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Gustafson, David I

CONTROLLED RELEASE TECHNOLOGY: DEVELOPMENT OF A SLOW
RELEASE SYSTEMIC REPELLENT FOR THE PROTECTION OF TREE
SEEDLINGS FROM DEER

University of Washington

Ph.D. 1983

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Controlled Release Technology:

Development of a Slow Release Systemic Repellent

For the Protection of Tree Seedlings from Deer

by

David I Gustafson

A dissertation submitted in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

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1983

Approved by G. Graham Allan
(Chairperson of Supervisory Committee)

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to Offer Degree Chemical Engineering

Date October 3, 1983

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NOMENCLATURE

A	Area, and a Constant Length Characterizing Soil Saturation
a	Constant
b	Constant
B	A Constant Length Characterizing Hydraulic Conductivity
BP0	Initial Pressure for Solution to Soil-Water Equation
BP1	Final Pressure for Similarity Solution to Soil-Water Equation
C	Molar Concentration of Selenium in Soil Solution
C_o	Concentration of Selenium in Dissolution Apparatus Sol'n
C_s	Aqueous Molar Solubility of Dimelamine Selenite
C_t	Concentration of Selenium at Pore Opening of Tablet
C_f	Selenium Concentration in the Foliage
$\underline{C}_f$	Foliar Selenium Concentration Nondimensionalized by K_m^a
C_L	Loading Concentration in the Higuchi Analysis
C_r	Selenium Concentration in the Roots
$\underline{C}_r$	Root Selenium Concentration Nondimensionalized by K_m^a
d	Absorption Rate Nondimensionalized by $V_r v_{max}^a$
D	Diffusion Coefficient
D_e	Effective Diffusion Coefficient of Selenium through the Soil
D_{er}	Effective Diffusivity in the Radial Direction from the Tablet
D_{ez}	Effective Diffusivity in the Axial Direction from the Tablet
D_o	Diffusion Coefficient of Selenite Ion in Pure Water
e	Basis of the Natural Logarithmic System, 2.7182818...

f	Ratio of Rate of Deactivation to the Rate of Absorption
F	Angular Velocity Function in the Levich Analysis
g	Acceleration Due to Gravity 980.829 cm/s ²
G	Radial Velocity Function in the Levich Analysis
h_{Tr}	Radial Thiele Modulus of Absorption $r_o (v_{max}^a / D_e K_m^a)^{1/2}$
h_{Tz}	Axial Thiele Modulus of Absorption $2z_o (v_{max}^a / D_e K_m^a)^{1/2}$
H	Height, Axial Velocity Function in the Levich Analysis
J	Molar Flux
k	Mass Transfer Coefficient
k_a	Se Solubility Divided by Michaelis Constant for Absorption
k_d	Se Solubility Divided by Michaelis Constant for Deactivation
k_e	Erosion Constant for Film
k_o	Hydraulic Conductivity at Saturation, Rate Constant of Selenium Release in the Dissolution Accelerator
k_r	Hydraulic Conductivity Divided by k_o
k_v	First Order Volatilization Rate Constant
K	Equilibrium Partition Coefficient
K_m^a	Michaelis Constant for Absorption
K_m^d	Michaelis Constant for Deactivation
L	Pore Length, a Characteristic Length, or a Film Thickness
M	Amount of Selenium that has left a Tablet
M_o	Amount of Releaseable Selenium in Tablet
MW	Molecular Weight

n_j	Moles of Solutes
n^0	Number of Neutrons
n_w	Moles of Water
N	Number of Members of a Population
p	Fraction of Tablet's Axial Face Covered by Pores
po	Porosity, Pore Volume Divided by Total Volume
P	Pressure
P_c	Capillary Pressure
P_o	Partial Pressure of Water
P_v	Vapor Pressure of Water (Saturated)
Q	Volumetric Flowrate, Total Efflux per unit Area
q_f	Ratio of Time Constants for Filling and Clearing the Foliage Compartment ($QK_m^a/V_f v_{max}^a$)
q_r	Ratio of Time Constants for Filling and Clearing the Root Compartment ($QK_m^a/V_r v_{max}^a$)
r	Radial Coordinate Measured from Axis of the Tablet
r_o	Radius of the Tablet
$\underline{r}$	Radial Position Nondimensionalized by Tablet Radius
R	Radius
R_a	Overall Instantaneous Rate of Selenium Absorption by Roots
Re	Reynold's Number, Ratio of Inertial to Viscous Forces
R_i	Rainfall on a Given Day
$s_{1,2}$	Geometric Mean of Two Popoulations' Averaged Deviations

S	Fractional Soil Saturation
S_r	Irreducible Saturation
t	Time, t Statistic
$\underline{t}$	Time Nondimensionalized by Absorption Time Constant (K_m^a/v_{max}^a)
t_c	Characteristic Time for Fluid Transport through Soil
T	Temperature
T.I.	Therapeutic Index
v	Nondimensional Volatilization Rate Constant ($k_v K_m^a/v_{max}^a$)
v_{max}^a	Maximum Rate of Selenium Absorption by the Roots
v_{max}^d	Maximum Rate of Selenium Deactivation in the Soil
v_r	Radial Velocity Near a Rotating Disk
v_w	Molar Volume of Water
v_z	Axial Velocity Near a Rotating Disk
ω	Angular Velocity Near a Rotating Disk
V	Volume
V_f	Volume of the Root Compartment
V_r	Volume of the Foliage Compartment
w_i	Weight Assigned to the i^{th} Data Point
x	Independent Variable, Mole Fraction
$\bar{X}$	Average Value of a Population
y	Independent Variable
z	Axial Position Measured from Central Plane of Tablet, and Vertical Position from the Soil Surface

z_0	Tablet Thickness
$\underline{z}$	Nondimensional Axial Position Defined by $(2z/z_0)$
∇^2	Laplacian Operator
Δ	Change in Value of a Variable
$-$	Averaged Value of a Variable over a Defined Domain
$'$	Time Rate of Change of a Variable, Dimensional Quantity
β	Relaxation Parameter
ζ	Nondimensional Height above Rotating Disk
η	Nondimensional Parameter Characterizing the Saturation
λ	Nondimensional Parameter Characterizing the Hydraulic Conductivity
μ	Viscosity
ν	Kinematic Viscosity
ξ	Similarity Variable (Boltzmann Transformation, $z/t^{1/2}$)
π	Ratio of Circle Circumference to Diameter, 3.14159265...
ρ	Density
τ	Tortuosity
ϕ	Water Potential Energy
ψ	Water Potential
ω	Angular Frequency

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CONTROLLED RELEASE TECHNOLOGY:
DEVELOPMENT OF A SLOW RELEASE SYSTEMIC REPELLENT
FOR THE PROTECTION OF TREE SEEDLINGS FROM DEER

The concept of controlled release, the prolonged delivery of active agents by formulation within an inert matrix, is a surprisingly new one given its many benefits. In pharmacology there are numerous advantages to be had; these include the avoidance of patient compliance problems, minimization of subcutaneous and intramuscular injury from injection, and localization of drug delivery to the target organ.⁽¹¹⁾ More recently, the favorable aspects of controlled release technology have been exploited in both agriculture and forestry. Fertilizers, pesticides and herbicides have all been successfully deployed in persistent forms.^(106, 127) The particular attractive features of sustained delivery systems to these disciplines include the lower application cost, the increased efficiency of utilization of the often expensive active ingredient and greatly reduced environmental contamination. The increasing chemical engineering interest in the field was recently underscored by the publication of an AIChE symposium entirely devoted to controlled release systems.⁽²⁶⁾

This thesis describes the specific application of a sustained delivery system for the protection of tree seedlings from browse damage by deer. A sparingly soluble tablet containing selenium, a systemic repellent, was synthesized and tested in a series of studies to determine its release rate characteristics, phytotoxic effects and its effectiveness as a long term repellent system in the field.

Foliar selenium content data were collected from trees grown under both carefully controlled environmental conditions and in the wild. These data provide a stringent test of the ability to predict, from first principles, the pattern of interaction between the sustained delivery system, the tree and the environment. The success achieved with the model presented in this work indicates that it may soon be possible to design controlled release systems with much more accuracy. This would eliminate much of the costly trial and error field testing which is now required in order to "size" a particular system. Such an advantage will become increasingly important as the use of these systems proliferates.

The major practical accomplishment of this work was the synthesis of a persistent system for the prolonged delivery of selenium to the soil solution surrounding the roots of the target seedling. There are many reasons why this was a difficult task. Selenium is a toxic material;^(48, 71, 107, 116, 152) thus one must be very careful to restrict the release rate from the device below the levels which cause harmful effects. An added complication was the fact that when this work was begun, this upper limit was unknown.

There is also a lower limit above which the release rate must be maintained in order to provide repellent action in the seedling. This lower limit on the release rate was also not established when the work began. In the pharmaceutical literature reference is often made to the Therapeutic Index, or T.I., which is the ratio of the toxic concentration in the body to the minimally effective

concentration.⁽⁹⁵⁾ The T.I. is a good indication of the safety with which a particular drug may be used. Drugs with low values for the T.I. are prime candidates for controlled release applications because it is very difficult for traditional dosage forms, such as either injections or pills, to maintain the active ingredient concentration within a narrow "window." The concentration window for selenium found in this study depends on the actual definition of the minimally effective concentration and phytotoxicity, but if 50% browse reduction is taken as the lowest acceptable protection and noticeable deceleration of the growth is taken as the phytotoxicity threshold, then the T.I. for selenium in Douglas-fir seedlings is approximately 50. This value is relatively high compared to the values prevalent in the drug industry, as indicated by the data found in Table 1.⁽⁹⁵⁾

The application of the particular form of selenium used in this study, the selenite ion, is complicated by the fact that SeO_2 and its hydrated acid form are both relatively strong oxidizing agents.⁽¹⁵⁰⁾ This means that nearly every material with which selenium is combined will lose electrons to the element, creating metallic Se, and other more reduced forms, which have been shown to be relatively unavailable for absorption through the roots of plants.^(7, 115) The redox reaction is easily seen in the lab by placing SeO_2 and almost any other material in an open beaker. Within a short time a pink color becomes apparent, which is characteristic of the formation of the most common metallic form of elemental selenium, which has a red hue.⁽³⁾

Table 1. Characteristic Values of the Therapeutic Index

DRUG	THERAPEUTIC INDEX (T.I.)
Aprobarbitol	5.3
Chlorpheniramine	1400
Digitoxin	2.0
Digoxin	2.2
Diphenhydramine	2300
Lidocaine	3.6
Lithium	2.6
Penicillin	100
Phenobarbitol	2.6
Phenytoin	2.0
Procainamide	2.0
Propanolol	2.5
Quinidine	2.5
Theophylline	1.6
Tripelennamine	19000

The most stringent requirement on a sustained selenium delivery system is that it be cheap, yet capable of providing the element in an absorbable form to the soil for at least three years. This period of time is required for the tree to attain a height at which it is no longer susceptible to serious browse damage.⁽³⁹⁾ This is a formidable task given the harsh environmental confines of the soil and the degradative tendencies of selenite ion which were just pointed out. These two constraints were met by the use of dimelamine selenite as the basis of the pellet.

Melamine (2,4,6-triamino-s-triazine) is a remarkable material, with physical properties that make it useful in applications as varied as the formation of tabletops and the fertilization of rice.⁽¹⁰⁶⁾ In this particular study the physical properties exploited were its low solubility and its phenomenal chemical stability. The solubility of free melamine is approximately 5 g/L (0.04 M) at room temperature, and the highly stable ring structure renders the molecule almost impervious to the action of oxidizing agents except under the most severe conditions. Dimelamine selenite has proved to have an unlimited shelf life, and with the addition of a small amount of aqueous formaldehyde solution as a binder, it can be pressed into a tablet form ideal for application to the soil.

The animal damage problem is one which is not unique to reforestation efforts, with the foliated pride and joy of fruit tree growers and home owners often succumbing to the attacks of foraging

herbivores.^(46, 101) In economic terms within the Northwest, however, it is the forest industry that is hardest hit by the voracious appetites of deer and other animals, most notably mountain beavers. (1, 2, 6, 8, 32-34, 39, 41, 42, 56, 72, 111, 122-124, 132)

It has been estimated that several million dollars worth of damage are done by deer each year to Douglas-fir seedlings in Washington and Oregon alone.⁽⁴¹⁾

The repellent system designed in this study could help accomplish a bailout of the selenium accumulators around the world, who currently generate about 1200 tons/yr of the material during the electrolytic refining of copper and have dreamed of new uses for the element since the turn of the century.⁽¹⁵⁰⁾ Selenium has photoconductive properties which make it very useful in xerography and certain other electrical devices.^(111, 150) The element began to find use as a systemic insecticide in the 1930's,^(9, 31, 59, 110, 142) but this application was killed in the United States in 1954 by a complete ban on all agricultural use of the material.⁽⁶²⁾ This ban was caused by a number of experiments which had purportedly shown that selenium was carcinogenic. This is ironic, however, because selenium is now actually being investigated as an inhibitor of cancer.⁽⁵³⁾

The major chemical engineering analysis involved in this study was the development of a mass transfer model to predict the effectiveness of the tablets in the field. This model represents an attempt to predict, from first principles, the foliar concentration of

selenium as a function of time following treatment with a sparingly soluble selenium tablet. Generality was retained during model development so that it could be applied to controlled release systems which supplied materials other than selenium to target plants other than Douglas-fir seedlings.

Several differential equations were solved numerically within the model, most notably the two dimensional diffusion equation in a cylindrical geometry with Michaelis-Menten kinetic expressions for consumption of the active ingredient. It was also necessary to solve the nonlinear equation which describes the moisture content of the partially saturated soil. The diffusion equation was handled by assuming no bulk flow and a pseudo-steady state. A finite difference representation of the equation was then derived, with a successive overrelaxation method used to solve the matrix.⁽⁵¹⁾ The soil saturation equation was solved by first neglecting the gravity term and applying a similarity transformation. This technique becomes less valid for long times and for distances far into the soil. The analysis in this model was restricted to day-long periods of time, and it was only the top 10-20 cm of the soil which were of interest.

The numerical solution which was obtained for diffusion away from the cylindrical pellet is of interest to other biological systems because the equation was solved with two competing Michaelis-Menten rate terms accounting for the disappearance of the active ingredient. When "turned inside out," the same solution would correspond to the diffusion-reaction problem within a cylindrical pellet. Such a

situation would arise for the case of cylindrically shaped particles impregnated with two types of immobilized enzymes, each competing for the same substrate.

The model developed in this work would be of special interest to those concerned with ground-water contamination, a problem which is certain to become increasingly important in the future. (47, 91, 117, 148, 151)

The question of whether selenium would infiltrate aquifers is one which has been addressed in this study, and it was both predicted from the model and confirmed by data obtained in the field that the use of the anti-browse tablets represented no threat to ground water supplies.

The mass transfer of ionic materials through porous media, especially charged porous media such as soils, is a highly complex web of phenomena, including molecular diffusion, convection, adsorption onto colloidal particles, chemical reaction with surface and solute molecules, and more esoteric processes such as thermodiffusion and osmosis. (17, 19, 21, 36, 66, 100)

The movement of selenite ion through soils is of increasing interest because of the discovery of several diseases induced by Se deficiencies. (4, 6, 7, 20-22, 38, 43, 60, 63, 71, 77, 82-84, 88, 94, 105, 108, 112, 125, 129-131, 133, 134, 136-138, 141, 143, 154-158, 161)

Soil application of selenium as a means of treating these seleno-paucities is sometimes confounded by the formation of highly insoluble complexes of HSeO_3^- with ferric hydroxide groups. (63, 73, 77, 82-84)

The results obtained through this investigation of selenite transport through the soil will be of

great interest to those attempting to treat selenium deficient soils.

In Chapter I an attempt is made to place this work in its proper historical perspective through a brief summary of previous investigations in the pertinent fields: controlled release technology, the animal damage problem and selenium biochemistry. The theoretical development of the equations required by the analysis is summarized in Chapter II. Many experimental projects were associated with the study, and these are described in Chapter III. Results of these studies in light of the theory developed in Chapter II are discussed in Chapter IV. Conclusions and recommendations for future work are examined in Chapter V. Appendix A contains listings of the important computer programs written during the study, and in Appendix B some of the mathematical details of the theoretical development are further illuminated.

Chapter I: Historical Perspective

In order to properly understand the significance of this work, it is necessary to view it in its proper historical perspective. Since this project spans many disciplines, we must consider the various research activities individually, and then finally indicate the manner in which they were combined to form this contribution. Both the language and the tools of chemical engineering are used to address the problem. The solution which is obtained demonstrates the rewards achievable through the application of chemical engineering fundamentals to situations not normally considered by practicing engineers.

Section 1.1: Timed Delivery Systems

The early 1950's brought the first published work on controlled release technology.⁽¹⁰²⁾ Dr. N.F. Cardarelli developed long lasting marine antifoulants by combination of the active ingredient with an inert rubber matrix. Dr. J. Folkman considered the sustained release of steroids from silicones at approximately the same time. Interest in the area quickly expanded as more researchers became aware of the distinct advantages of such systems. Most of the current research is concerned with the development of pharmaceuticals for humans, but extensive studies are being initiated to investigate the performance of slow release devices applied to the soil.

The essential attributes of a sustained release device may be listed in the following manner:⁽¹²⁸⁾ 1) a platform, the physical

backbone of the device; it must be stable for the duration of active agent delivery, and must therefore be compatible with any living tissue it may contact; 2) a reservoir, the stable storage region which maintains the active ingredient in its desired chemical form up until delivery; 3) a program, the duration and rate of release which is required to effect optimal therapeutic activity; 4) a rate controller, the system which meters release of the agent at the particular rate dictated by the program; and 5) an energy device, the source of power which drives the entire system. These five very general requirements may be met by a variety of devices, a few of which are described below.

Section 1.1.1: Types of Sustained Delivery Systems

A number of sustained delivery systems are based on osmotic pressure. The prototypic apparatus for visualizing the osmotic phenomenon is shown in Fig. 1. Two solutions of different solute concentration are separated by a membrane through which only solvent molecules may pass. At equilibrium a pressure is built up within the more concentrated (in terms of solute) phase, because the diffusive flux of solvent must be counterbalanced by a mechanically induced flow. This pressure will remain constant as long as the permeability of the membrane remains unchanged and the molar concentration of solute remains constant on either side of the barrier. The value of this pressure difference is given by the following expression:

$$P_1 - P_2 = \frac{RT}{v_{sol'n}} \ln(x_1/x_2) \quad (1-1)$$

One device which exploits this phenomenon is shown in Fig. 2.⁽¹²⁸⁾ In this controlled release system the salt solution is maintained at saturation by supplying excess solute. If the solvent molarity of the external solution remains constant then zero-order release of material should be observed as the gel containing the active ingredient is slowly squeezed out through the portal. Zero-order, or constant release is generally the goal of controlled release systems in pharmaceutical applications.⁽¹¹⁾

Other systems which make use of the osmotic phenomenon include certain so-called "monolithic" devices in which soluble packets of material are dispersed within an insoluble matrix such as lignin.⁽¹²⁷⁾ Water which is able to penetrate the matrix forces its way into the voids which contain the soluble material. If these packets are closed, then great osmotic pressures build within them as water continues to be drawn in, finally resulting in catastrophic rupture and break-up of the monolithic device into what might be called a polyolithic dispersion.

A final system which exploits the osmotic phenomenon is a slightly more refined version of the device just described.⁽⁶⁸⁾ In this case a salt is dispersed evenly throughout a hydrophobic polymer matrix which also contains dispersed drug. The mechanical properties of the polymer are adjusted such that when water is osmotically imbibed by the presence of the salt, the polymer swells rather than

THE OSMOTIC PHENOMENON

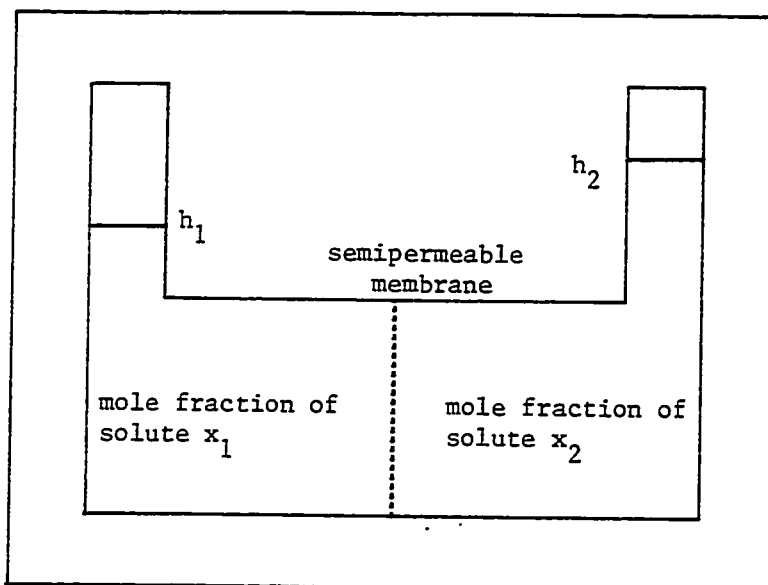


Figure 1. An Apparatus for the Observation of Osmosis.

