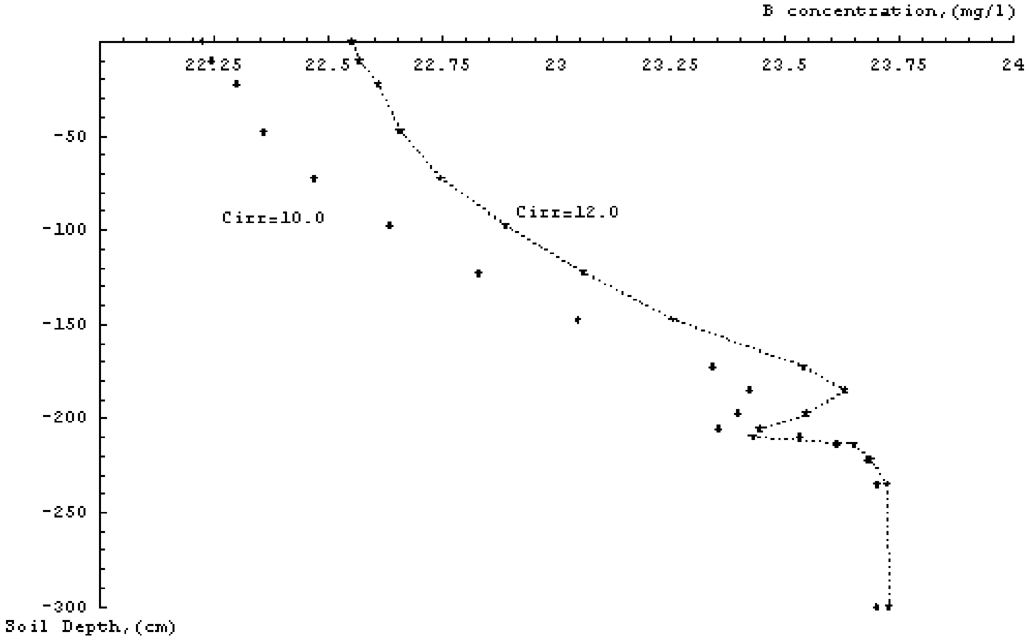

Figure 3.10. The effect of C_{irr} on Boron concentration distribution

3.4.5. Root absorption coefficient, λ:

As seen in Figure.3.11, as the root absorption coefficient increases the boron concentration decreases, which means as the plant uptakes the boron the accumulation of boron in soil decreases.

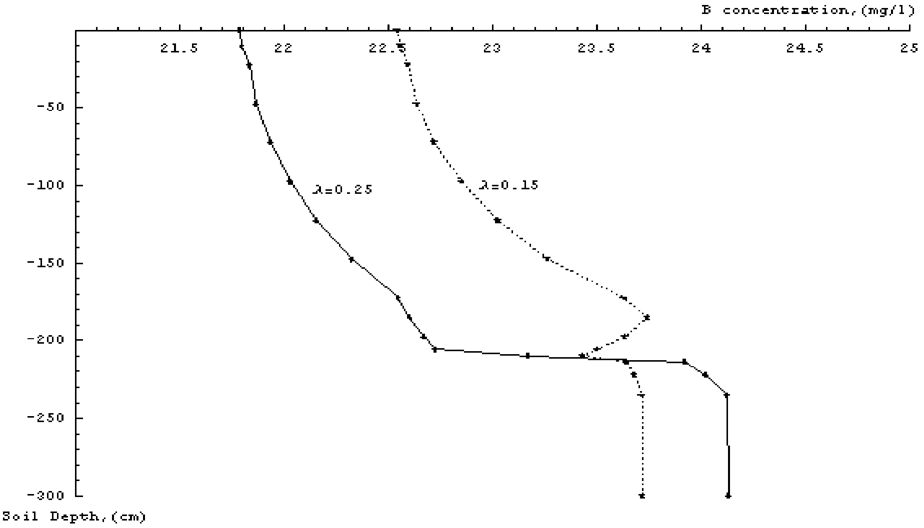

Figure 3.11. The effect of root absorption coefficient on B concentration distribution

3.4.6. Model Application to Laboratory Experiments

The model was applied to investigate the boron concentration behavior in three different soils, sandy loam, silt loam, and clay loam.

As seen in Figure.3.12 the boron concentration in the solution phase is lower in silt loam than that in sandy loam and clay loam. That means boron adsorption is higher in silt loam than that in the other soils. It is also seen in Figure.3.12 that, though the boron adsorption is higher in clay loam than that in sandy loam, this difference is not significant. These results are in agreement with Tanji (1970).

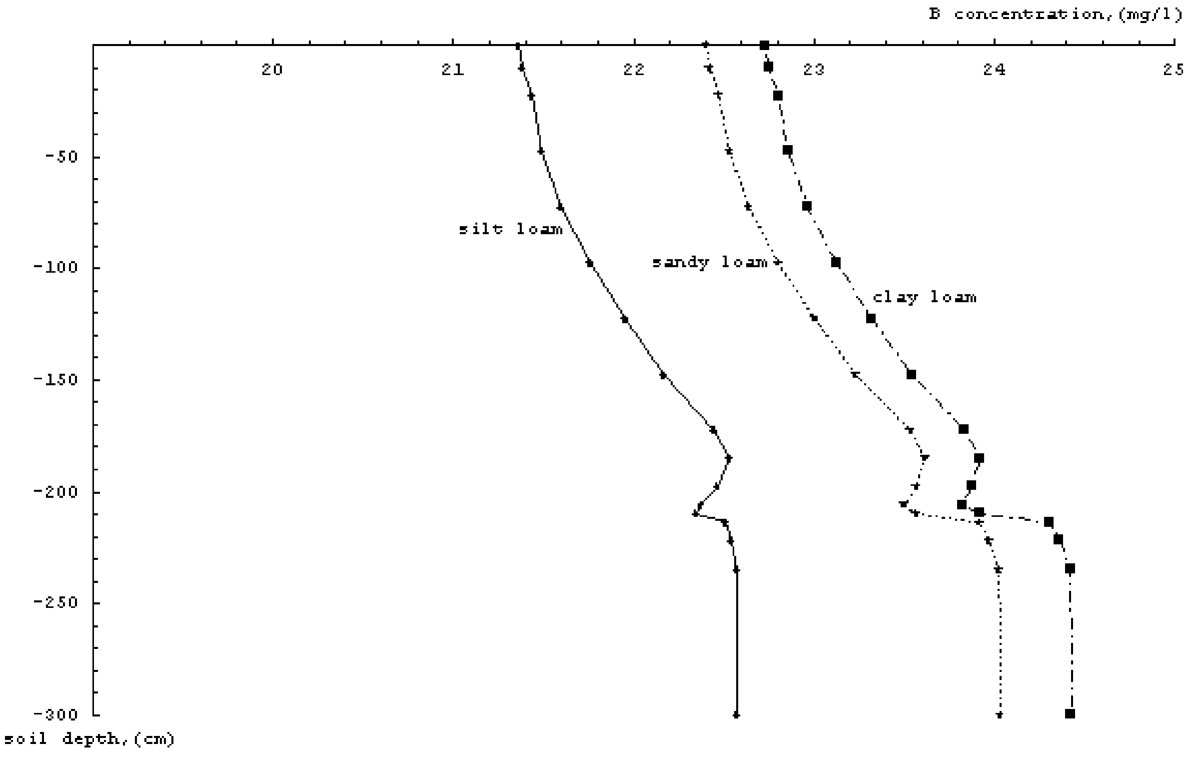

Figure 3.12. Results of model application to three different soils

CHAPTER 4

A NUMERICAL MODEL FOR SELENIUM TRANSPORT

4.1.Mathematical development

4.1.1.Flow Transport

The equation which models the flow in saturated-unsaturated zone in two dimensions is expressed as (Neuman, 1973; Nour el Din et al., 1987; and Karajeh et al., 1994):

$$\left(\lambda\ S_s + \frac{\partial \theta}{\partial p}\right)\ \frac{\partial p}{\partial t} = \frac{\partial}{\partial x}\left[K_r \frac{k_{xx}}{\mu}\ \frac{\partial p}{\partial x}\right] + \frac{\partial}{\partial z}\left[K_r \frac{k_{zz}}{\mu}\ \left(\frac{\partial p}{\partial z} - \rho g\right)\right] \mp Q \qquad (4.1)$$

where λ = a coefficient taken as unity in the case of saturated flow and zero in the case of unsaturated flow; Ss = the storage coefficient that describes the volume of water released from storage under a unit decline in hydraulic head; θ = volumetric water content; p = soil-water pressure; Kr = relative hydraulic conductivity (0 < Kr < 1); kxx = saturated hydraulic conductivity tensor in x-direction; kzz = saturated hydraulic conductivity tensor in z-direction; μ = kinematic viscosity; ρ = the density of water; g = the gravitational acceleration; and Q = the strength of all sources and sinks in the system.