AN OSMOTIC RELEASE DEVICE

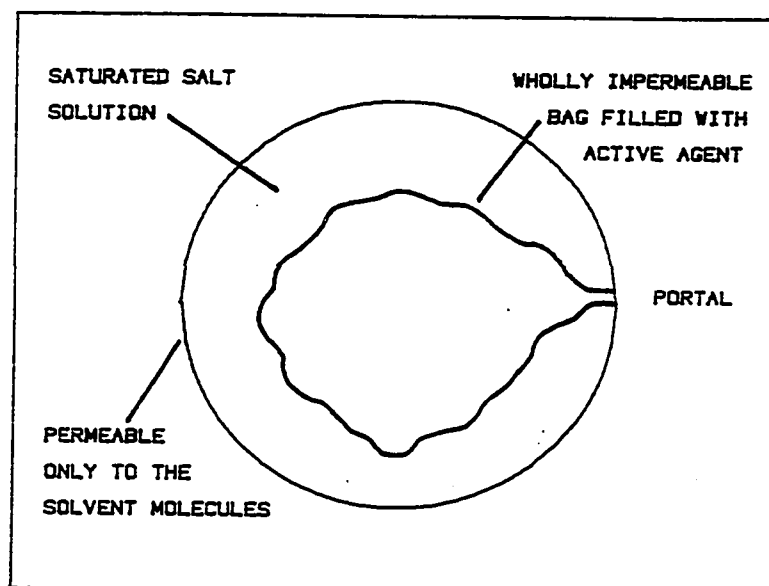


Figure 2. An Osmotically Based Release System.

collapsing as in the cruder system. This swelling increases the effective diffusivity of the drug by orders of magnitude; thus it leaves freely as the swelling front advances through the matrix. Zero-order release has been maintained for significant lengths of time from devices designed according to these principles.⁽⁶⁸⁾

Elastic systems rely on simple mechanically induced pressures to deliver the active ingredient. In essence, the gel which contains the drug is placed in a balloon. If the balloon is right cylindrical, then the release will be zero-order because of the constant hoop stresses present in the structure.⁽¹²⁸⁾

Erosion based devices are produced by dispersion of the active agent throughout an erodible matrix. Several different polymers have been used for these applications; among the most common are poly(3-hydroxybutyrate) or PHB, poly(DL-lactide), poly(ortho-esters), substituted polysaccharides, poly(oxyethylene glycol), poly(vinyl alcohol), and various combinations of these.⁽⁷⁶⁾ The release rate observed from such devices depends on their geometry. Zero-order release is achievable with disk shaped devices, which undergo relatively little surface area loss as they erode, but only if the edges of the disk are nonerosive. The characteristic types of curves obtained with different geometries are summarized in Fig. 3. These curves are generated with the assumption that each face of the device erodes at the same rate. The differential equation which thus governs the surface area (and hence the release rate) is then:

$$\frac{dV}{dt} = -kA \quad (1-2)$$

The volume of the device is denoted by V , and its surface area is given by A . The k in this equation is simply a mass transfer coefficient, and the relationship states mathematically that the release rate from the eroding device is proportional to its surface area. For a cube of length L along each edge, this equation becomes:

$$\frac{d(L^3)}{dt} = -6kL^2 \quad (1-3)$$

For a cube of initial edge length L_0 , the solution to this equation is easily shown to be:

$$L = L_0 - 2kt \quad (1-4)$$

If the initial geometry is that of a sphere of radius R , then equation (1-2) becomes:

$$\frac{d(\frac{4}{3}\pi R^3)}{dt} = -4k\pi R^2 \quad (1-5)$$

The solution for an initial radius R_0 is then:

$$R = R_0 - kt \quad (1-6)$$

Of special interest to this study is the cylindrical geometry, as

this was chosen for the selenium pellet. As will be shown later, the release from the tablet did not proceed by simple erosion, but if it had, then the height, H , and the radius, R , would have been governed by the following differential equation:

$$\frac{d}{dt}(\pi R^2 H) = -2k\pi R(R+H) \quad (1-7)$$

The assumption that each face erodes at the same rate allows the rate of change of the height, H' , to be related to the rate of change of the radius, R' , through the following equation:

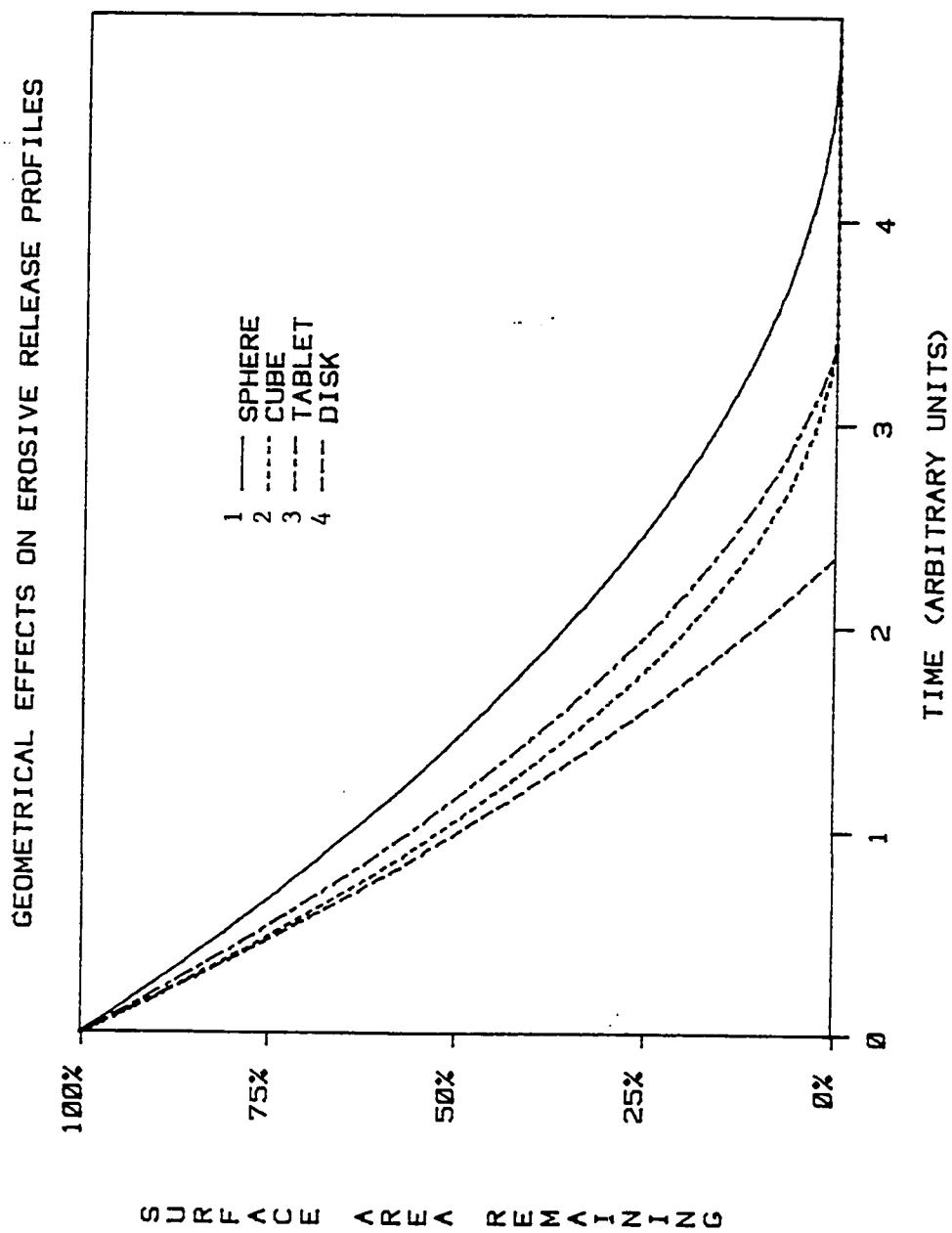
$$\frac{dH}{dt} = 2\frac{dR}{dt} \quad (1-8)$$

Eq. (1-7) is then soluble for the time dependence of the height and radius of the tablet, with the answer given by:

$$R = R_0 - kt \quad H = H_0 - 2kt \quad (1-9)$$

Notice that for the special case $2R=H$, this equation reduces to the same relationship as was given for a sphere. It is sometimes erroneously stated that forcing the ratio, R/H , to take on very high values, such that a disk-type geometry is achieved, will give approximately zero-order release. This is not true, however, for the case in which the radial face is allowed to erode, as has been assumed here. In fact, the flattest profiles possible with a homogeneous

Figure 3. Erosive Release Profiles from Various Geometries.



eroding cylinder are for the special case mentioned, in which the release from a sphere is mimicked. The two profiles shown for cylinders in Fig. 3 demonstrate this phenomenon. Curve number 3 is for a cylinder with the same dimensions as the selenium pellet synthesized in this study, and curve number 4 is for a disk in which R/H is 50.

A complication occurs when the active component is able to diffuse through the eroding matrix. In that case concentration profiles develop within the device which drive a diffusive flux that occurs in parallel with the erosive flux.

Many sustained delivery systems are based on diffusion limited barriers. In these devices the active ingredient diffuses from a reservoir through a membrane of well characterized thickness and permeability (see Fig. 4). The release rate observed from such systems is given by the following equation:⁽⁹⁵⁾

$$J = \frac{DKAC}{\tau L} \quad (1-10)$$

where J is a flux, D is the diffusion coefficient of the active ingredient (a.i.) through the membrane material, K is an equilibrium partition coefficient for the a.i. between the membrane and the surroundings, C is the driving force across the membrane, L is the membrane thickness and τ is the tortuosity of the membrane, defined as the actual diffusive path length divided by the nominal displacement.

Of particular interest to this study is the case in which the membrane may erode. Rather than being a constant, the thickness, L , is then a decreasing function of time. It can be seen from eq. (1-10) that the flux would therefore increase as the diffusive barrier became thinner.

When the active agent is dispersed throughout an insoluble matrix, then the cumulative flux of material from the device increases as the square root of time. This behavior has been accounted for analytically by the so-called Higuchi analysis.⁽⁹⁵⁾ The assumptions built into this analysis include the following:

- * A pseudo-steady state is maintained during release (means that partial derivatives with respect to time are neglected).
- * The external solution is a perfect sink.
- * The diffusivity of the active agent remains constant.
- * The porosity of the insoluble matrix is constant.
- * The loading concentration, C_L , is much greater than the active agent's solubility.
- * There are no chemical interactions between the active agent and the matrix.

Consistent use of these assumptions leads to the following relationship between the cumulative flux from the device, Q [mass/unit area], and the system properties:

$$Q = \sqrt{\frac{Dp_0}{\tau}(2C_L - p_0C_S)C_S t} \quad (1-11)$$

It will be seen that this expression adequately describes the behavior of many of the sustained delivery systems synthesized in this study.

The dimelamine selenite tablet which was synthesized in this work is unique among currently available delivery systems in that the major mode of release of the active agent is through ion exchange. Some free salt is delivered to the soil solution through simple dissolution processes, but the majority of the melamine is tied up in a three-dimensional polymer by the formaldehyde. Selenite ion is ionically bound to this anion exchange resin and is freed when negatively charged species from solution replace it in the matrix. Delivery of selenium by the tablet is thus described by mathematical relations which have not previously been applied in the controlled release literature.

Section 1.1.2: Special Demands on Controlled Release

Devices Applied to the Soil Environment

In contrast to pharmaceutical applications, it is often desirable in both agricultural and forestry applications to have release rates other than simply zero-order. The systemic animal repellent devised in this study, for instance, would have ideally been endowed with the property that the release rate was an increasing function of time. This is because as the tree grows it will presumably require more and

more of the active ingredient since there is more and more foliage to protect. This requirement may be alleviated, however, by the observation that the incidence of browsing falls quickly with tree height, reaching nearly 0% terminal damage at a height of 1 m.⁽⁷²⁾

There are many ways that such an increasing release rate may be achieved, but none of them fall within the practical price range dictated by the forestry application under consideration, with two possible exceptions. The first is a diffusion limited device with an eroding membrane, which could theoretically yield an increasing flux for a certain length of time. The other possibility is a device laden with fibers. If a monolithic erodible device were to be constructed with fibers throughout, then it is conceivable that the fibers would be biodegraded at a much faster rate than the bulk matrix, thus resulting in an increase of the available surface area. Whether either device could maintain such increasing delivery rates over the entire period of active agent delivery is a question that could be answered only through experiment.

Section 1.1.3: Characterization of the Performance Of Sustained Delivery Systems

The characterization of controlled release systems is a young, but surprisingly well developed science. The first step in the analysis parallels the first step in the interaction of the sustained delivery system with the treated organism, which is a characterization of the actual release rate observed from the device in vivo.^(95, 128)

A DIFFUSION LIMITED RELEASE DEVICE

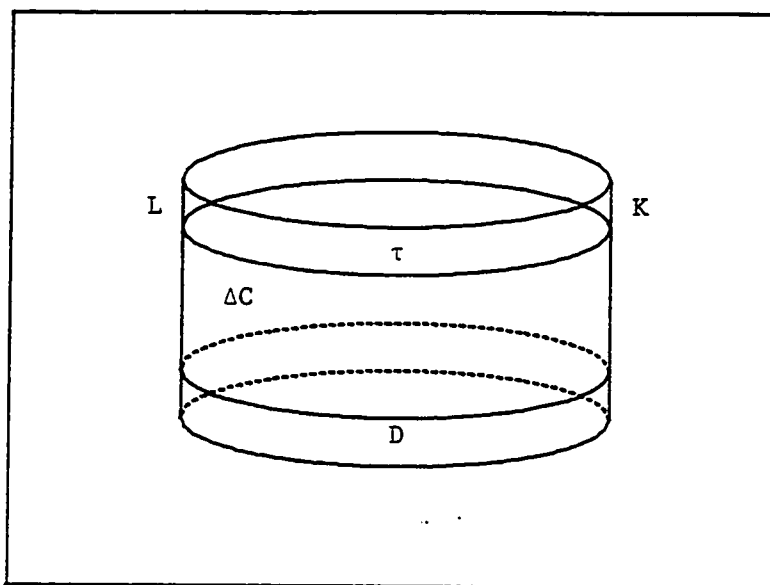


Figure 4. Controlled Release through a Diffusive Barrier.

A COMPARTMENTAL MODEL OF ACTIVE AGENT DISTRIBUTION

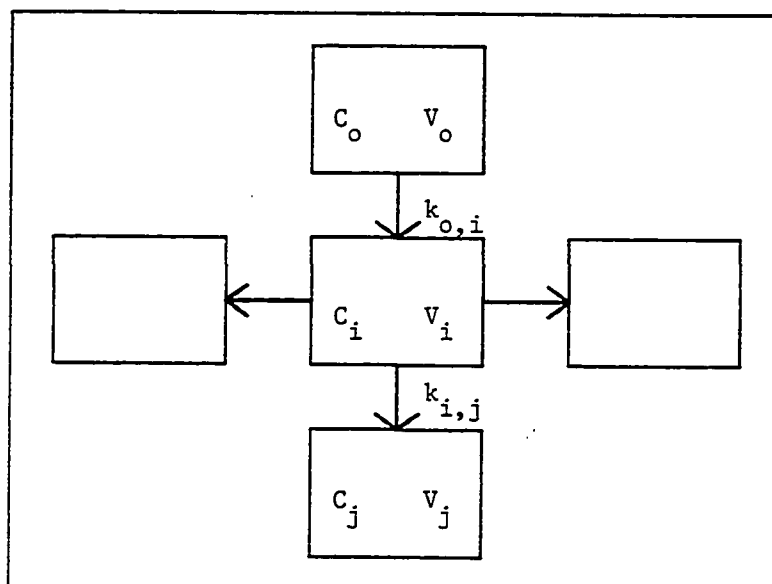


Figure 5. A Pharmacokinetic Model of Drug Distribution.

Determination of the release rate from the device is only the first step in fully characterizing the performance of the sustained delivery system, however, because the active ingredient often distributes in a manner that is quite different than what was originally intended.⁽¹²⁸⁾ The way that this distribution has normally been analyzed is with so-called "compartmental" models (see Fig. 5). In the language of chemical engineering, one assumes that the organism consists of a number of interconnected stirred tank reactors. Within each reactor the active ingredient can be either converted to a different form, passed on unchanged to the next reactor, or perhaps eliminated from the organism. Such a compartmental model has proved useful in this study as a means of characterizing the rate at which selenium passes through the tree and is eliminated.

Section 1.2: The Animal Damage Problem

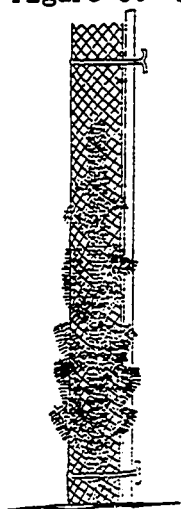
Modern forest management requires cost-effective regeneration of lumber-producing plantations on harvested sites. Newly planted seedlings are exposed to many harmful natural phenomena, including fire, disease, competitive vegetation and drought. However, studies of a number of reforestation attempts have shown that animal damage is often the single most important impediment to healthy seedling growth.⁽⁴²⁾ The relative importance of browse can only be enhanced by the increasing use of herbicides, which tends to knock down alternate feed material, making the seedling even more tempting forage. Many

animals have been identified as possible consumers of seedlings planted in the Northwest, including rabbits, mice, mountain beavers, pocket gophers and shrews. But it is deer, however, which are most commonly complained about by managers of reforestation programs. The Cooperative Animal Damage Survey (CADS) identified many particular problem areas around the West, and arrived at a monetary figure of approximately \$5,000,000/year damage done to Douglas-fir seedlings by deer in Washington and Oregon alone.⁽⁴¹⁾

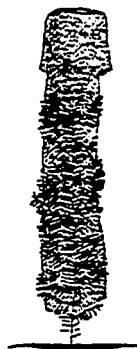
Section 1.2.1: Mechanical Barriers

This significant financial impact has led to the development of sometimes elaborate systems for the protection of tree seedlings from animal attack.⁽¹⁴⁴⁾ Everything from human hair to lion dung appears to have been tried, and the number of repellent systems found is roughly equal to the number of people with browse problems. The commercially available systems may be broadly classified as either mechanical barriers or chemical contact repellents.⁽⁴⁶⁾ Among the former are such devices as (see Fig. 6):⁽³⁹⁾ (1) a rigid, cylindrical, polypropylene mesh (Vexar^R tubing, E.I. du Pont & de Nemours & Co., Wilmington, DE) which forms a fence around the tree; (2) an elastic version of (1), known as Vexar^R netting and available from the same source, which fits the tree much like a nylon stocking; (3) leader tubes, which are small versions of (1) that protect only the leader and are not secured to the ground as the larger tubes must be; (4) paper bud caps, which consist of water resistant sheets that are

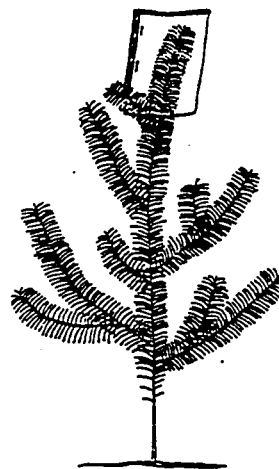
Figure 6. Mechanical Barriers to Animal Damage.



Vexar^R Tube

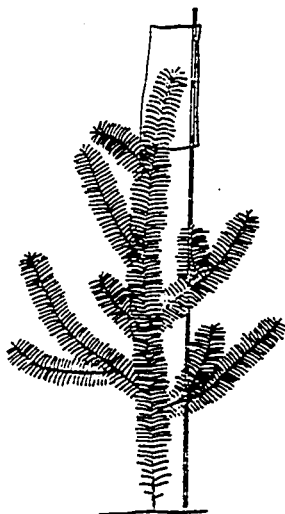


Vexar^R Netting



Paper Bud Cap

Reemay^R Sleeve



Reemay^R Bud Cap



Vexar^R Leader Tube



No Nibble^R



rolled up and stapled around the seedling's leader (the main terminal); (5) nonwoven polyester fabric (Reemay^R sleeve, E.I. du Pont & de Nemours & Co., Wilmington, DE) sewn in the form of a sock and simply slipped over the tree; (6) a smaller version of (5) which is spun with slightly heavier fabric and is stapled onto the leader much like a paper bud cap; and (7) No Nibbles^R, small polypropylene covers, shaped much like the shuttlecocks used in badminton, which are placed directly on the leader. All these devices have operational inadequacies that render them ineffective unless much care is taken during application to the seedling.^(8, 39) The time required to take this extra care translates into excessive labor costs of field application, which is not attractive to an industry, such as forestry, that does not have lots of free capital to throw at problems.