Equation (1) is nonlinear since the hydraulic conductivity and soil water content are functions of pressure. In order to solve equation (1) initial and boundary conditions need to be specified. Initial spatial distribution of the pressure needs to be specified as the initial condition. The boundary conditions can be either Dirichlet-type or Neuman-type for specified pressure or specified flux, respectively.

4.1.2. Selenium Transport:

The Se transport and transformation processes in soil column under transient flow conditions are complex. Several complicating factors like pore water velocity gradient, hydraulic conductivity, evaporation and transpiration fluxes, concentration gradient, and seasonal rise and fall of water table control the transport of different Se species. In general, Se is transported in soil by the ways of convection and dispersion which are the result of mass flow and concentration gradient. Se transformation processes in soil systems are oxidation/reduction, adsorption/desorption, plant uptake, menarilazation/immobilization, and volatilization. Figure 2.1 shows some of the Se transport and transformation processes and the factors affecting each of the processes.

The rate of transformation of Se from selenite to selanate and vice versa through oxidation/reduction processes is very slow, but oxidation of elemental Se to selenite is somewhat more pronounced (Cary and Allaway, 1969). Rate of oxidation/reduction of different species depends on the factors such as Eh, pH, oxygen status of soil, soil temperature, microbial activity, and soil water content. In general, in alkaline soils of semi-arid areas Se exists in the selenate form. However, under acid and reducing conditions, as in humid regions, Se may exist dominantly in the selenite form.

The process of selenate and selenite adsorption and desorption plays a crucial role in governing soil Se mobility in most acidic and neutral soils. This, in turn, affects the other Se processes in the soil especially, Se availability to plant uptake and volatilization. Since selenious acid is weaker acid than the selenic acid selenite is retained more strongly by soils than selenate (Balistrieri and Chao, 1987; Neal and Sposito, 1989; Fio and Fujii, 1990; and Shifang, 1991). Factors affecting the processes of adsorption and desorption are the properties of adsorbents, the solution pH, competitive anion such as PO_4^{3-}, and the concentration of soil amendment (CaCO3 and CaSO4) (Hamdy and Gissel-Nielson, 1977; and Neal et al. 1987). The properties of adsorbents affect Se adsorption and desorption because of specific affinity sites and total surface area. Selenite adsorption was found to be positively correlated with specific area and organic carbon. pH is very sensitive factor with respect to Se adsorption since it affects both surface electrochemical potential and Se redox potential (Hamdy and Gissel-Nielson, 1977).

Se volatilization from soils has often been reported as a result of microbial processes. The conversion of added Se to volatile gases was enhanced when soils were amended with organic matter (Karlson and Frankenberger, 1989; Thampson-Eagle and Frankenberger, 1990). Factors affecting the volatilization of soil Se are soil pH, soil temperature, organic matter content, liming and moisture content, microbial activity, and plant growth (Gissler-Nielson, 1976; Hamdy and Gissel-Nielson, 1977; Mushak, 1985; Thompson-Eagle and Frankenberger, 1990; Biggar and Jayaweera, 1990). Gissel-Nielson (1976) from their studies concluded that the change in soil moisture content and increase in liming, organic matter content, temperature, carbon sources, and protein sources increase the volatilization.

Se is absorbed by plants in both the inorganic form, such as selenate and selenite, and the organic form as selenomethionine (Johnson et al., 1967; Statman, 1974; and Gissel-Nielsen, 1973). The factors affecting the Se uptake by plants are: soil moisture content, plant type, soil pH, soil texture, soil solution salinity, organic matter content, competitive anions such as SO_4^{2-} and PO_4^{3-} , tillage and fertilizer (Gissler-Nielson, 1976; Hamdy and Gissler-Nielsen, 1977; Carter et al., 1972; Westerman and Robbins, 1974). In soils with a high content of organic matter and iron oxides the selenite is very strongly fixed and thereby unavailable to plants (Gissler-Nielson, 1976; and Hamdy and Gissler-Nielsen, 1977). Sandy soil retain less Se than clay soil but more available for plant uptake. Low pH favors the fixation of selenite to the clay minerals, while high pH favors the oxidation of selenite to the far more easily extractable selenates. Carter et al. (1972) suggested that plant uptake of selenite might be increased by phosphate (PO_4^{3-}), probably because of adsorbed selenite displacement, increased root growth and enhanced microbial activities. Se concentration in plant decreases with additions of SO_4^{2-} , because of Se-SO_4^{2-} antagonism effects. Soil solution salinity decreases Se uptake, tillage and fertilizer increases Se uptake due to soil aeration and stimulation of microbial activities and root growth (Westerman and Robbins, 1974).

In the following section the equations expressing selenate, selenite and selenomethionine transport in two dimensions are given. Each equation comprised of advection diffusion terms and all the possible sink and source terms resulting from transformations and plant uptake.

4.1.2.1. Selenate Transport

$$\frac{\partial}{\partial t}\left(R_1 C_1\right) = \frac{\partial}{\partial x}\left[\theta\ D_{1x}\ \frac{\partial C_1}{\partial x}\right] + \frac{\partial}{\partial z}\left[\theta\ D_{1z}\ \frac{\partial C_1}{\partial z}\right] - \frac{\partial}{\partial x}\left(C_1\ q_x\right) - \frac{\partial}{\partial z}\left(C_1\ q_z\right) -$$

$$\left(\lambda_{a1}\ \alpha_1\ U\ C_1\right) - \left[\left(K_{r1} + K_{v1} + K_{b1}\right)\theta\ C_1\right] + \left(\rho_s\ K_{m1} S_o\right) \qquad (4.2)$$

where

$$R_1 = \left[\theta + \rho_s\left(K_{a1}\ n\ C_1^{n-1}\right)\right] \qquad (4.3)$$

where C_1 = selenate concentration (mg/L); R_1 = retardation factor for selenate; ρ_s = bulk density of the porous medium (kg/m^3); K_{a1} = adsorption coefficient for selenate (L/kg); n = nonequilibrium exponent for selenate; D_{1x} = total diffusion coefficient for selenate in x-direction (cm^2/day); D_{1z} = toal diffusion coefficient for selenate in z-direction (cm^2/day); q_x = Darcy flux in x-direction ($q_x = \theta v_x$, where v_x =pore water velocity in x-direction) (cm/day); q_z = Darcy flux in z-direction ($q_z = \theta\ v_z$, where v_z = pore water velocity in z-direction) (cm/day); λ_{a1} = root absorption coefficient for selenate; α_1 = coefficient for SO_4^{2-} anatagonism effect for selenate; U = root water extraction (1/day); K_{r1} = transformation rate constant for reduction of selenate (1/day); K_{v1} =

volatilization rate constant of selenate (1/day); K_{b1} = transformation rate constant for immobilization of selenate (1/day); K_{m1} = transformation rate constant for mineralization of selenate (1/day); and S_o = organic selenium concentration (mg/kg).

4.1.2.2. Selenite Transport:

$$\frac{\partial}{\partial t}(R_2C_2) = \frac{\partial}{\partial x}\left[\theta\ D_{2x}\ \frac{\partial C_2}{\partial x}\right] + \frac{\partial}{\partial z}\left[\theta\ D_{2z}\ \frac{\partial C_2}{\partial z}\right] - \frac{\partial}{\partial x}\left(C_2\ q_x\right) - \frac{\partial}{\partial z}\left(C_2\ q_z\right) -$$

$$\left(\lambda_{a2}\ \alpha_2\ U\ C_2\right) - \left[\left(K_{r2} + K_{v2} + K_{b2}\right)\ \theta\ C_2\right] + \left(\rho_s\ K_{m2}S_o\right) + \left(K_{r1}\theta\, C_1\right) \qquad (4.4)$$

where

$$R_2 = \left[\theta + \rho_s\left(K_{a2}\ w\ C_2^{w-1}\right)\right] \qquad (4.5)$$