Even when the trouble is taken to properly deploy mechanical barriers, however, there is a whole host of shortcomings which often become evident with time.⁽³⁹⁾ The rigid devices can cause contorted growth of the tree and thereby introduce kinks in the trunk which render the tree of little future use.⁽⁸⁾ The socks, caps and sleeves all reflect significant quantities of light (>60%) and thus reduce the amount of energy available for photosynthesis. The main terminals of seedlings are very tender during early spring and can sometimes be damaged by even the slight extra force exerted downwards and laterally by sleeves or socks which rest on top of the tree. Finally, many of the devices are open at the top, such that when the leader protrudes it is likely to be browsed because the remainder of the tree is

unavailable.⁽¹⁴⁴⁾

A browsed seedling tip induces the formation of multiple leaders, such that several iterations of the browse process can transform the tree into a shrub.⁽³²⁻³⁴⁾ Such a plant would look fine as an ornamental bush nestled beside a residential home, but it has limited potential as a lumber producer for the forestry industry.

Section 1.2.2: Chemical Contact Repellents

To avoid the difficulties and limitations associated with the mechanical barriers, attention has turned to chemical deterrents. These efforts have resulted in the current availability, in the U.S.A., of two major products.^(1, 2, 46, 153) These chemical contact repellents are simply sprayed on the seedling in conjunction with an adhesive, and due to either their taste or their odor will reduce browse damage.^(1, 144) One strongly odored concoction consists of 37% putrescent whole egg solids (BGR^R Repellent, McGlaughlin-Gormley-King Company, Minneapolis, MN). The other malodorous material commonly used is Thiram (tetramethylthiuram disulphide), available from numerous sources. The use of Thiram is becoming less widespread, however, because of the close similarity of the material with a substance used to treat alcoholics that induces severe nausea upon the ingestion of any ethanolic beverages when it is present in trace amounts within the body. Problems have arisen with planters getting small amounts on their hands, improperly washing before lunch, and then getting violently ill at the bar after work. They have become

understandably irate about this.

Notwithstanding this limitation, contact repellents suffer in the field because of their relatively ephemeral lifetime on the foliage to which they are applied. (1, 144, 153) They weather fairly well if rainfall is not too great and the temperatures are not too extreme, but even under the optimal environmental conditions, the producers recommend that they be reapplied every six to eight weeks. (1, 144) This is necessary because the contact repellents protect only the particular foliage to which they adhere, and any new foliage which appears after application is not affected. (144) This shortcoming is crucial because the leader is made up of new growth and is the most frequently browsed portion of young trees.

Section 1.2.3: The Desirability of a Systemic Repellent

The essential drawbacks of both mechanical and chemical systems have led to the search for a systemic deer repellent. (46) Such a chemical should ideally be absorbed by the tree, metabolized, translocated to the foliage and eliminated in a form which is somehow repugnant to the browsing species. Only those chemicals which are able to exhibit this behavior without harming the tree's normal growth and development would be acceptable. Such a material would be ideal for protecting the new foliage, as this is where the major metabolic activity is taking place, and the systemic repellent would be consistently volatilized from the critical seedling leader. Hundreds of possible compounds have been investigated, but until recently, none

has been shown to decrease browsing at non-phytotoxic treatment levels. Among the candidates considered, selenium is particularly attractive because it is a natural ingredient of soils in large areas of the United States and elsewhere.⁽¹²⁹⁾ Animals accustomed to foraging in a seleniferous region are apparently able to detect the organoselenium odor exuded by selenized plants, and avoid eating the foliage.^(129, 146)

Section 1.3: The Wonders of Selenium

Truly living up to its name (from Greek for "moon", selēnē) selenium has waxed and waned as a commercially important material. Selenium possesses unique photo-conductive properties which make it quite useful for applications in xerography, and it is finding increasing use in second-generation semiconductor devices.⁽¹⁵⁰⁾ It is the biological activity of selenium, however, which has recently come under intense scrutiny, with much of this interest due to the observation of an inverse correlation between the incidence of several forms of cancer and the amount of Se in the diet.^(28, 53, 135) This is ironic, as the element was labeled as a carcinogen in the early 1950's, which resulted in a complete ban on the agricultural use of selenium in the United States. Only quite recently (August 1981), did the weight of experiments demonstrating the therapeutic effects of trace amounts of selenium in the diet result in a partial lifting of

and lambs is now routinely practiced in regions where selenium responsive diseases (especially white muscle dystrophies) are present.

Ever since selenium was first isolated by Berzelius in 1817, chemists working with the element have acquired a certain "air" about them that was somewhat unpleasant to their acquaintances.⁽¹⁵⁰⁾ The origin of this scent turned out to be the strong, garlic odor of seleno-organic compounds. The human body, as most biological organisms, converts selenium to a volatile form (in this case dimethyl selenide) in order to eliminate the element from the system^(25, 125, 150, 162) This same type of detoxification through methylation and subsequent volatilization has been observed for metallic elements other than selenium, most notably arsenic.⁽²⁵⁾

It should be noted, however, that although selenium is toxic at high concentrations in the body, there are many beneficial effects on humans at trace levels.^(4, 53) Paavo Airola, "America's foremost nutritionist," reports in his book, The Miracle of Garlic, that this common spice contains 0.44 ppm Se on a dry weight basis. Garlic is thus the best-known natural source of the element in the diet. The selenium component of garlic has been credited with many of the "miraculous" properties which the food purportedly has. The antioxidant capabilities of selenium in the body are primary among these benefits. Selenium appears to be a cofactor in the activity of vitamin E (tocopherol), and in the activity of the enzyme glutathione peroxidase.^(43, 130, 133, 136-138) The antioxidant properties are required in membranes, especially in red blood cells, across which

much oxygen diffuses. The inhibition of heavy metal poisoning by garlic has been attributed to its high sulfur and selenium contents. Protection against infections and the lowering of high blood pressure have also been linked with selenium, but these last two findings are less well corroborated. There is general agreement among nutritionists, however, that selenium is an essential nutrient, albeit in trace quantities, and a daily dose of 50 to 200 micrograms per day is recommended by the National Research Council as "safe and adequate." (157)

The ability of plants to convert selenium to foul smelling compounds has been known since the 1930's. (13-15, 49, 78, 79, 97, 98, 146)

An investigation of history texts reveals, however, that Marco Polo apparently gave the first (ca. 1295) written account of the avoidance of selenized foliage by foraging animals. (129)

Throughout all the mountainous parts of it [Tibet] the most excellent kind of rhubarb is produced, in large quantities, and the merchants who come to buy it convey it to all parts of the world. It is a fact that when they take that road, they cannot venture amongst the mountains with any beasts of burden excepting those accustomed to the country, on account of a poisonous plant growing there, which, if eaten by them, has the effect of causing the hoofs of the animal to drop off. Those of the country, however, being aware of its dangerous quality, take care to avoid it.

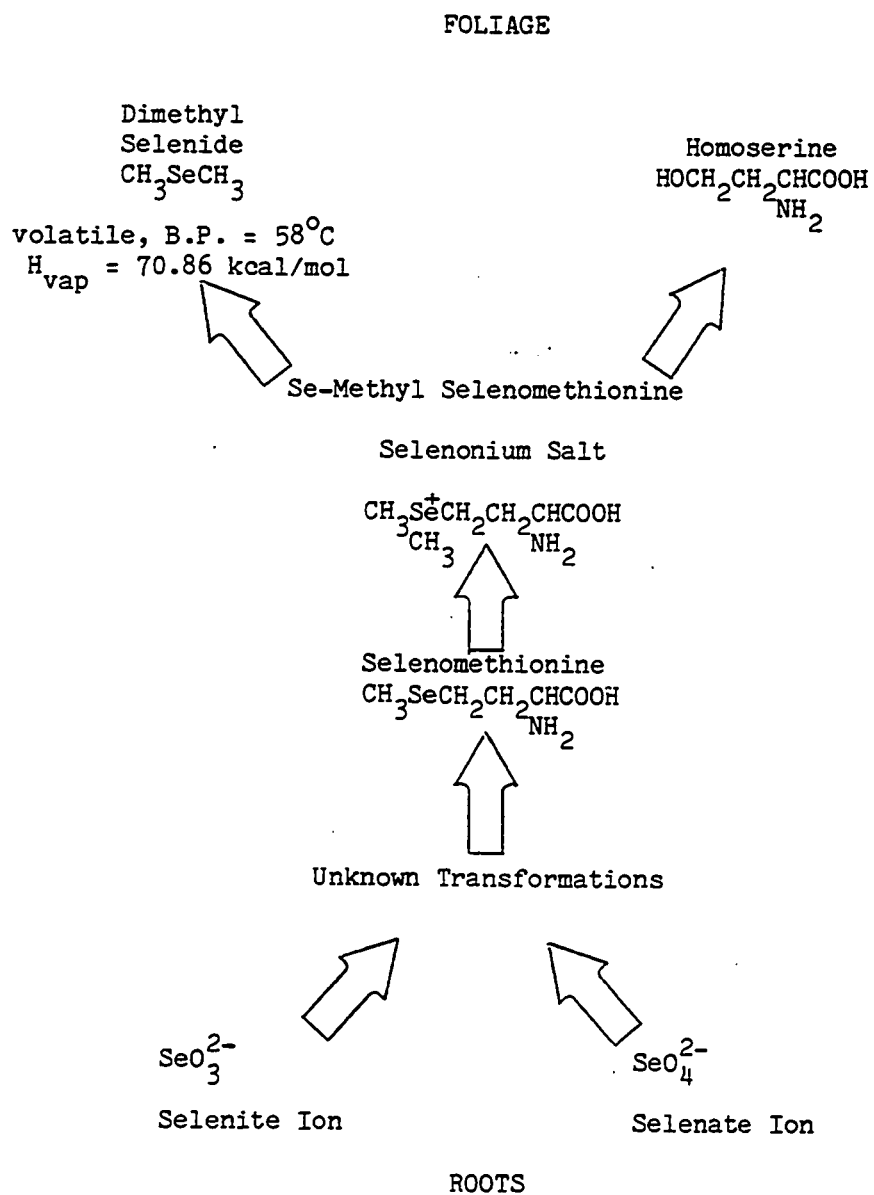
This disease which afflicts animals that have consumed large amounts of selenium is still known by the misnomer with which it was originally penned: "alkali disease." (48, 71, 107, 116, 152) This malady is observed in certain animals that forage among the Rocky Mountain regions of the United States, portions of which have soils

that are rich in selenium.⁽¹²⁹⁾

Only a few plant species are able to develop the foliar concentrations of selenium (> 1000 ppm) required to induce either alkali disease or other forms of selenosis.⁽¹²⁹⁾ Such plants have imaginatively been named selenium accumulators. The great majority of plants, however, including all commercially important species and certainly Douglas-fir (*Pseudotsuga menziesii*), are non-accumulators. As such, they are unable to tolerate foliar concentrations in excess of 100 ppm without suffering ill effects.^(6, 111, 129)

The metabolic steps involved in the processing of selenium by non-accumulating species which have so far been identified are shown in Fig. 7.⁽⁵⁴⁾ Very little is known about the first few steps following absorption of either the selenite or selenate ion. It has been shown, however, that the selenate ion is absorbed somewhat faster.^(17, 58, 79, 98, 155) Eventually, most of the absorbed selenium is incorporated as the seleno-analog of methionine. As shown in Fig. 7, this amino acid is then methylated to yield an unstable selenonium salt, and finally enzymatically cleaved to give dimethyl selenide and homoserine. Once in the plant, the selenate ion appears to exert a more severely phytotoxic effect than the selenite species, and the plant tends to retain selenium introduced in the more highly oxidized state, while more readily eliminating selenium absorbed as SeO_3^{2-} .^(79, 98) The toxicity of selenium appears to result from the inclusion of Se into proteins as analogs of methionine and cysteine.^(48, 82, 112, 129, 137-140, 152) The very slow kinetics of

Figure 7. Metabolism of Selenium by Nonaccumulating Plants.



the reduction of Se^{VI} to Se^{IV} (7) is probably responsible for the enhanced toxicity of the selenate ion, since this step must presumably occur before any of the subsequent detoxification reactions may take place.

These relatively recent findings explain the failure of the first attempts, by Rediske and Lawrence, to use selenium as a systemic repellent.⁽¹²⁶⁾ Only selenate ion formulations were used, and beneficial deterrent effects could not be demonstrated at non-phytotoxic selenium foliar levels. Selenite compounds were not tested as possible repellents because it was thought that the selenite ion would be quickly reduced in the acidic conifer planting soils which thermodynamically favor selenide formation. As earlier noted, these reduced forms are not generally available for absorption into the plant^(7, 115) Selenite ion can form insoluble complexes with compounds such as ferric hydroxides present in the soil,⁽⁷³⁾ but the formation of such species is reversible, and the selenium is still available for eventual absorption into the plant. Rediske and Lawrence also suggested (p. 147) that the selenite species are more toxic than the selenates, although this is contrary to the findings of most other workers.^(23, 79, 98, 129, 136-138)

Section 1.4: Summary of Past Work and Goals of this Project

Though highly touted by its proponents, the application of controlled release systems to both agricultural and forestry problems has been sluggish at best. Few sustained delivery products have made

a commercial impact in fields other than the pharmaceutical industry. The animal damage problem in reforestation is obviously a prime opportunity to deploy a timed release device to the soil, and thereby demonstrate that products designed from these new principles can have clearcut advantages over the conventional techniques.

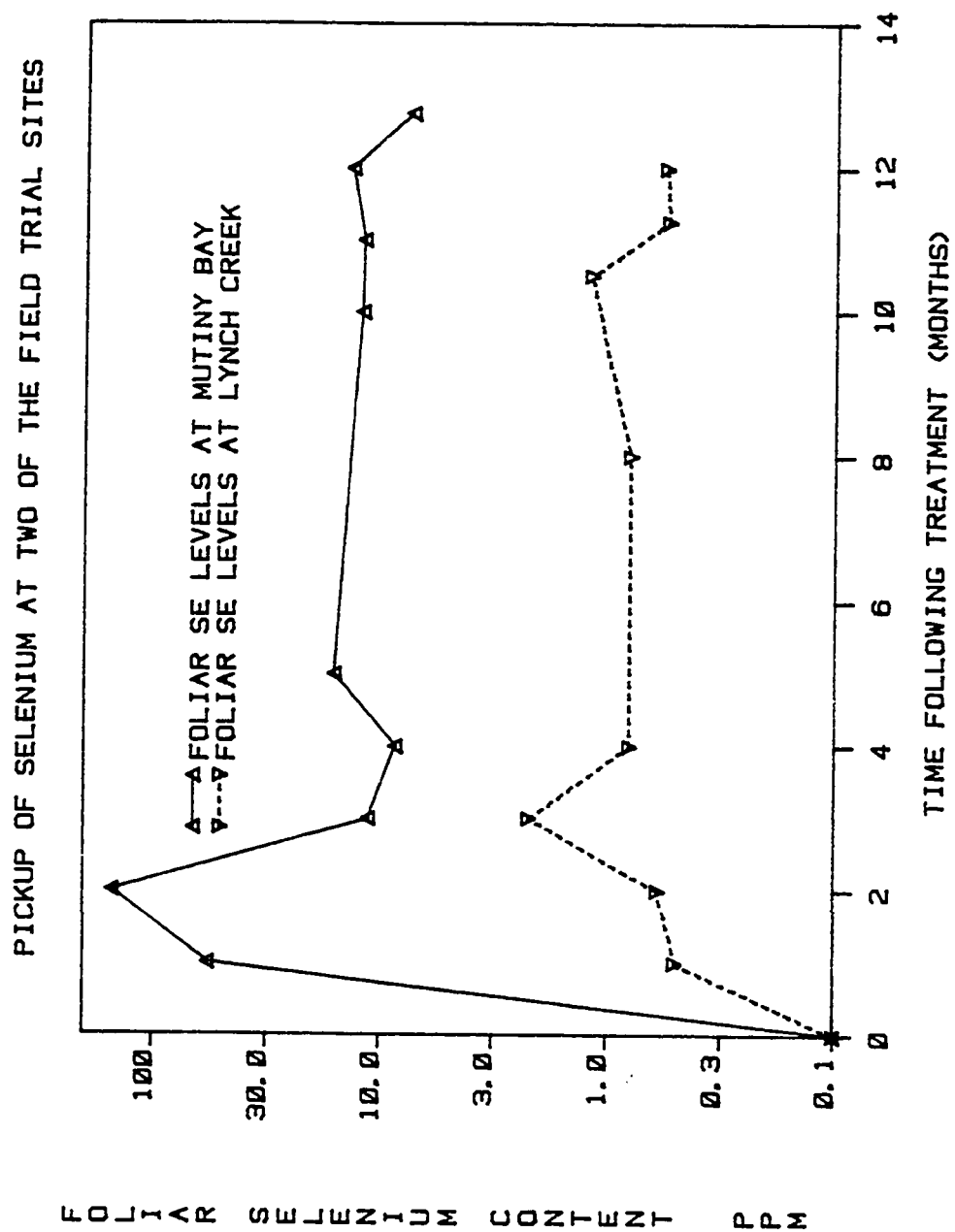
The characterization of such systems has been far from quantitative thus far,^(52, 151) and the application of chemical engineering principles to the problem has not yet been reported. A primary goal of the project was to carry out such an analysis, and arrive at a method for engineering sustained delivery systems in a more rational manner.

Chapter II: Theoretical Development

The formulation of a mathematical model which is able to make quantitative predictions about the behavior of any biological response is a formidable task. The myriad of biochemical pathways present in a living system is stupefying. Many simplifying assumptions will be required in order to simply write down any equations. These assumptions will be addressed in turn as they arise in the analysis, and conclusions will be reached concerning their consequences and validity. The success achieved at the end of the process, measured in terms of the model's ability to predict the response of Douglas-fir seedlings in the field to treatment with the selenium tablets will be taken as a de facto confirmation of the validity of the approach.

As a preview of the difficulties which will be encountered in the attempt to model the mass transfer of selenium within the soil/plant system, consider the data shown in Fig. 8. The upper curve represents the observed foliar Se content as a function of time following the treatment of trees with a selenium tablet at a field trial on Whidbey Island (Mutiny Bay). The lower curve indicates the foliar Se concentrations observed at a site (Lynch Creek) near Eatonville after treatment with precisely the same tablet formulation. The details of the experimental set-up are illustrated later, but for now it is sufficient to point out how different the results are. At the Mutiny Bay site the foliage contained well over 100 ppm Se in just a few weeks following the treatment, while at the Lynch Creek site no tree has ever been observed to contain more than 10 ppm Se in its foliage.

Figure 8. Pickup of Selenium at two of the Field Trial Sites.



The only difference between the two was that the tablets at Mutiny Bay had been placed in quite intimate contact with the root ball of the seedlings, which were planted on the very same day that they were treated. At Lynch Creek, however, the trees had been in the ground one year prior to treatment with the tablets, and the tablets were placed in small holes about an inch from the stem of the seedling.

The sensitivity of the response of the Douglas-fir seedlings to the manner in which they were treated was very surprising. This again points out the complexity of biological systems and highlights the difficulty of modeling their behavior. It is the goal of this theoretical development to derive equations which accurately describe the interaction of the sustained delivery system with the plant.

Section 2.1: Statement of the Problem

The mass transfer process to be described is a sequential series of steps including the following: 1) delivery of the active ingredient, in this case the selenite ion, to the soil solution; 2) diffusion of the active ingredient through the porous medium to the target area, which is an absorption site on the root; 3) absorption of the active ingredient from the soil solution across the root interface; 4) metabolism and translocation of selenium to the foliage; 5) volatilization of selenium away from the tree. In many agricultural applications it is only steps 1), 2) and 3) which are of interest, but as this should be a unidirectional process with

negligible feedback, no generality is lost by including steps 4) and 5), which are crucial to the performance of this systemic repellent. The important phenomena within each step of this process are described below.