where C_2 = selenite concentration (mg/L); R_2 = retardation factor for selenite; K_{a2} = adsorption coefficient for selenite (L/kg); w = nonequilibrium exponent for selenite; D_{2x} = total diffusion coefficient for selenite in x-direction (cm^2/day); D_{2z} = total diffusion coefficient for selenite in z-direction (cm^2/day); λ_{a2} = root absorption coefficient for selenite; α_2 = coefficient for SO_4^{2-} anatagonism effect for selenite; K_{r2} = transformation rate constant for reduction of selenite (1/day); K_{v2} = volatilization rate constant of selenite (1/day); K_{b2} = transformation rate constant for immobilization of selenite (1/day); and K_{m2} = transformation rate constant for mineralization of selenite (1/day).

4.1.2.3. Selenomethionine Transport:

$$\frac{\partial}{\partial t}(R_3C_3) = \frac{\partial}{\partial x}\left[\theta\ D_{3x}\ \frac{\partial C_3}{\partial x}\right] + \frac{\partial}{\partial z}\left[\theta\ D_{3z}\ \frac{\partial C_3}{\partial z}\right] - \frac{\partial}{\partial x}\left(C_3\ q_x\right) - \frac{\partial}{\partial z}\left(C_3\ q_z\right) -$$

$$\left(\lambda_{a3}\ \alpha_3\ U\ C_3\right) - \left(K_{v3}\ \theta\ C_3\right) + \left(\rho_s\ K_{m3}S_o\right) \qquad (4.6)$$

where

$$R_3 = \left[\theta + \rho_s \left(K_{a3}\ l\ C_3^{l-1}\right)\right] \tag{4.7}$$

where C_3 = selenomethionine concentration (mg/L); R_3 = retardation factor for selenomethionine; K_{a3}= adsorption coefficient for selenomethionine (L/kg); l = nonequilibrium exponent for selenomethionine; D_{3x} = total diffusion coefficient for selenomethionine in x-direction (cm^2/day); D_{3z} = total diffusion coefficient for selenomethionine in z-direction (cm^2/day); λ_{a3} = root absorption coefficient for selenomethionine; α_3 = coefficient for SO_4^{2-} anatagonism effect for selenomethionine; K_{v3} = volatilization rate constant of selenomethionine (1/day); and K_{m3} = transformation rate constant for mineralization of selenomethionine (1/day).

The rate of change in organic selenium can be expressed as:

$$\frac{\partial S_o}{\partial t} = \frac{\theta}{\rho_s} K_{b1} C_1 + \frac{\theta}{\rho_s} K_{b2} C_2 - K_{m1} S_o - K_{m2} S_o - K_{m3} S_o \tag{4.8}$$

The rate of change in gaseous selenium can be expressed as:

$$\frac{\partial G}{\partial t} = \frac{\theta}{\rho_s} K_{v1} C_1 + \frac{\theta}{\rho_s} K_{v2} C_2 + \frac{\theta}{\rho_s} K_{v3} C_3 \tag{4.9}$$

where G is gaseous selenium concentration (μg/kg).

CHAPTER 5

RESULTS AND DISCUSSION

The model was applied to the observed data set obtained from Mendota site. The data belong to the 1985-1990 plantations. The experimental site consist of fine textured silt clay (0-60cm) to clay soils (60-300cm) underlain by a impermeable clay layer at 3 to 3.7m depths over the entire plantation. The irrigation was applied in every 10 days for about 24 hours. The irrigation application efficiency was about 0.85.

It has been seen in the modeling of Mendota II (1990 observations), that the model extended with Langmuir isotherm(Figure.5.2.) for adsorption has given slightly better result versus the model with Freundlich (Figure.5.1.).

Table.5.1. The results of the B transport model for Mendota I (1987 observations)

Depth (cm)	53	110	158	210
Observed data B(mg/l)	17	22	25	30
Model results B(mg/l)	22.819	23.823	23.820	24.955

The results given in Table.5.1. are for the model extended with Langmuir for the estimation of 1987 observations. Due to the lack of input data belonging to Mendota I agroforestry site, the model results are not satisfactory in a zone where there is rapid changes in concentration. Although there is only observations for 4 points which are the root-zone quartiles, the model is in good compliance within the depths of 110cm and 158cm.

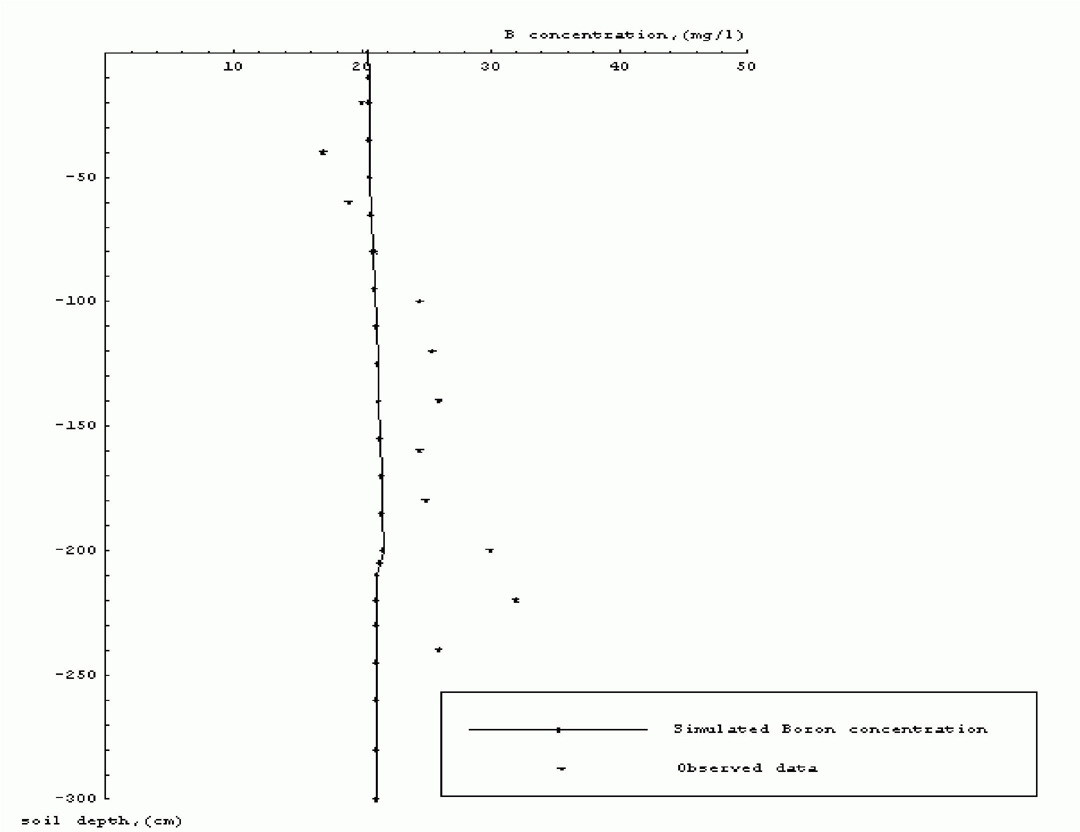

Figure.5.1. The B distribution for the model extended with freundlich isotherm(Mendota II,1990)

The effects of some physical parameters on boron transport are investigated by the model. The irrigation scheduling and the irrigation water quality have been found to be very important for boron accumulation in the site. Also the adsorption isotherm parameters, which show us the soil properties are also found to be important for the boron movement in the site.