Section 2.1.1: Dissolution of Selenite Ion from the Tablet

Because of the method in which the tablets were produced, there are two mechanisms by which selenite ion leaves the tablet surface to enter into the soil solution. The first is simple dissolution of the free dimelamine salt that is present in the tablet. The second is ion exchange between soil anions and the cationic resin formed during pellet formation (see Section 3.5, Preparation of Sustained Release Selenium Tablets...). The two processes are not completely independent because ion exchange occurs at a rate governed by the concentrations of the exchanging species, and the concentration of the selenite ion will of course be increased by the occurrence of the dissolution process near a region where ion exchange is taking place. Electric fields are generated whenever ions diffuse at different rates, and this is indeed the case with one of the tablets in the soil solution environment. Such fields act to slow the faster moving species. In terms of the mathematical model, these phenomena will contribute to the boundary condition for the selenite ion concentration at the surface of the tablet.

Section 2.1.2: Transfer of Selenium Through the Soil

Once in the soil solution, the selenite ion diffuses as all other soil anions, with the significant exception that it can form quite insoluble complexes with certain chemical species present in the soil. The most common, and most important to the process of interest, is the reaction of selenite ion with ferric hydroxide groups to form complexes of very low solubility.⁽⁷³⁾ These species have been blamed for the failure of efforts to alleviate selenium deficiencies in New Zealand by soil application of selenite ion.^(154, 155) This type of behavior has traditionally been handled mathematically by the addition a sorptive term for the disappearance of the diffusing ion from the soil solution. In the model developed here the sorptive term is accounted for by the inclusion of a second reaction term in the reaction/diffusion equation, one which competes in parallel with the root absorption sites for the selenite ion.

Even in the absence of chemical effects, however, the diffusion of materials in partially saturated soils is a problem of labyrinthian complexity to handle mathematically. In the field, the physical properties of the soil are never known precisely, i.e. local porosity, tortuosity, presence of voids, etc., such that it is never certain exactly how material will be displaced. The effective diffusion coefficient of the selenite ion is also a strong function of the fractional saturation of the soil, and the value for this moisture content of the soil is not readily available.⁽¹⁴⁵⁾ Operationally, it should be possible to arrive at a reasonable value for the saturation

through solution of the soil water equations with boundary conditions appropriate to the particular environmental data which bear on this, including evaporation rate, temperature, and of course precipitation. Unfortunately, evaporation rate data are very rarely available, and it is often necessary to be satisfied with simply diurnal high temperature, low temperature and precipitation. Convective flows can potentially become important if the soil is completely saturated, rainfall is heavy, and there are plentiful voids near the tablet, but the major modes of transport will be through molecular diffusion and wicking flows. In doing a worst case analysis, however, possibly to answer questions about ground water contamination, it would be prudent to include convective effects.

Section 2.1.3: Absorption of Selenium by the Roots

The absorption of ions by plant roots has been extensively studied and is relatively well understood. The kinetics of selenite ion absorption were not known at the start of this study, but have been shown to be well-described by the Michaelis-Menten analysis. The values determined for the rate constants were found in nutrient solution in the absence of diffusion effects, and were calculated on a per gram of root basis. Thus in order to apply these data correctly in the field, one requires some knowledge of the root distribution through the soil. This is a question which has been studied in detail for Douglas-fir seedlings, and it has been found, as might be expected, that there is great variability in the types of root

distributions found.⁽⁵⁰⁾ This variability will introduce "noise" into all of the data which are obtained in the field.

Section 2.1.4: Internal Biokinetics of Selenium Metabolism

The internal biokinetics of selenium metabolism are mostly unknown, and would take many person-years of study to fully elucidate. For the purposes of modeling the transport of the element through the seedling, however, it is sufficient to note that time constants for water transport through the seedling are significantly greater than any time constants one could reasonably hypothesize for the rates of chemical conversion. This means that by the time selenium is transported to the foliage of the tree, it should have already undergone most of its transformations, and the mainly physical process of water uptake dominates the rate at which volatile selenium appears in the foliage.

Section 2.1.5: Volatilization of Selenium from the Foliage

Once in the foliage, volatilization of the element occurs as dimethyl selenide is split off from an unstable selenonium salt. The rate at which this occurs was unknown when the work began, but reasonable values for an effective first order volatilization rate constant may be extracted from data obtained in both this and earlier studies. Temperature is of primary importance in determining the actual rate at which dimethyl selenide leaves the needles, as the vapor pressure of the liquid is a strong function of T.

Section 2.2: Model Development

The model of selenium transport through the tablet-soil-plant system will be developed in a series of steps, which roughly correspond with the steps involved physically. A model relating the soil water to the available precipitation and temperature data will first be developed. A description then follows of the analytical techniques used to relate the accelerated dissolution studies to the performance of the tablets in the soil environment. The question of internal diffusive resistances within the tablet is then addressed. A two dimensional model of selenium diffusion from the cylindrical tablet is then derived, and the computer program based on the model is extensively tested. The rate of water transport through the seedling is thought to be the phenomenon which determines the rate at which selenium moves from the roots to the foliage, and a model is therefore derived to calculate this flow from meteorological data. Finally, a compartmental model of the type normally seen in the pharmacokinetic literature is used to describe the concentrations of selenium in both the root and foliar tissue.

Section 2.2.1: Soil Water Relationships

The interaction of water with soil is a complex series of phenomena beyond the reach of exact analytical description because of the nonuniformities present in all natural soils. Nevertheless, important progress has been made in the analysis of soil water physics

by means of simplifying assumptions that have varying degrees of validity.

The most relevant aspect of soil water movement to this project is the vertical movement of water in response to either rainfall or evaporation. The vertical infiltration of water into soil has been shown to be well characterized by the Boltzmann similarity transformation for short distances into the soil.⁽⁷⁰⁾ Evaporation has been observed to occur in three relatively distinct stages. During the first the evaporative flux remains relatively constant as the soil moisture content curve attains a more severely curved shape near the evaporative surface. This curvature increase is necessary in order to maintain a constant flux since the hydraulic conductivity falls with moisture content. When the moisture content curve becomes sufficiently sharp the evaporative flux falls as the moisture content gradients level off, no longer able to respond to the atmospheric demand for water. In a final drying stage the water table actually begins to drop, but this stage is rarely observed, especially in the western Washington soils considered in this study.⁽⁵⁰⁾

As noted earlier, the moisture content of the soil has a very strong effect on the effective diffusivity of an active ingredient, in this case the selenite ion. Reasonably accurate solution of the reaction/diffusion problem will require that a value for the effective diffusivity be obtained. This necessitates solution of the equations that govern the moisture content of partially saturated soil. The following form of Darcy's law has been given as just such an

equation: (51)

$$-\frac{dS}{dP_c} \frac{\partial P}{\partial t} = \frac{\partial}{\partial z} \left(k_r \frac{\partial P}{\partial z} \right) - \frac{\partial k_r}{\partial z} \quad (2-1)$$

This is a nondimensional form of Darcy's law in which the pressure has been nondimensionalized with respect to ρgL , where ρ is the density of the fluid, g is the gravitational acceleration and L is a characteristic depth. The vertical position, z , has been made dimensionless through division by L . Time has been divided by a characteristic time constant, t_c given by:

$$t_c = \frac{\rho_o L \mu}{k_o \rho g} \quad (2-2)$$

Soil porosity has been denoted by ρ_o , fluid viscosity by μ , and the soil permeability at complete saturation by k_o . The relative permeability of the soil, $k_r = k/k_o$, is dependent on the capillary pressure (P_c , defined as the air pressure minus the water pressure) in the following manner:

$$k_r = \frac{1}{1 + (P_c L/B)^\lambda} \quad (2-3)$$

The constants which appear in this equation must be determined experimentally (see Section 3.15, Determination of Soil Properties). The saturation of the soil may also be related to the capillary pressure through a similar empirical relationship:

$$\frac{S-S_r}{1-S_r} = \frac{1}{1 + (P_c L/A)^\eta} \quad (2-4)$$

Here the quantity S_r is the so-called irreducible saturation, a moisture content below which the soil may not be dried. It should be noted that a hysteresis phenomenon is often observed for both the permeability and the saturation of porous media, such that the wetting value of either the saturation or permeability at a given capillary pressure will be different depending on whether the soil is wetting or drying. The magnitude of the difference between the wetting and drying curves depends on the particular soil, but representative behavior of the type normally seen is portrayed in Figures 9 and 10.

The method chosen to solve the soil saturation equation involved a major simplification at the outset: neglecting the gravity term. With this assumption a similarity transformation to the equation may be obtained with a variable of the characteristic Boltzmann form, $\xi = z/(t^{1/2})$. The partial differential equation is thus reduced to an ordinary differential equation in the similarity variable:

$$\frac{d}{d\xi} \left(k_r \frac{dP}{d\xi} \right) - \frac{\xi}{2} \frac{dS}{dP} \frac{dP}{d\xi} = 0 \quad (2-5)$$

In addition to losing the gravitational effects, this simplification restricts the type of boundary conditions which may now be applied to the solution; in particular, the pressure must be set equal to a constant at both $\xi = 0$ and $\xi \rightarrow \infty$. Physically this corresponds to a situation in which the pressure is initially uniform

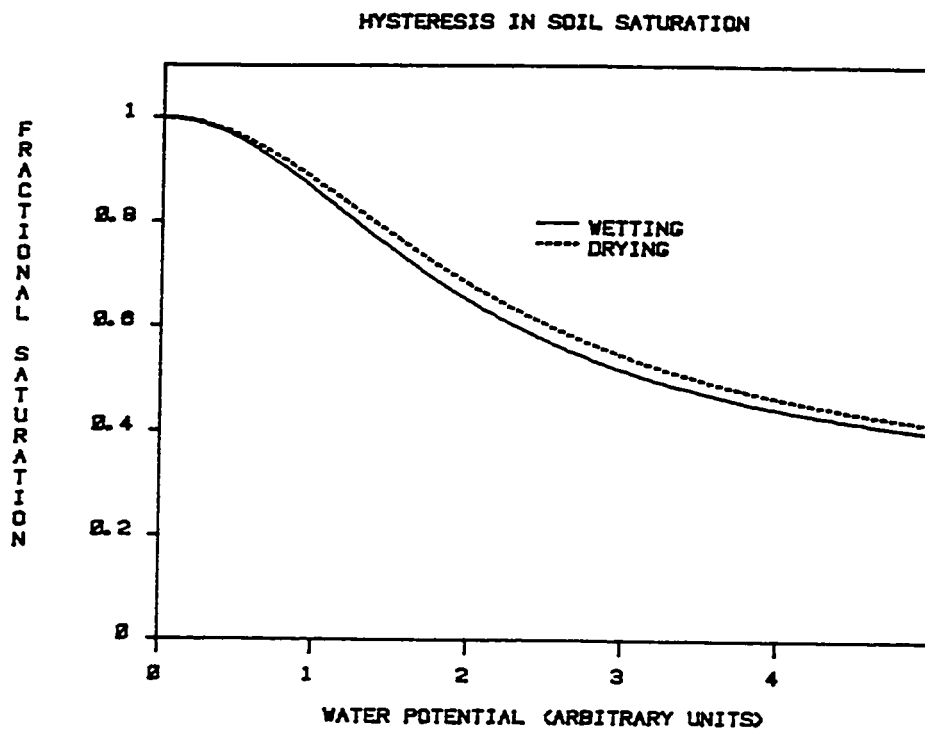


Figure 9. Saturation as a Function of Water Potential.

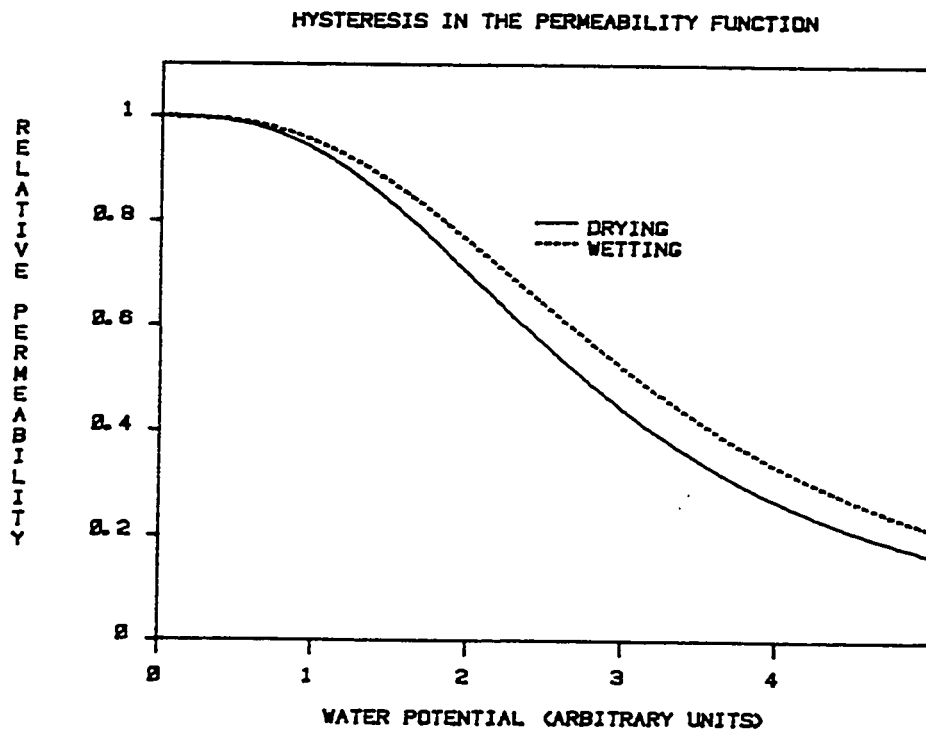


Figure 10. Hydraulic Conductivity as a Function of Water Potential.

in z , and a step change is introduced at $z=0$ at time $t=0$ to a new constant value. This generates a front which then propagates through the porous medium. This will obviously only be valid for relatively small values of L , the characteristic length, because if L becomes large then there must be a significant hydrostatic head. The system of current interest, however, involves a tablet placed about 2 cm beneath the surface of the soil. As shown later, the active agent diffuses only about 1 cm into the soil. Thus the hydrostatic head that is generated under the most severe conditions is only ($\rho \times g \times 3$ cm) or 0.003 atm.

Numerical solution of equation (2-5) is required because of the highly nonlinear nature of both the permeability and saturation dependences on capillary pressure. It is most convenient to transform the domain from ξ to a new variable $y=e^{-\xi}$ such that the boundary conditions are given at finite values of the independent variable. In terms of this new variable the differential equation becomes:

$$\frac{dk_r}{dy} \frac{dP}{dy} y^2 + k_r \frac{d^2P}{dy^2} + \frac{dP}{dy} y + \frac{y}{2\ln(1/y)} \frac{dS}{dP} \frac{dP}{dy} = 0 \quad (2-6)$$

If the initial pressure throughout the porous medium is BP_0 and the pressure to which the boundary is changed to at time $t=0$ is BP_1 , then the boundary conditions to which this equation is subject are:

$$P(y=0) = BP_1$$

(2-7)

(2-8)

$$P(y=1) = BP0$$

A finite difference representation of the equation is now easily derived by replacing second-order difference expressions for the derivatives that appear. This substitution gives the following nonlinear difference equation:

$$\begin{aligned} & \frac{(k_{r_{i+1}} - k_{r_{i-1}})}{2\Delta y} \left(\frac{P_{i+1} - P_{i-1}}{2\Delta y} \right) y_i^2 + k_{r_i} \left(\frac{P_{i+1} - 2P_i + P_{i-1}}{\Delta y^2} \right) y_i^2 + \left(\frac{P_{i+1} - P_{i-1}}{\Delta y} \right) y_i \\ & + \frac{dS}{dP_{c_i}} \left(\frac{P_{i+1} - P_{i-1}}{\Delta y} \right) \frac{y_i}{2\ln(1/y_i)} = 0 \end{aligned} \quad (2-9)$$

The boundary conditions simply force both P_0 and P_n to take on the values at the ends of the domain. An iterative technique was applied to solve the matrix which is generated (see Appendix A for a listing of the program). The pressures at each of the grid points were initialized by a simple ramp function between BP0 and BP1. At each iteration the new value for P_i was given by:

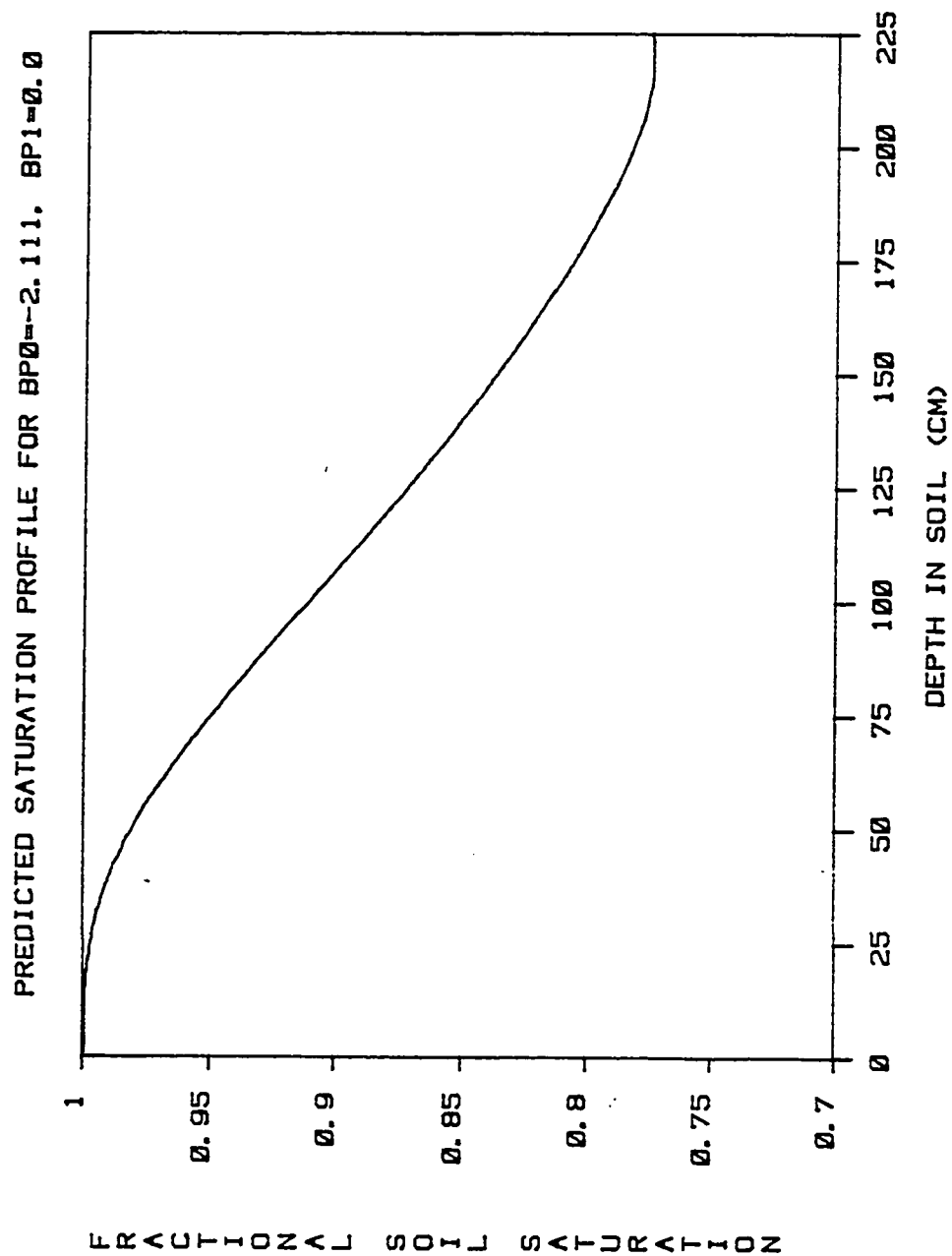
$$P_i = \left(\frac{\Delta y^2}{2k_{r_i}} \right) \left(\frac{(k_{r_{i+1}} - k_{r_{i-1}})}{2\Delta y} \right) \left(\frac{P_{i+1} - P_{i-1}}{2\Delta y} \right) y_i^2 + \left(\frac{P_{i+1} - P_{i-1}}{\Delta y} \right) y_i + \quad (2-10)$$

$$\frac{dS}{dP_{c_i}} \left(\frac{P_{i+1} - P_{i-1}}{\Delta y} \right) \frac{y_i}{2\ln(1/y_i)} + k_{r_i} y_i^2 \left(\frac{P_{i+1} + P_{i-1}}{\Delta y^2} \right)$$

which is simply the equation that results from isolating P_i to one side of equation (2-9).