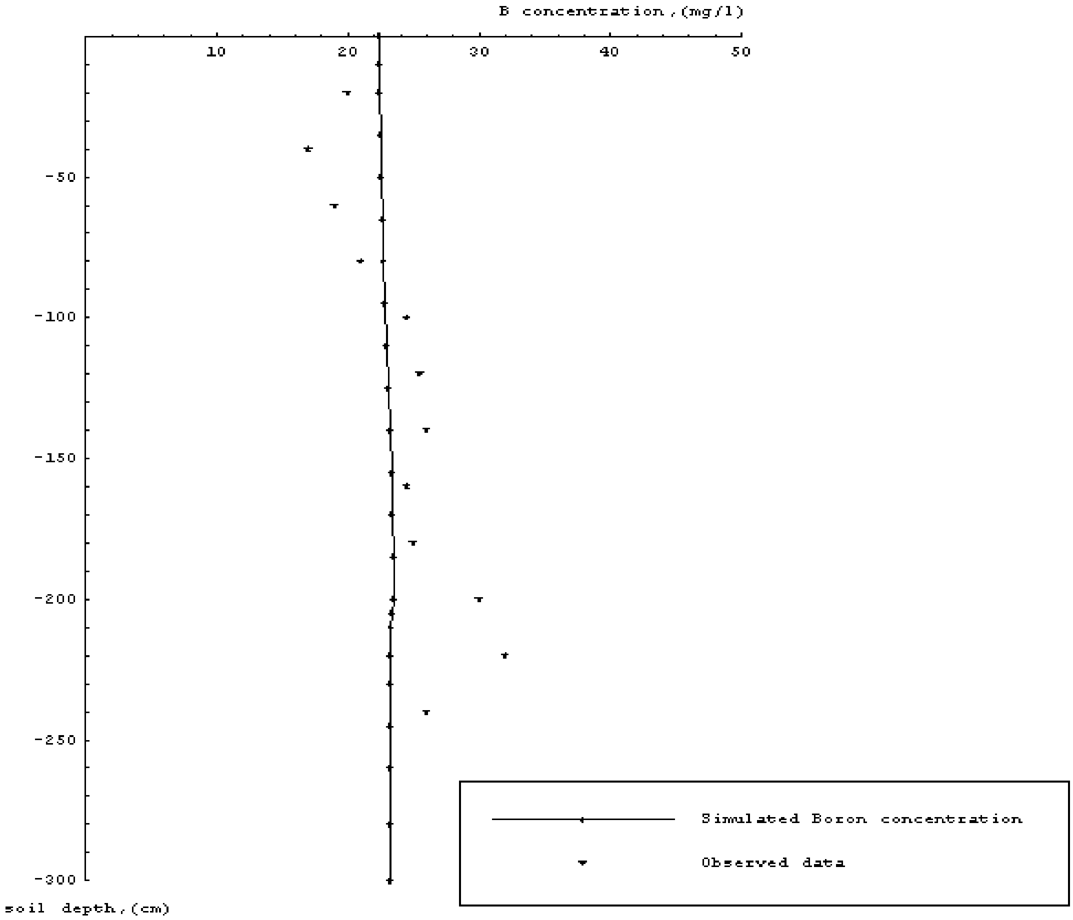

Figure.5.2. The B distribution for the model extended with Langmuir isotherm (Mendota II,1990)

In the modeling of selenium transport in the soil, the need for too many parameters made the problem very complex. Table 5.2. shows the observed data belonging to Mendota I(1987 observations) and the model predictions for selenium. Since the lack of observations and too much parameters affecting the selenium transport, the results are not so good when compared with boron transport model.

Table 5.2. The results of the Se transport model for Mendota I (1987 observations)

Depth (cm)	53	110	158	210
Observed data Se(μg/l)	500	550	600	800
Model results Se(μg/l)	543.2	550.6	552	557.4

Due to the lack of observations Table 5.2. shows us that the selenium transport model can not handle the rapid concentration variations at critical depths. The critical depth occurs in the zone where the water flow is comparatively high. In our problem these critical depths are at the surface of the soil and at the depth where the tile drainage is set.

CHAPTER 6

CONCLUSIONS

In this study, 2 dimensional finite element models were developed to simulate boron and selenium transport in an agroforestry system. The models can simulate seasonal variations of soil water content and the concentration distributions in irrigated and under-drained agroforestry systems. The model was developed by modifying the model D-HYSAM which simulates salt transport. There are two different developed models which are considering Freundlich and Langmuir isotherms for boron adsorption/desorption process.

The extended D-HYSAM program reads the input data and all the topology for the problem from an input file. It would be better for the program to have a graphical interface which would decrease the user errors and save time.

The model results showed a good accuracy for a solute transport problem in soil, where the problems are hard to model due to the complexity of the dynamics.

The performance of the model for Boron transport is satisfactory. The model can be a practical tool for research and management of agroforestry sites.

The model results for selenium transport highlighted the need for accurate measurements for the parameters affecting the selenium transport.

Due to the lack of input data belonging to Mendota I (1987 observations) agroforestry site, the model results of both boron and selenium are not quite satisfactory in a region where there is rapid changes in concentration.

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