An example of the type of saturation profiles predicted by the similarity solution is shown in Fig. 11 for the following parameter

Figure 11. Soil Saturation as a Function of Depth at the End of a One Day Period with $BP_0 = -2.111$, $BP_1 = 0.0$.



values:

$$\begin{array}{lll} L = 100 \text{ cm} & S_r = 0.32 & \eta = 3.65 \\ A = 231 \text{ cm} & p_o = 0.485 & \lambda = 6.65 \\ B = 146 \text{ cm} & k_o = 0.5 \mu^2 & \end{array}$$

The shape of the profile is relatively sensitive to the particular soil properties (hydraulic conductivity, etc.) which are used to generate the profiles.

The effective diffusivity of the selenite ion may then be calculated from this value for the saturation. Different physical processes become responsible for the movement of the selenite ion as the saturation takes on different values. At complete saturation, the effective diffusivity of the selenite ion would best be given by its value in pure water divided by the tortuosity. When gradients of saturation exist in an unsaturated soil, however, then molecular diffusion becomes relatively less important compared to the wicking flows which are at work in the soil, and an enhancement of the effective diffusivity would be expected over what would be observed due to statistical fluxes alone. The most valid approach would be to solve the convective-diffusion equation with non-zero velocity terms in order to properly account for this enhancement to the mass transfer. The complexity of the velocity profiles encountered in porous media prevented such a technique within the scope of this initial study, however, and the effective diffusivity was approximated by the following ad hoc equation:

$$D_e = \frac{SD_o}{\tau} + \frac{(1 - S)}{(1 - S_r)} \frac{k\phi gL}{\mu} \quad (2-11)$$

This equation expresses mathematically the intuitive expectation that mobility near saturation will be dominated by molecular diffusion, and that at dry conditions near S_r transport is essentially due to the wicking flows and the effective mobility is equal to that of the water. As will be seen in Chapter IV, the soils in western Washington are generally quite damp, so that the only major contribution is from the first term in eq. (2-11). Thus the second term, which has no theoretical basis, is of negligible importance to the current study. It might prove helpful, however, in the analysis of dry soils.

Section 2.2.2: Theoretical Description of the Mass Transfer

From a Tablet in the Dissolution Accelerator

A crucial value which is required in order to accurately characterize the release of selenium from a tablet placed in the soil is the concentration of selenite ion at its surface. If the tablet were simply dimelamine selenite alone, then it could safely be assumed that this value was the solubility of the salt. The situation is somewhat more complicated, however, because the method used to form the tablets resulted in the creation of an ion exchange resin as the polymeric backbone of the pellet.

In order to experimentally determine the effect of ion exchange on the release of selenium from the tablet, an apparatus was

constructed in which the tablet was rotated at high speed (~1000 rpm). This rotation rate effectively accelerated the delivery of selenium from a process measured in terms of years to a process measured in terms of hours. The enhancement of the delivery rate can be quantified in terms of a mass transfer coefficient for the particular geometry involved.

The geometry involved in the dissolution accelerator is shown in Fig. 41. This geometry has certain similarities to the rotating disk problem considered by Levich, in which a "uniformly accessible surface" is predicted theoretically and achieved experimentally.⁽⁹⁶⁾ A brief summary of his analysis follows.

A solution to the equations of motion is sought through the hypothesis of the following functionalities for the velocity components and the pressure:

$$v_r = r\omega F(\zeta) \quad (2-12)$$

$$v_\phi = r\omega G(\zeta) \quad (2-13)$$

$$v_z = \sqrt{v\omega} H(\zeta) \quad (2-14)$$

$$P = -\rho v\omega p(\zeta) \quad (2-15)$$

where the height above the pellet has been nondimensionalized through the definition $\zeta = \sqrt{\omega/\nu} z$. These substitutions yield a set of nonlinear

ordinary differential equations for the four hypothesized functions:

$$F^2 - G^2 + F'H = F'' \quad (2-16)$$

$$2FG + G'H = G' \quad (2-17)$$

$$HH' = p' + H'' \quad (2-18)$$

$$2F + H' = 0 \quad (2-19)$$

The boundary conditions are fixed by the particular geometry which Levich considered, in which there is no-slip at the disk surface and a uniform velocity of fluid towards the disk at distances far from its surface. Mathematically, this yields:

$$F(0) = 0 \quad F \rightarrow 0 \text{ as } \zeta \rightarrow \infty \quad (2-20)$$

$$G(0) = 1 \quad G \rightarrow 0 \text{ as } \zeta \rightarrow \infty \quad (2-21)$$

$$H(0) = 0 \quad H \rightarrow -\alpha \text{ as } \zeta \rightarrow \infty \quad (2-22)$$

$$p(0) = p_0 \quad p \rightarrow \beta \text{ as } \zeta \rightarrow \infty \quad (2-23)$$

Asymptotic solutions to the equations have been obtained as a series of exponentials for large ζ , and as a power series for small

ζ . The particular form of the velocity functions are shown in Fig. 12. When this author plotted the expansions reported by Levich for the velocity functions, it was observed that they did not match satisfactorily. The best fit that could be obtained with the constants given by him is shown in Fig. 12. The data in Fig. 13 demonstrate that a slight alteration in the value of two of his constants, "a" and "b," made for a much better fit. Nevertheless, the important result is that a boundary layer forms near the disk, and this boundary layer has a thickness which is essentially independent of radial position. The actual thickness of the boundary layer is of course somewhat arbitrary, but at a position $\zeta = 3.6$, the axial velocity has reached 80% of its limiting value and the angular velocity has decayed to 5% of the disk velocity. For small distances from the surface of the disk, the velocity towards the disk is well approximated by the leading term in the power series:

$$v_z \approx -0.51 \sqrt{\omega^3/\nu} z^2 \quad (2-24)$$

Two criteria must be met for this solution to retain its validity. As the edge effects have been ignored, one requires that the boundary layer thickness must be significantly less than the disk radius. Laminar, steady flow has also been assumed, and this has been found to be valid up to Reynold's numbers (based on disk radius and the angular velocity) on the order of 10,000. For extremely well polished and well centered disks, laminar character can be retained as

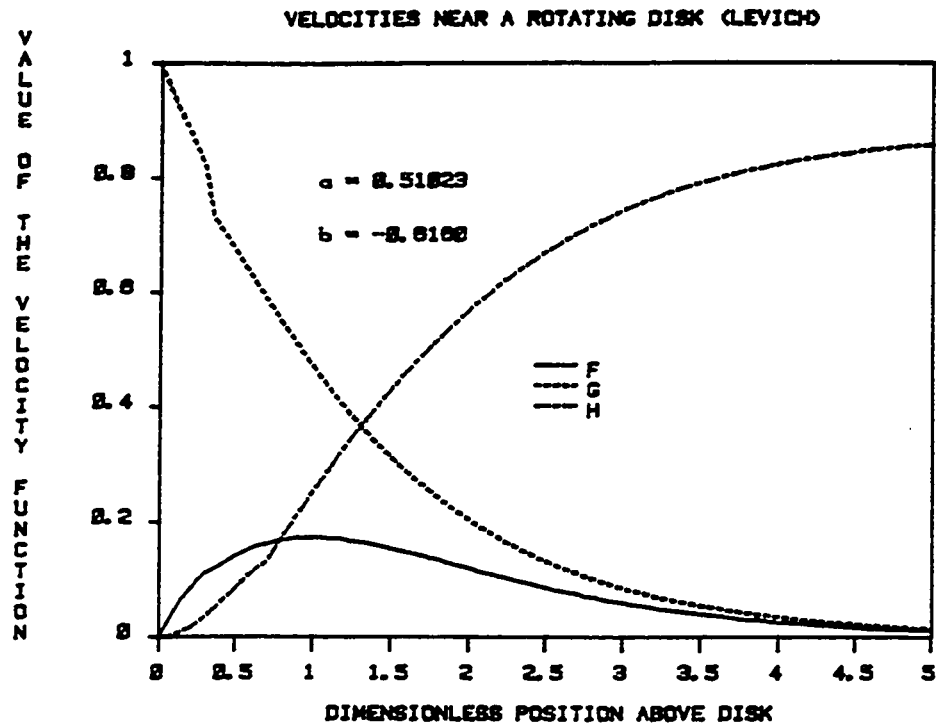


Figure 12. Velocity Profiles Near a Rotating Disk (Levich).

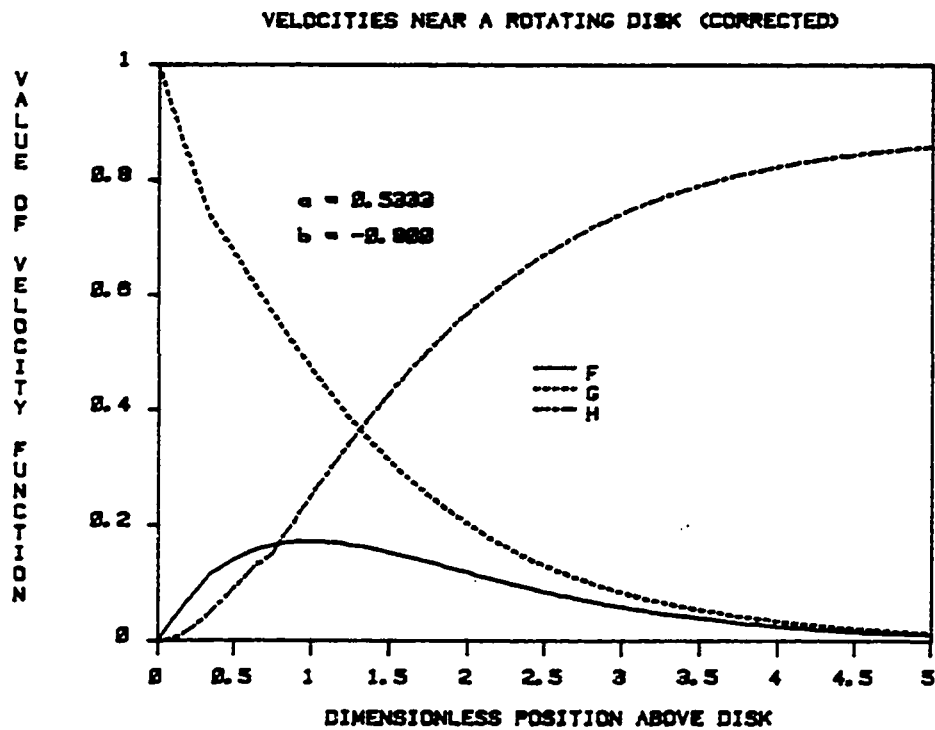


Figure 13. Velocity Profiles Near a Rotating Disk (Corrected).

high as $Re=100,000$.⁽⁹⁶⁾

Mass transfer to or from such a rotating disk system is well characterized. The mass transfer coefficient is constant across the disk surface because the hydrodynamic boundary layer thickness is independent of radial position. A simple analysis using the leading term in the power series for v_z (valid for high Schmidt numbers) suggests that the mass flux from the disk surface should be (with a slight correction as noted earlier):

$$J = 0.617 \frac{D^{2/3} \omega^{1/2}}{\nu^{1/6}} C_s \quad (2-25)$$

In principle then, C_s could be determined by the measurement of all the other terms in this equation. Unfortunately, however, the tablet installed in the dissolution apparatus does not have the same geometrical configuration. In particular, there is the radial face which is also exposed to solution. Mass transfer from this type of geometry has not been fully reported in the literature, but a simple analysis may be applied to an infinitely long rotating cylinder. At steady state there is no enhancement to the mass transfer because there is no radial component to the velocity, and all mass transfer is in the radial direction. Because of the edge effects, however, there are both axial and radial components to the velocity near the tablet rim, but experiments with injected dye suggest that this effect is not of significance. More convincing are the scanning electron micrographs shown in Plates I-IV, which clearly demonstrate that an

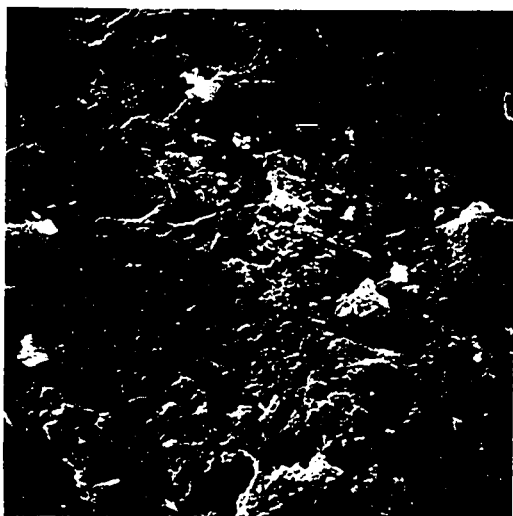


Plate I. Radial Face Before
Dissolution (x1020).

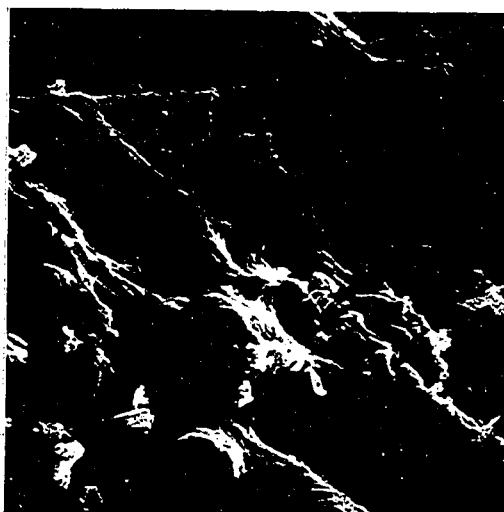


Plate II. Axial Face Before
Dissolution (x969).

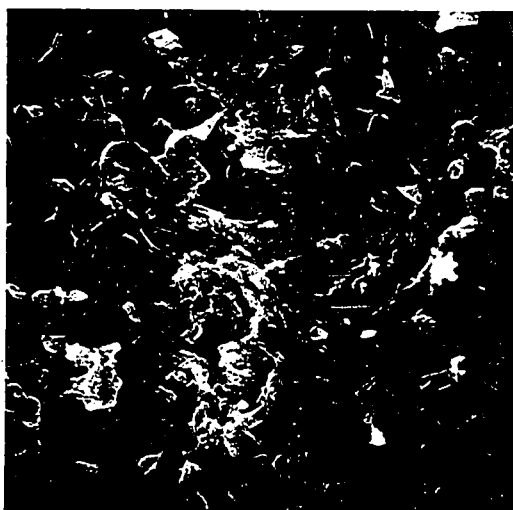


Plate III. Radial Face After
Dissolution (x1046).

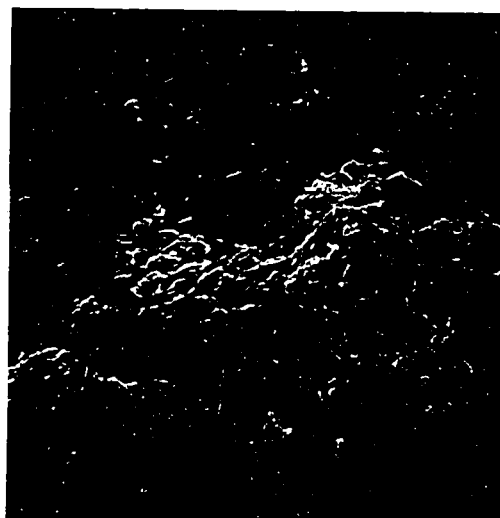


Plate IV. Axial Face After
Dissolution (x1003).

elaborate pore structure builds within the axial face of the tablet during dissolution, while the radial face remains relatively unscathed. The radial face actually appears to have become smoother (cf. Plates I and III) during the dissolution process. Thus it is reasonable to retain the Levich analysis as a first order approximation to the mass transfer coefficient.

Section 2.2.3: Modeling Diffusion within the Tablet

A phenomenon occurs in the dissolution process which quickly makes the major resistance to mass transfer appear within the tablet. This is because as the dimelamine selenite enters the solution phase, it leaves behind a more and more porous matrix, the diffusion through which soon constitutes the major resistance to mass transfer. Exact analytical description of this process would require more information about the nature of the tablet morphology than is currently available, but the following simplified approach has proven successful at providing a reasonable fit to the collected data.

Consider first a right cylindrical pore (of length L) as it develops within the tablet. Mass transfer through this pore can be approximated by the following equation:

$$J_{\text{pore}} = \frac{DC_s}{L} \quad (2-26)$$

The solubility of the material is denoted by C_s ; and its diffusivity is given by D . Several assumptions have been made in

writing down this equation, including a pseudo-steady state, a perfect sink in the external solution, and constant diffusivity. The molar flux, J , can also be related to the depth of the pore through a simple mass balance. This exercise yields the following differential equation:

$$J_{\text{pore}} = \frac{\rho}{MW} \frac{dL}{dt} \quad (2-27)$$

The molecular weight of the material is given by MW ; its density is ρ and d/dt is a derivative with respect to time. Substituting the various terms which make up the molar flux and separating, we obtain an equation which may be integrated to give the time dependence of the "infiltration distance," L . If the assumptions of constant diffusivity and a perfect sink are retained, then the analysis suggests that L increases as the square root of time (similar to the Higuchi analysis).

A more realistic assumption is to recognize that the flux through the pore is coupled with the external mass transfer considered in the previous section (see Fig. 14). This coupling may be quantified by defining p to be that fraction of the pellet's axial face which is made up of pores. Then the flux through all of the pores, as given by either of eq's. (2-26) or (2-27), may be related to the flux through the external boundary layer. This exercise is equivalent to an abandonment of the infinite sink assumption. Defining C_t to be the concentration at the pore mouth, the driving force for the internal

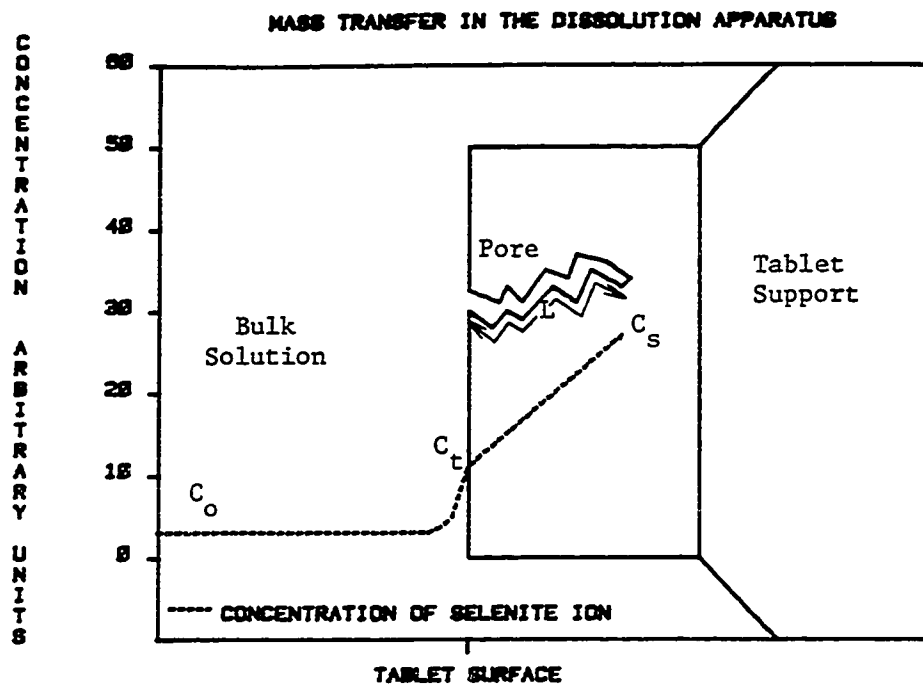


Figure 14. Mass Transfer in the Dissolution Apparatus.

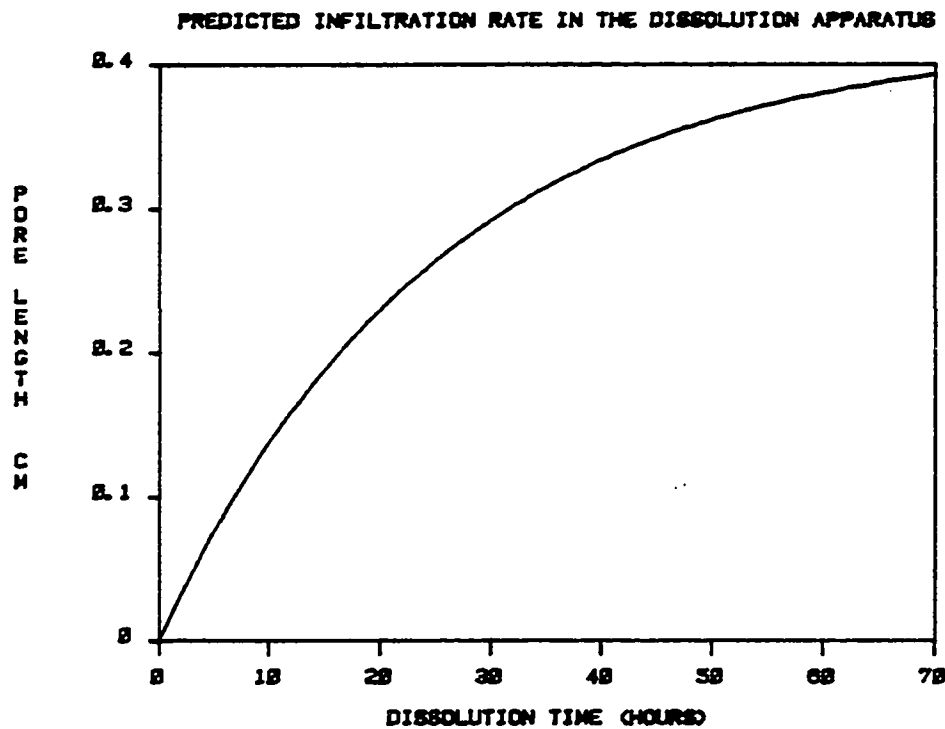


Figure 15. Predicted Time Dependence of the Pore Length.

mass transfer becomes $C_s - C_t$, and the driving force for the external mass transfer becomes $C_t - C_o$, where C_o is the concentration of selenium in the bulk solution. This concentration in the bulk solution can be related to the flux and the geometry of the dissolution device used (see Appendix B). A differential equation for L , the pore length, is then obtained through manipulation of eq's. (2-25) - (2-27), (see Appendix B for a full derivation):

$$C_s - \frac{pA\phi L}{V MW} = \left(\frac{L}{pDC_s} + \frac{1}{k} \right) \frac{p\phi}{MW} \frac{dL}{dt} \quad (2-28)$$

When integrated this equation yields an exponential time dependence for the infiltration distance:

$$t = \frac{1}{p} \left(\left(\frac{V}{A\phi} \right)^2 \left(\frac{C_s MW}{D\rho} \right) + \frac{V}{A k} \right) \ln \left(\frac{1}{1 - \frac{p L A \phi}{V MW C_s}} \right) - \frac{L V}{D A p} \quad (2-29)$$

The flux that is then predicted from the tablet as a function of time is directly proportional to L . An example is shown in Fig. 15 for the following parameters:

$$\begin{array}{lll} p = 0.5 & C_s = 2.5 \times 10^{-5} \text{ mol/cm}^3 & D = 3.0 \times 10^{-6} \text{ cm}^2/\text{s} \\ V = 8 \text{ L} & \rho = 1.315 \text{ g/cm}^3 & k = 1.397 \times 10^{-3} \text{ cm/s} \\ A = 1.267 \text{ cm}^2 & & \end{array}$$

Justification of this model is found in the excellent agreement between the flux predicted and the results obtained in the dissolution studies.

It is important to note that this model is overly simplified for the ion exchange process under consideration. As the gradients of exchanging ions develop within the tablet there are electric fields generated. This phenomenon occurs because the more mobile ions diffuse faster, which would result in a net charge buildup were it not for the electrostatic force. As this net charge builds an electric field evolves which acts to oppose the movement of the more mobile species until a dynamic equilibrium is established between the statistically generated diffusive flux and the electrostatically driven flux. The actual diffusivities observed in such a system have been predicted theoretically to be roughly equal to that of the slower species, and this is in fact what has been observed. (66, 67)

The full equation which has been derived for the dependence of the diffusivities on concentration is the following:

$$D_{AB} = \frac{D_A D_B (z_A^2 C_A + z_B^2 C_B)}{z_A^2 C_A D_A + z_B^2 C_B D_B} \quad (2-30)$$

Since the selenite ion was found to have a very low diffusion coefficient, this equation suggests that the effective ionic mobility during any ion exchange process involving the selenite species will be equal to $D(\text{HSeO}_3^-)$.

Section 2.2.4: Modeling the Diffusion of Selenium Through the Soil

When a sparingly soluble tablet is placed in the soil, the material leaches away from the tablet surface in a manner which should

be governed by the continuity and convective diffusion equations. If bulk flow is ignored and steady state is assumed, then an elliptic boundary value problem arises for the active ingredient (a. i.) concentration, C:

$$D_e \nabla^2 C - R(C) = 0 \quad (2-31)$$

$C = C_t$ at tablet surface
 $C \rightarrow 0$ far from the tablet

The effective diffusivity of the selenite ion is denoted by D_e . As noted earlier, the value of this coefficient is dependent on the soil moisture content, and this will restrict the validity of the steady state solution to time intervals in which the saturation is constant. The kinetic parameters that make up the $R(C)$ term will vary with temperature, in a manner dependent on the value of the pertinent effective activation energies, and this will also limit the steady state analysis to time intervals of relatively constant climactic conditions. The active agent is removed from the soil solution at a rate given by $R(C)$, which is assumed to be made up of two competing Michaelis-Menten rate expressions. The boundary condition at the surface of the tablet merely forces the selenite ion to be in equilibrium with the tablet. For a simple salt tablet this concentration would be the agent's solubility. In this case, however, the equilibrium delivery concentration is a function of soil solution ionic strength and the amount of selenium which has already left the tablet. The behavior of this parameter has been obtained as a

function of these variables through the accelerated dissolution experiments as discussed earlier, and will be regarded as known throughout the rest of the analysis. It is important at this point to carefully define what is meant by the concentration of the active ingredient. The concentration of selenite ion in a beaker of water may be unambiguously defined as the grams or moles of selenium per unit volume. In an unsaturated soil, however, the situation is somewhat muddled. It shall be the convention throughout this analysis that C is given as the moles of selenite ion per unit volume (generally cm^3) of water. The "bulk" concentration of selenium in the soil, on a volumetric basis, is thus obtained by multiplying this concentration by the factor ($S \cdot p_o$), where p_o is the fractional pore volume and S is the fractional saturation. For example, if a soil has a porosity of 0.5 and a saturation of 0.5, in which the water is saturated with dimelamine selenite ($\sim 0.025 \text{ M}$), then there is actually a bulk concentration of selenium in the soil of $0.025 \cdot 0.5 \cdot 0.5 \text{ M}$, or about 0.006 moles of selenium per liter of soil.

Far away from the tablet this concentration falls to zero, or possibly to its environmental value (which is essentially zero for the soils considered in this study).

For a cylindrical tablet of radius, r_o , and thickness, z_o , eq. (2-31) becomes:

$$D_e \left(\frac{\partial^2 C'}{\partial r'^2} + \frac{1}{r'} \frac{\partial C'}{\partial r'} + \frac{\partial^2 C'}{\partial z'^2} \right) - \left(\frac{v_{\max}^a C'}{K_m^a + C'} + \frac{v_{\max}^d C'}{K_m^d + C'} \right) = 0 \quad (2-32)$$

$$C' = C_t \text{ at } r' = 0 \text{ for } -z_o/2 < z' < z_o/2 \\ \text{and at } z' = z_o/2 \text{ for } 0 < r' < r_o \quad C' \rightarrow 0 \text{ as } r' \text{ and } z' \rightarrow \infty$$

Dimensional variables have now been primed and the Michaelis-Menten (mildly nonlinear) kinetics have been inserted for absorption and deactivation of the active agent. It has been assumed that the reactive sites are uniformly distributed, obviously a somewhat questionable assumption. The equation is nondimensionalized with the following definitions:

$$C = C'/C_t \quad (2-33)$$

$$r = r'/r_o \quad (2-34)$$

$$z = 2z'/z_o \quad (2-35)$$

The delivery concentration of selenium at the tablet surface is given by C_t , and the other constants have been previously defined.

These substitutions yield the nondimensional equation:

$$\frac{1}{h_{Tr}^2} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) + \frac{1}{h_{Tz}^2} \frac{\partial^2 C}{\partial z^2} - \left(\frac{C}{1+k_a C} + \frac{fC}{1+k_d C} \right) = 0 \quad (2-36)$$

$C \rightarrow 0$ as r and $z \rightarrow \infty$

$C = 1$ $r = 1$ for $-1 < z < 1$

and at $z = 1$ for $0 < r < 1$

with the following definitions:

$$h_{Tr}^2 = \frac{r_o^2 v_{max}^a}{D_e K_m^a} \quad (2-37)$$

$$h_{Tz}^2 = \frac{4z_o^2 v_{max}^a}{D_e K_m^a} \quad (2-38)$$

$$f = \frac{v_{\max}^d K_m^a}{v_{\max}^a K_m^d} \quad (2-39)$$

$$k_a = C_t / K_m^a \quad (2-40)$$

$$k_d = C_t / K_m^d \quad (2-41)$$

Five dimensionless parameters arise. Two are Thiele moduli, with the usual physical interpretation. The nondimensional kinetic saturation constants, k_a and k_d , determine whether the system behaves in a quasi-linear manner. If these two parameters are very small, then the kinetics are essentially first order, and the equation is linear. If they are very large, then zero-order kinetics prevail over most of the domain, and the equation is again linear. The efficiency of pickup is determined by the value of f . When f is large, most of the selenium is consumed by competing chemical reactions and not absorbed by the plant.

The boundary conditions at large r and large z are somewhat problematic to a numerical solution scheme, thus the domain is transformed by defining new independent variables, x and y , given by:

$$x = e^{-r} \quad (2-42)$$

$$y = e^{-z} \quad (2-43)$$

In terms of these new variables, the differential equation

becomes:

$$\frac{1}{h_{Tr}^2} \left(x^2 \frac{\partial^2 C}{\partial x^2} + \left(x - \frac{x}{\ln(1/x)} \right) \frac{\partial C}{\partial x} \right) + \frac{1}{h_{Tz}^2} \left(y^2 \frac{\partial^2 C}{\partial y^2} + y \frac{\partial C}{\partial y} \right) - \left(\frac{C}{1+k_a} + \frac{fC}{1+k_d} \right) = 0 \quad (2-44)$$

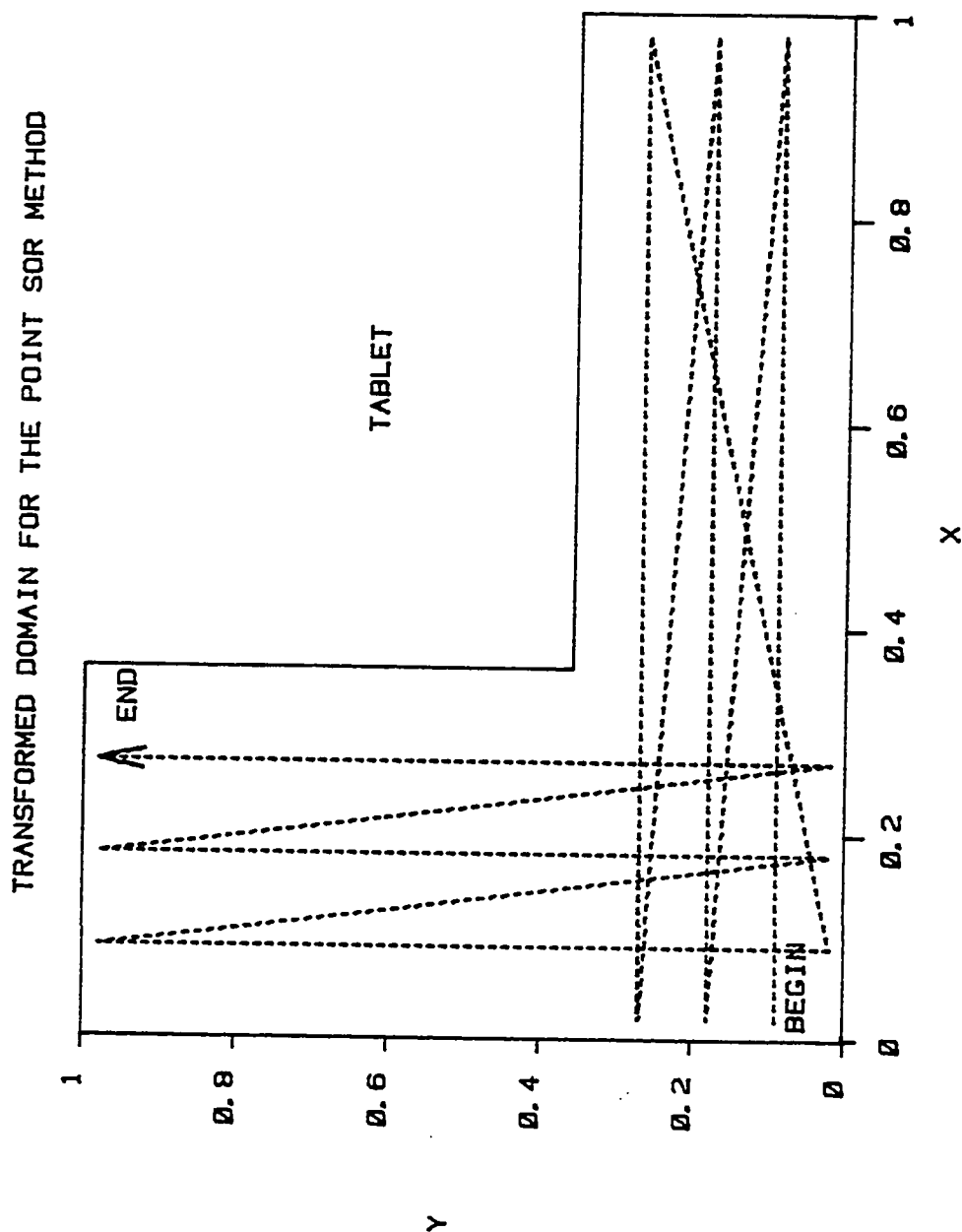
$C = 0$ at $x = 0$ for $0 < y < 1$
 and $y = 0$ for $0 < x < 1$
 $C = 1$ at $x = 1/e$ for $1/e < y < 1$
 and $y = 1/e$ for $1/e < x < 1$

The problem is now confined to a finite, convenient domain, as shown in Fig. 16, in which the symmetry properties have been exploited in order to reduce the size of the problem. The two new portions of the boundary are axes of symmetry, thus the flux normal to these boundaries must vanish. A finite difference representation of eq. (2-44) constructed on uniform, square elements corresponds to solving the problem with an exponentially expanding mesh in the original domain. Defining $C_{i,j} = C(x_i, y_j)$, one may write down the FD representation of eq. (2-44) as:

$$\frac{1}{h_{Tr}^2} \left(x_i^2 \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{\Delta x^2} + \left(x_i - \frac{x_i}{\ln(1/x_i)} \right) \frac{C_{i+1,j} - C_{i-1,j}}{2\Delta x} \right) + \frac{1}{h_{Tz}^2} \left(y_j^2 \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta y^2} + y_j \frac{C_{i,j+1} - C_{i,j-1}}{2\Delta y} \right) - \left(\frac{C_{i,j}}{1+k_a} + \frac{fC_{i,j}}{1+k_d} \right) = 0 \quad (2-45)$$

A point-by-point successive overrelaxation (SOR) method⁽⁵¹⁾ was chosen to solve the problem (see Appendix A for a print out of the program). The mesh had 50 uniform elements over both the x and y intervals. The pair of singularities at 0 and 1 (the $1/(\ln(1/x))$ term) were initially avoided by limiting the mesh points to between 0.001 and 0.999 in the numerical scheme. The concentration was kept

Figure 16. Transformed Domain (Showing Sweep Method) for the Successive Overrelaxation Solution of the Two Dimensional Diffusion Equation.



at 0 along both of the first rows, and it was kept at 1 along the portion of the 18th row which corresponded to the tablet surface. The internal points were initialized by linear ramp functions connecting the two boundaries. The SOR method involved sweeping through each 'leg of the L' in the domain as indicated in Fig. 16. After the penultimate element of a row had been reached, the last element in that row was filled to meet the symmetry criterion. The second-order one sided derivative formula was used to meet this boundary condition and thus fill the last element.

The nonlinearity of eq. (2-45) was handled with a modified Newton method. The entire equation was identified as $F(C)$, and an approximate partial derivative with respect to $C_{i,j}$ was taken. The approximation involved linearization of the reaction rate terms. Two options are possible; the derivatives of each may either be set equal to zero (corresponds to very large nondimensional kinetic saturation constants), or first order kinetics are assumed, which yields $1/f$ as the partial-derivative of $R(C)$. The latter, more conservative option was chosen in order to ensure convergence. In the SOR method, the $C_{i,j}$ found from eq. (2-45) is given an asterisk in order to show that it is merely a guess that is then extrapolated to give the "real" $C_{i,j}$. The values of C at points already calculated in the current sweep are used in the calculation of C^* (the Gauss-Seidel improvement), and the modified Newton method that was then used can be written as:

$$C_{i,j}^{*(k+1)} = C_{i,j}^{*(k)} - \frac{F(C_{i,j}^{*(k)}, C_{i+1,j}, C_{i-1,j}, C_{i,j+1}, C_{i,j-1})}{\frac{\partial F}{\partial C_{i,j}}} \quad (2-46)$$

Iteration of eq. (2-46) was executed 5 times for each $C_{i,j}$ before proceeding farther through the program, unless the change in C^* was less than 10^{-7} between iterations. The value of $C_{i,j}$ was then calculated with overrelaxation as shown in eq. (2-47):

$$C_{ij}^{s+1} = C_{ij}^s + \beta(C_{ij}^* - C_{ij}^s) \quad (2-47)$$

Section 2.2.4.1: Numerical Tests of the Method

The first trial run of the program was selected in order to compare the results with an approximate solution that had already been obtained through the assumption of a spherical tablet. Such an assumption yields a two point boundary value problem in one dimension:

$$\frac{2}{r} \frac{dC}{dr} + \frac{d^2C}{dr^2} = h_{Tr}^2 \left(\frac{C}{1+k_a C} + \frac{fC}{1+k_d C} \right) \quad (2-48)$$

$C = 1$ at $r = 1$
 $C \rightarrow 0$ as $r \rightarrow \infty$

The equation was solved with an iterative method analogous to the analysis just developed, with second order difference expressions for the derivatives and 100 intervals, stretching from $r = 1.0$ to $r = 22.0$. The Thiele modulus for this one dimensional model was set to 1, as was f . The kinetic saturation parameters, k_a and k_d were set to

10, and the solution obtained both for this h_T and for moduli of 10 and 0.1 are shown in Fig. 17.

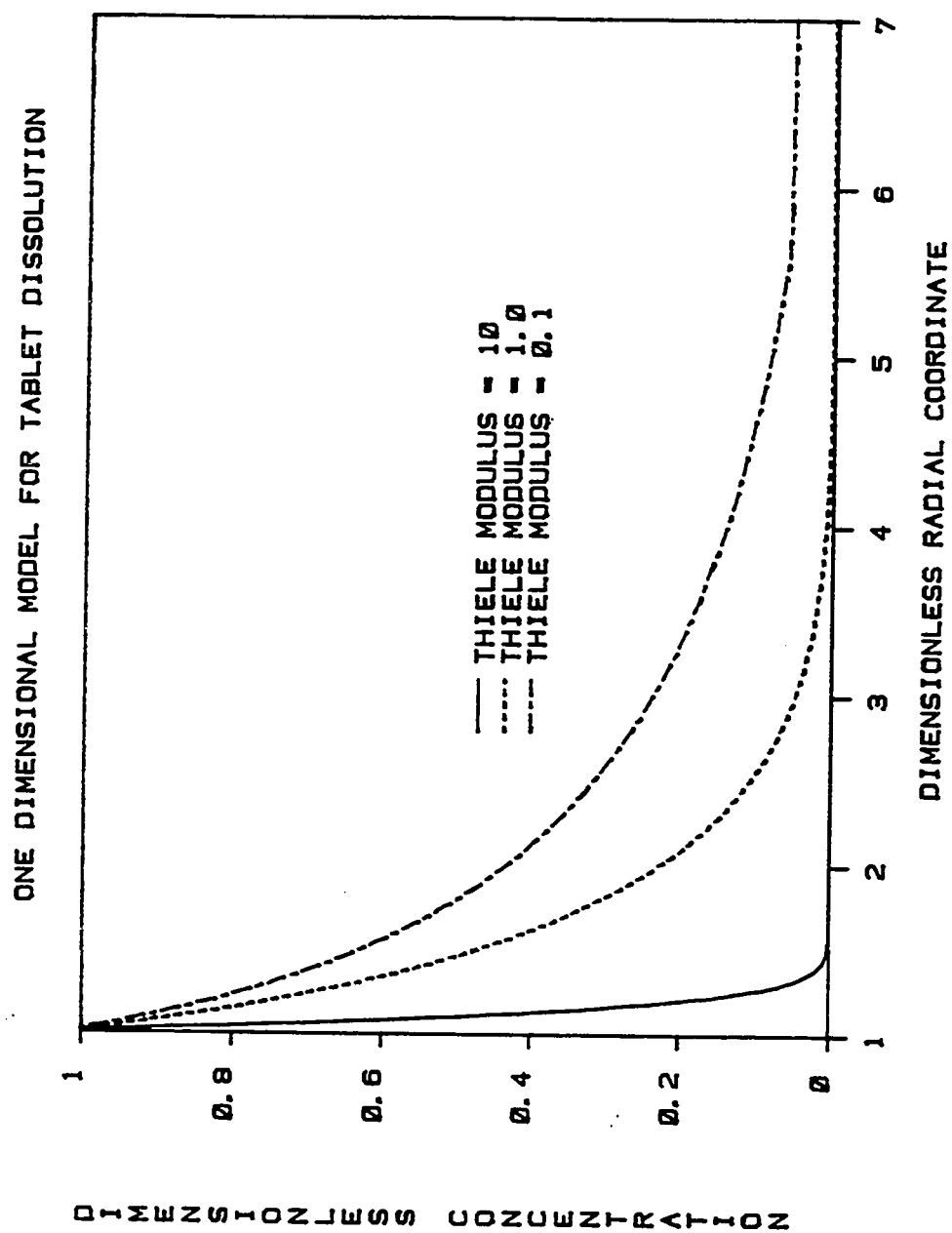
This solution provided a benchmark against which to test the 2-D model program. The parameter values used for the 2-D test were:

$$h_{Tr}^2 = h_{Tz}^2 = f = 1 \quad k_a = k_d = 10$$

These values were entirely analogous to those chosen for the 1-D model, and the results were indeed very similar (see Fig's. 18 and 19 for the axial and radial profiles respectively).

An optimal value for the overrelaxation parameter, beta, was chosen by summing the absolute values of the residuals at the internal grid points after a fixed number of iterations. The results of this procedure are shown in Fig. 20 for 30 iterations with beta varying from 1.1 to 1.9. The minimum total residual occurs near beta = 1.7 in this plot. When the number of iterations was increased to 50, however, the minimum appeared to shift to the right, as shown in Fig. 21. This behavior continued as the number of iterations was increased. The final solution for this run was obtained with beta = 1.862, and the total residual decreased monotonically with increasing iterations until about 600 iterations, as shown in Table 2. After 600 iterations the method seemed unable to converge any further. The reason for this was not determined, but it seems possible that a revision in the value of beta at that point in the solution might have completed the convergence. This possibility was not investigated, and it is conceivable that machine accuracy limited further convergence.

Figure 17. One Dimensional Model for Dissolution from the Tablet.



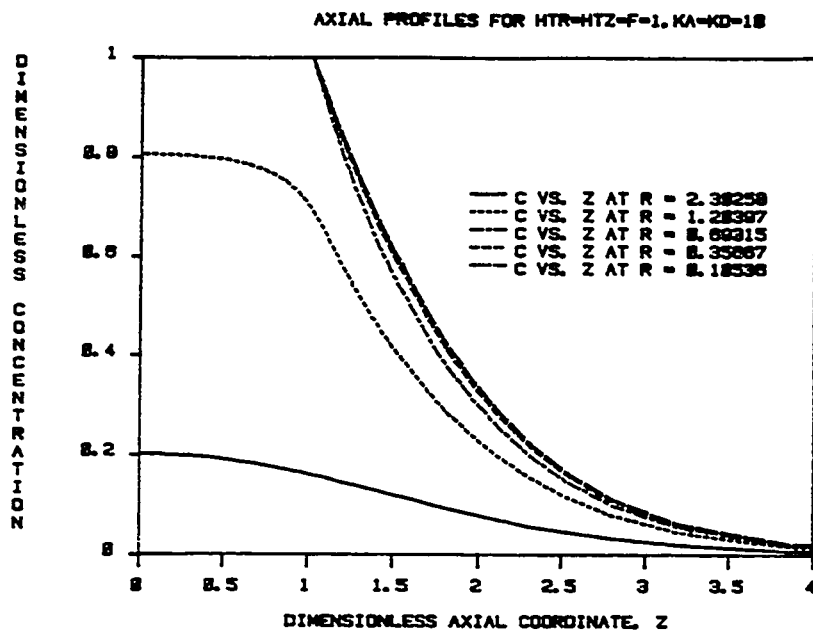


Figure 18. Test of the Axial Profiles.

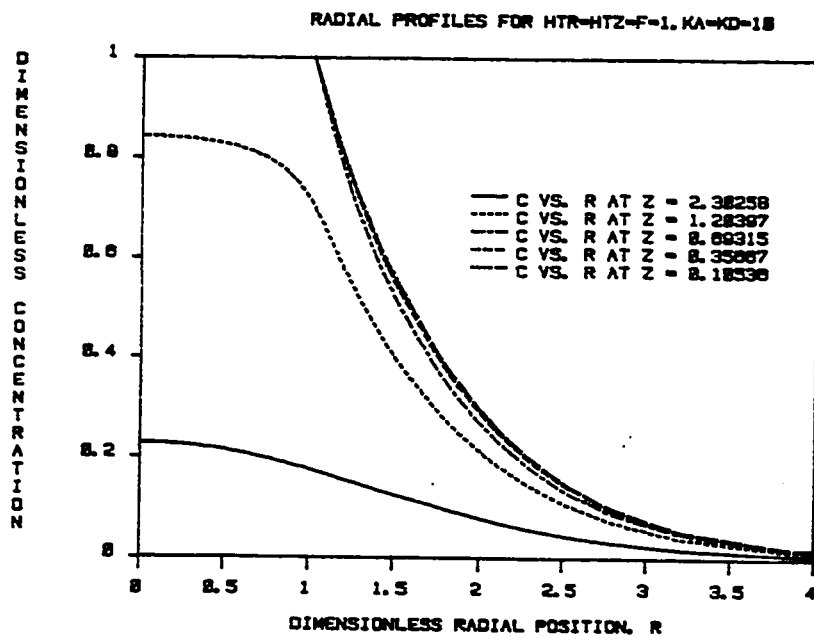


Figure 19. Test of the Radial Profiles.

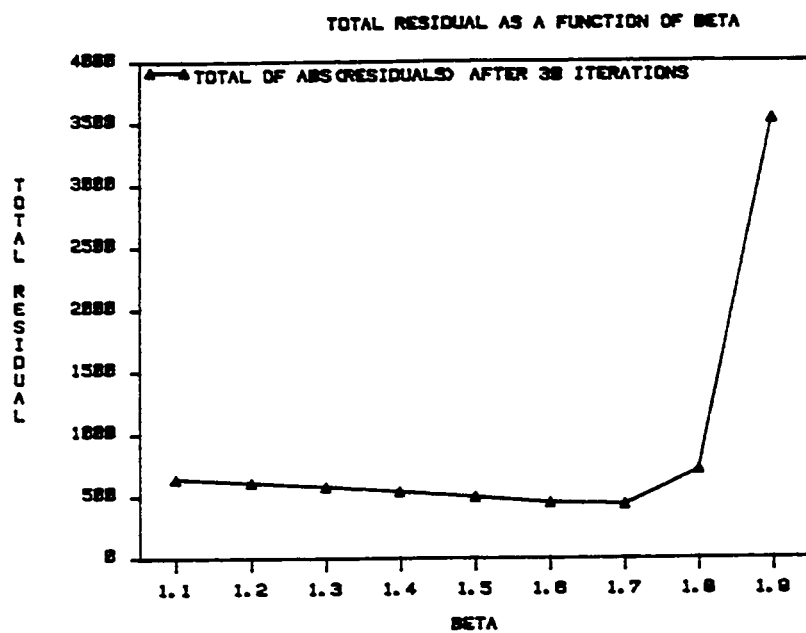


Figure 20. Total Residual after 30 Iterations.

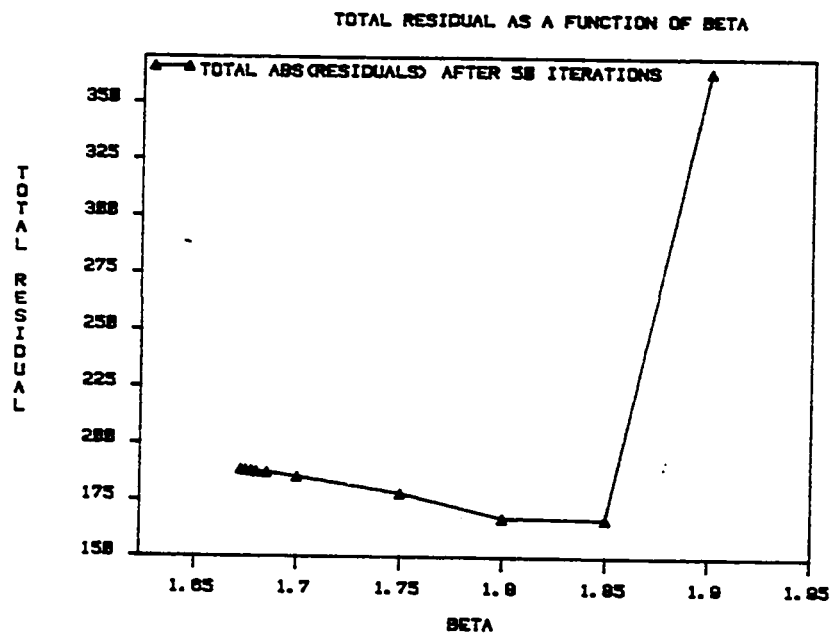


Figure 21. Total Residual after 50 Iterations.

Table 2. Convergence Results For Beta = 1.862

$$h_{Tr}^2 = h_{Tz}^2 = 1$$

$$f = 1, k_a = k_d = 10$$

No. of Iterations	100	199	298	397	496	595	694	793	892	999
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Total Residual	46.66	8.388	1.843	.4833	.1981	.1508	.1513	.1402	.1449	.1550
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Table 3. Convergence Results for Beta = 1.44

$$h_{Tr}^2 = h_{Tz}^2 = 10$$

$$f = 1, k_a = k_d = 1$$

No. of Iterations	100	199	298	397	496	595	694	793	892	999
----------------------	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Total Residual	19.75	1.172	.0690	.0055	.0015	.0008	.0008	.0007	.0008	.0008
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Table 4. Convergence Results for Beta = 1.862 (Coarse Mesh)

$$h_{Tr}^2 = h_{Tz}^2 = 1$$

$$f = 1, k_a = k_d = 10$$

No. of Iterations	100	199	298	397	496	595	694	793	892	999
----------------------	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

Total Residual	.0695	.0058	.0057	.0065	.0063	.0055	.0061	.0062	.0068	.0057
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The radial and axial profiles obtained were nearly identical in appearance, and they predict that the selenium vanishes at a dimensionless coordinate of four, in excellent agreement with the results of the spherical geometry solution.

A second example was run with much smaller nondimensional kinetic saturation constants, $k_a = k_d = 0.1$, in order to convert the kinetics from roughly zero order to roughly first order. The same technique was used to select an optimal beta. The results were quite similar to the first example. The optimal beta appeared to shift to higher values as the number of iterations was increased. The final value of beta chosen for this run was 1.922.

The numerical scheme converged much more quickly than did the first run. This was probably due to the choice of beta rather than to the relative difficulty of the two problems. The inability of the numerical scheme to reduce the total residual below about 0.16 was repeated in this run. The profiles found for these smaller nondimensional Michaelis constants were nearly identical to those earlier obtained.

These first two runs corresponded to nearly linear problems, in which the reaction rate term was either first order or zero order. In order to see the effect of a nonlinear reaction term, a third run with the dimensionless kinetic saturation constants equal to 1 was executed. All other parameters remained the same.

The behavior of the total residual as a function of beta was virtually identical to the first two runs. It is thought that the

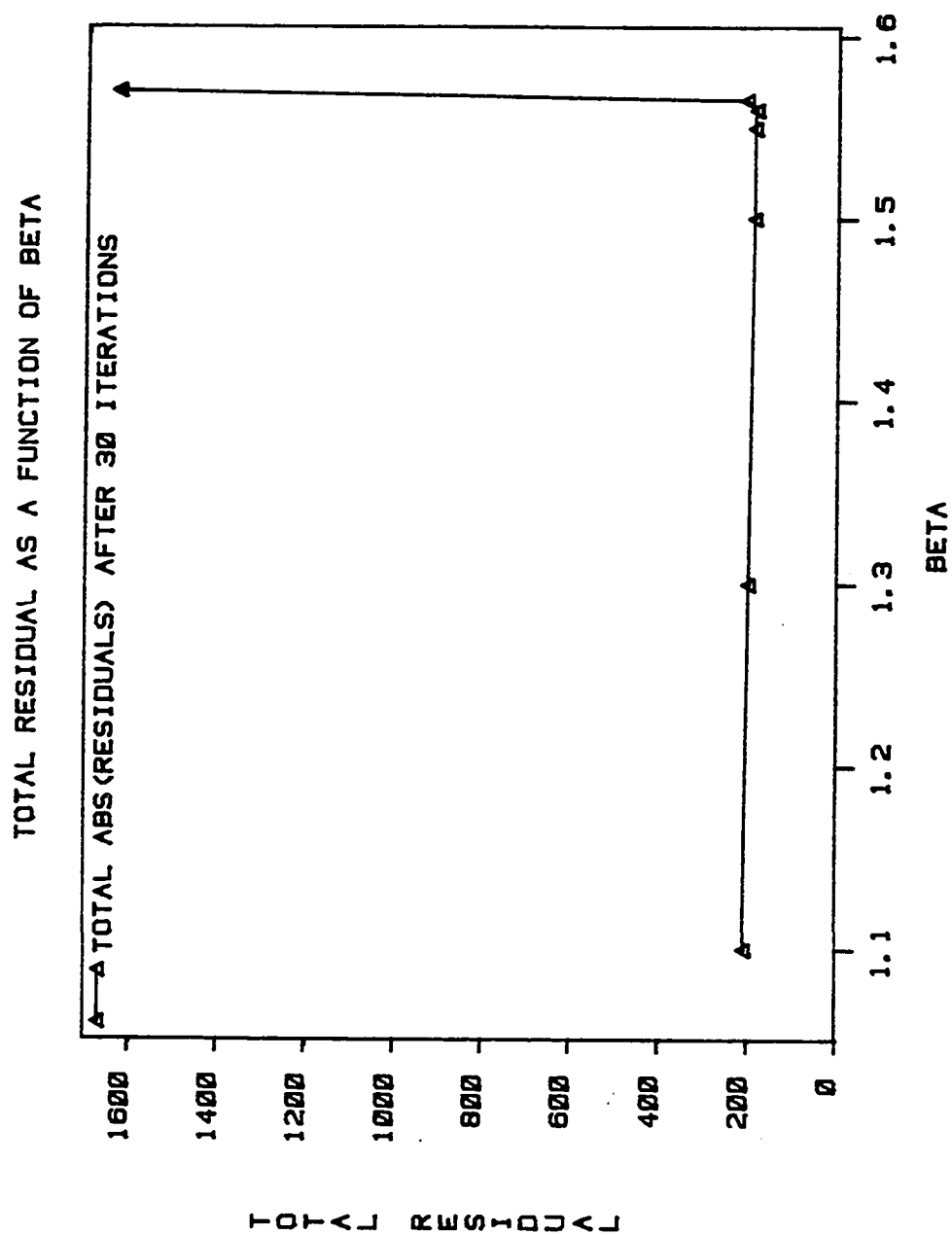
shift in the optimal beta value that was observed as the number of iterations was increased is probably due to the nonlinearity of the difference equation. The method converged in roughly the same fashion as in the second run.

The residual was not lowered by increasing iterations after about 300, as in the second run. The concentration profiles obtained for this mildly nonlinear reaction rate term were again nearly identical to those in Fig's. 18 and 19. The one conclusion which is possible at this point is to note that there seems to be very little effect of the reaction rate order on either the convergence rate or the resulting profiles. It could be expected that much larger changes would be effected through changes in the Thiele moduli. For large values of the h_T 's, it is expected that the profiles will be quite steep, making convergence more difficult. Low values of the Thiele modulus will stretch out the profiles, necessitating an expansion of the domain.

Both the Thiele moduli squared were set to 10, with $f = k_a = k_d = 1$ for the next run. The total absolute residuals obtained after 30 iterations with various values of beta are shown in Fig. 22. Somewhat unexpectedly, the total residual after this fixed number of iterations was smaller than it had been for the smaller Thiele moduli, but only for $\beta < 1.58$. Above this value, the method diverged rapidly, with a total absolute residual of 2.85×10^{30} after 30 iterations at $\beta = 1.9$. This is quite remarkable, as this same beta was nearly optimal for the same system with smaller Thiele moduli.

A solution was obtained with an overrelaxation parameter of 1.44,

Figure 22. Total Residual after 30 Iterations for Thiele Moduli = 10.



and the total absolute residual fell to much lower values than had been obtained for lower Thiele moduli. These results are summarized in Table 3.

It is not certain why the numerical scheme was able to reduce the total residuals to such a low value in this run. It is probable, however, that the large number of concentration values near zero merely weighted the total residuals down to lower values, but without a more detailed look at the residual distribution this is not certain. The profiles which resulted from this solution are shown in Figures 23 and 24. An interesting feature of these plots is that the axial profiles drop off much more quickly than the radial profiles. The radial concentration profile at $z = 2.30258$ is just barely perceptible in Fig. 23, while the axial profile at $r = 2.30258$ rises to a value of $C \sim 0.16$ at $z = 0$. A check of the data files revealed that the program was being fed the correct numbers, such that this appears to be a "real" result. It is disturbingly counter-intuitive, however, and another run at slightly higher Thiele moduli squared (both 20) was undertaken to check the result.

The steepness of the profiles became prohibitive for these higher Thiele moduli, however, and it was necessary to abandon the linear ramp functions as initial values. Instead, the converged solution from the run with the Thiele moduli squared equal to 10 was used to initialize the grid. The results obtained with $\beta = 1.14$ after 300 iterations (total absolute residual = 0.0357) repeated the earlier trends. Again, the axial profiles tended to decay much faster than

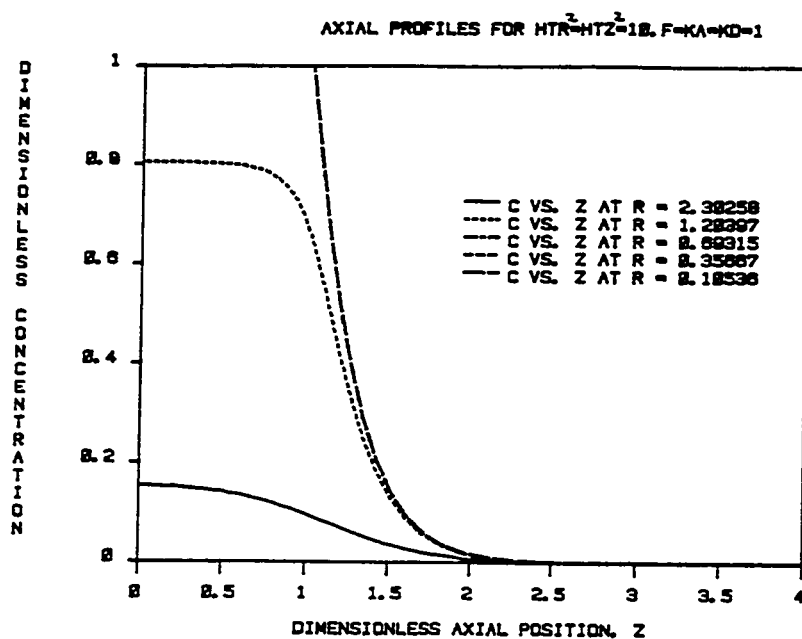


Figure 23. Axial Profiles for $h_T^2 = 10$.

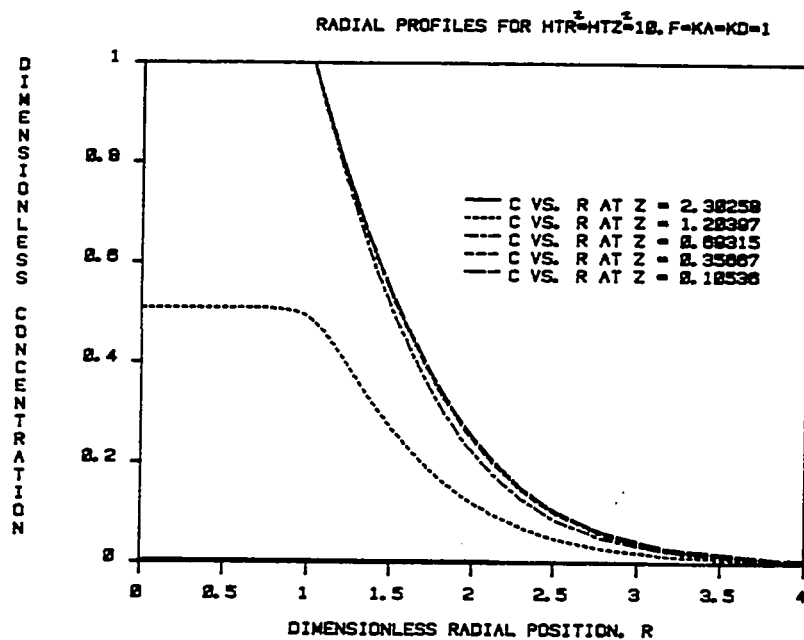


Figure 24. Radial Profiles for $h_T^2 = 10$.

the radial profiles.

Initial efforts to obtain convergent solutions for higher values of the Thiele moduli all failed, and it was thought that a larger mesh would be required. The PDP-11 used in the study would not accept larger meshes, however, and so this technique was not attempted. It was subsequently found that the use of beta values lower than 1 would give convergent solutions at much higher values of the Thiele moduli.

The use of lower Thiele moduli necessitated an extension of the domain, as the former version of the program was limited to $x = y = 0.001$, which transforms to a point "far away" from the tablet of only about 6.9 in dimensionless coordinates. This is easily changed by starting the domain at 10^{-9} , which puts the point "infinitely" far from the tablet at 20.7 in dimensionless coordinates.

The new domain was used to solve a problem in which the Thiele moduli squared had the value 0.001, and the other parameters were held at their former value (unity). The linear ramp functions were again used as the initial values, as these gave faster convergence than any profiles previously generated. The solution obtained for $\beta = 1.807$ after 480 iterations (total absolute residual = 111.9) is illustrated by the data shown in Figures 25 and 26. These profiles were not spread out nearly as much as was expected. It is not clear that convergence had yet been obtained, but the total residual was being reduced so slowly that further iterations were not deemed worthwhile until it was shown that these were relevant to the current study. The axial profiles seemed to be relatively more affected by the altered

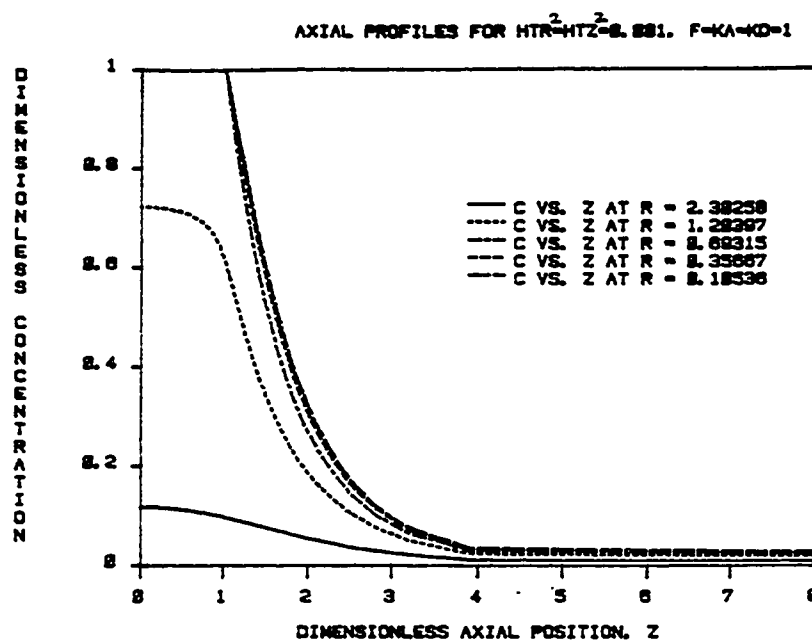


Figure 25. Axial Profiles for $h_T^2 = 0.001$.

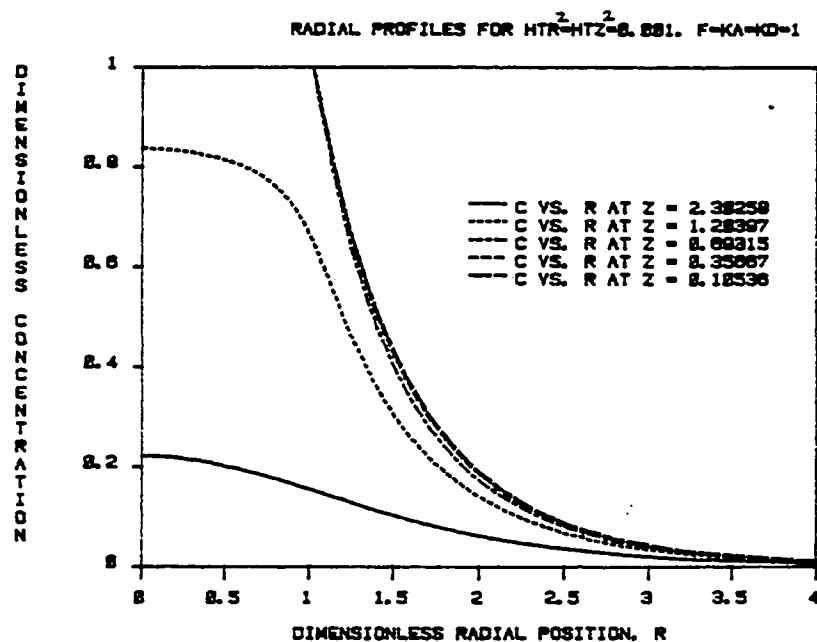


Figure 26. Radial Profiles for $h_T^2 = 0.001$.

Thiele modulus, however, as they seemed to retain a small, finite value at distances far from the tablet (past $z = 5$).

The rather large value of the total absolute residual is very suspicious, but no other value of β could be found which gave better convergence. The program appeared to take a lot more CPU time on these runs, but quantitative data on the CPU time for each run were not gathered. An effort to lower this total residual by altering the value of the error criterion in the modified Newton method from 10^{-7} to 10^{-11} did not affect the results. This indicates that the iteration of eq. (2-27) was continuing through 5 steps for each point, meaning that it had not converged to within 10^{-7} . It might be possible to increase this upper bound on the number of Newton iterations in order to get better convergence, but this was not investigated. Yet another possible explanation for the failures at these lower values of the Thiele moduli was that the exponentially transformed domain was accentuating errors in the far reaches where the concentration values had formerly all been zero.

Another test of a finite difference scheme is to vary the mesh size. The former discretization scheme had pushed the PDP-11 to its memory limits, such that the only option was to go to a coarser grid. This was accomplished by merely doubling the length of each element, which gave 25 elements along the interval 0 to 1. The ninth row then became the edge of the tablet.

The first run with the new mesh was a repeat of the very first run of the program, with the Thiele moduli squared equal to unity, $f =$

1, and the dimensionless kinetic saturation parameters equal to 10. A plot of the total absolute residuals after 30 iterations as a function of beta is shown in Fig. 27 for the coarser mesh. This plot is the analog of Fig. 20, and it can immediately be seen that the magnitude of the residuals has been greatly reduced. This is not due to any increased accuracy, but rather is due to the fact that fewer residual values (320 instead of 1377) are summed for the new mesh. The analog of Fig. 21, which shows the residual after 50 iterations, is given in Fig. 28 for the coarse scheme. The optimal beta again shifted to higher values with increasing iterations. The convergence of the solution for $\beta = 1.862$ is illustrated in Table 3, which again points out that the numerical scheme is unable to lower, after 300 iterations, the total residual below a certain value (which happens to be lower here than it was for the fine mesh with the same beta, for the reason given above).

The profiles obtained from this run are shown in Figures 29 and 30. They are nearly identical to the analogous curves given in Figures 18 and 19. The only immediately perceptible difference is the slightly less smooth nature of the profiles. From this observation, it can be concluded only that the finer mesh is required to get a better approximation of the true solution, but without further refining the mesh, the absolute accuracy of the solution can not be known.

The coarse mesh was significantly more convenient to use on this relatively small computer. The execution time appeared to be roughly

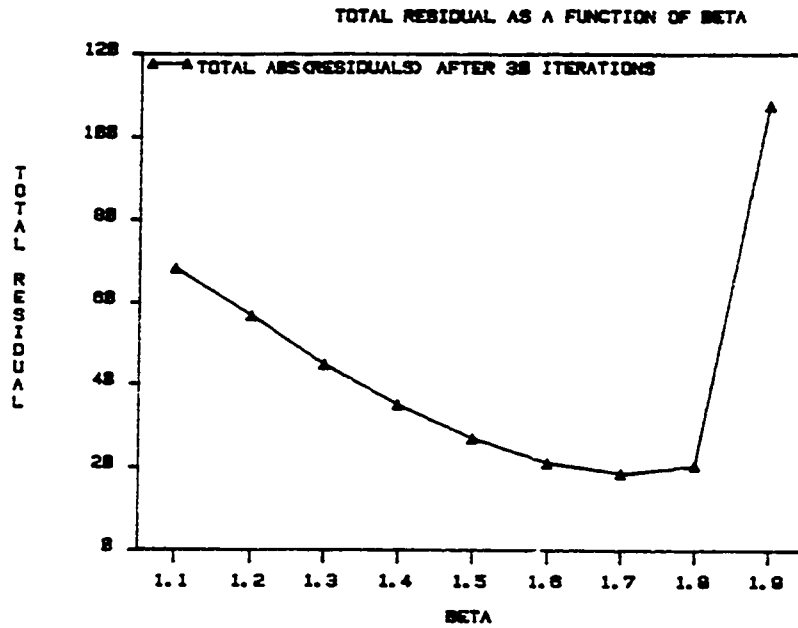


Figure 27. Total Residuals after 30 Iterations (Coarse Mesh).

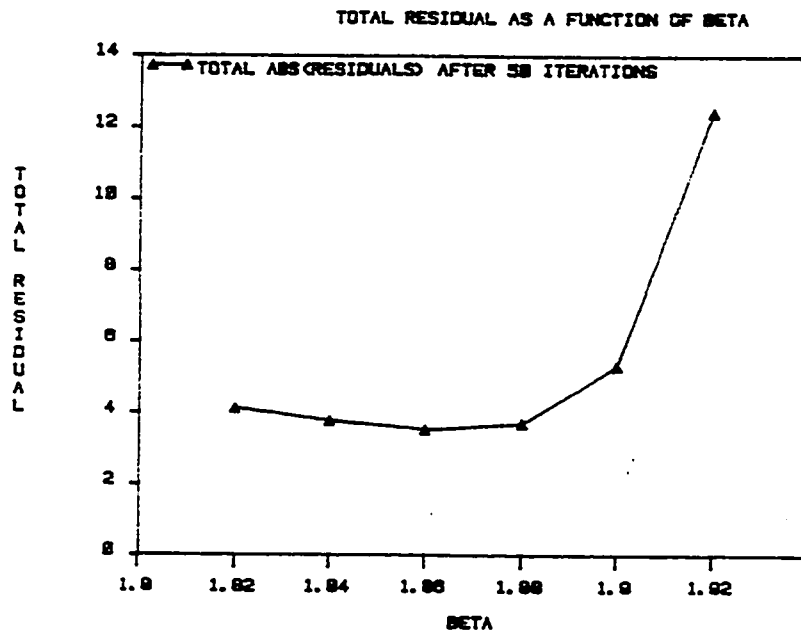


Figure 28. Total Residual after 50 Iterations (Coarse Mesh).

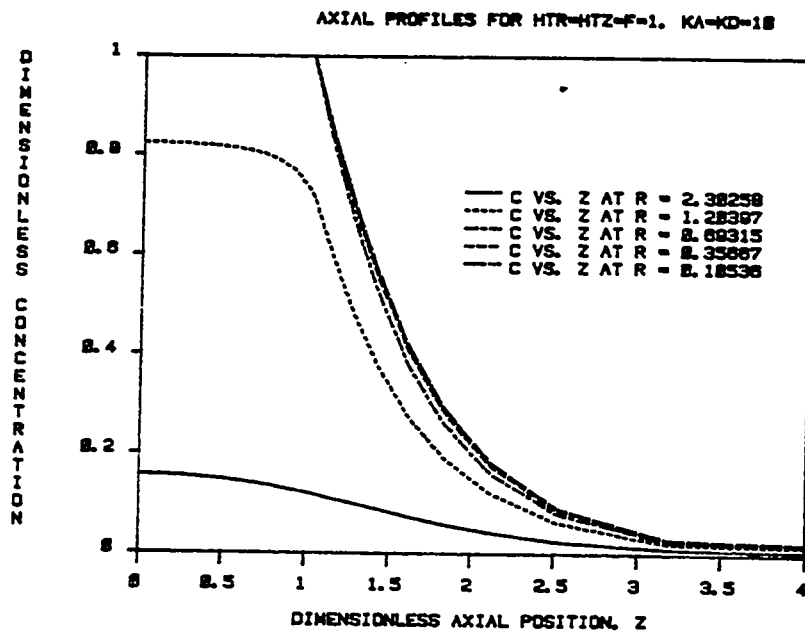


Figure 29. Axial Profiles with the Coarse Mesh.

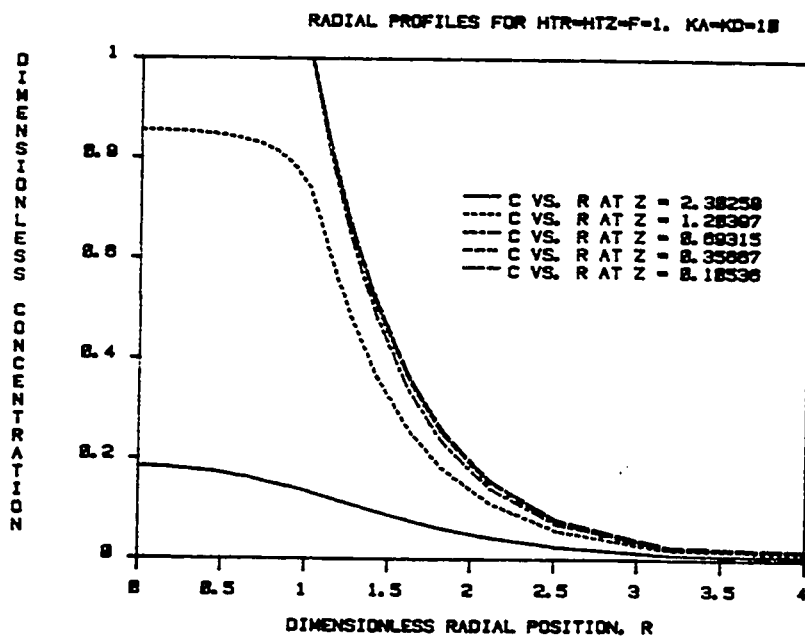


Figure 30. Radial Profiles with the Coarse Mesh.

20% of that required for the fine mesh, as would be expected from the number of grid points in each.

The "robustness" of the fine mesh was now further tested by allowing anisotropies in the effective diffusion coefficient. This is quite reasonable physically, as soils are often encountered in which the effective vertical mobility is much greater than the lateral mobility. Depending on the orientation of the cylindrical tablet in the soil, this fact could alter the relative values of the Thiele moduli. This presents potential numerical difficulties because gradients in one direction will then be much greater than those in the other direction. A trial run was thus executed with the following parameters:

$$h_{Tr}^2 = 0.1 \quad h_{Tz}^2 = 10 \quad f = 1 \quad k_a = k_d = 10$$

The fine mesh was used, with the actual grid points extending from 10^{-9} to 0.999999999 as in the examples shown in Figures 25 and 26.

The optimal value of beta was found through a two-step procedure that made use of the coarse/fine mesh comparison results. During those runs it had been discovered that the optimal beta, defined as that which gave the lowest total absolute residuals, was unchanged by the mesh size, thus the optimal beta was selected with the coarse mesh. This greatly reduced the computer time required. As before, the minimum shifted slightly with increasing iterations, but it shifted to the left this time. A convergent solution was obtained on

the fine grid with an overrelaxation parameter of 1.72.

Somewhat surprisingly, the numerical scheme was able to converge to a quite small value of the total absolute residual. The profiles obtained are portrayed in Figures 31 and 32. As expected, the axial profiles are much steeper than the radial profiles, due to the disparity in the two Thiele moduli. The point SOR turned out to be a very adequate method for solving the problem with these anisotropic parameters.

Section 2.2.4.2: Results of the Numerical Tests

The program appeared capable of providing a quite accurate representation of the solution for Thiele moduli of about 20 and smaller when the mesh size was kept at 50 intervals on each side of the domain. A coarser mesh of 25 intervals on each side gave much less smooth profiles, although its much lower computing time (~20%) made it useful for a purpose detailed below.

The mildly nonlinear Michaelis-Menten reaction term had little effect on either the rate of convergence or the profiles generated by the program, at least for Thiele moduli equal to one. Perhaps with much smaller Thiele moduli, larger effects upon varying the effective reaction order from zero to one could be seen.

The optimal value of the overrelaxation parameter, β , (defined as the value which minimized the summed absolute residuals for a fixed number of iterations) exhibited interesting behavior. Increasing the number of iterations resulted in a change in the optimal β , most

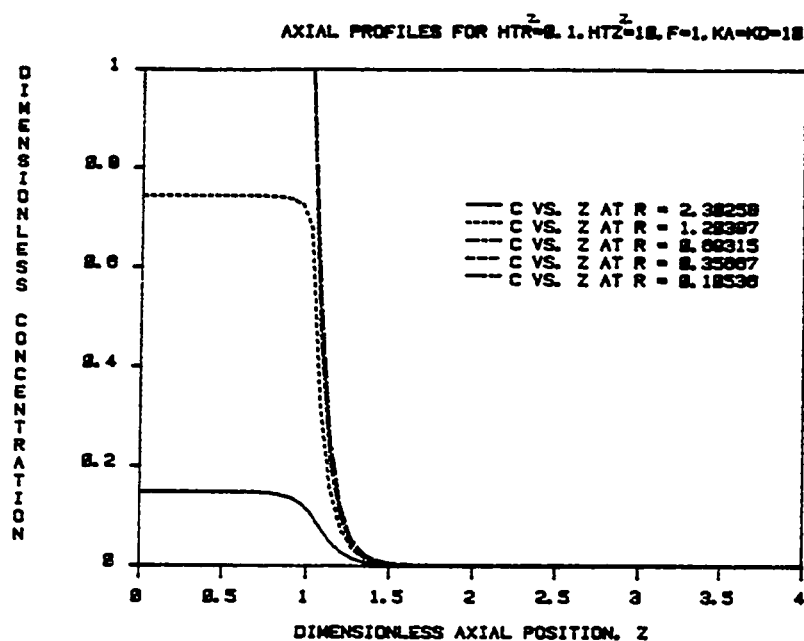


Figure 31. Axial Profiles with Anisotropic Transport.

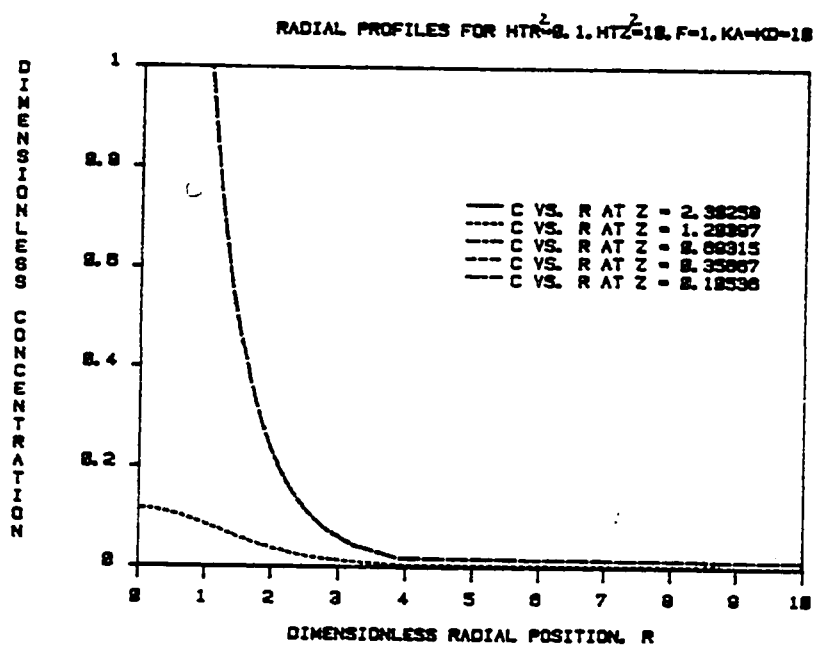


Figure 32. Radial Profiles with Anisotropic Transport.

often to higher values, but it shifted to the left in the last run with the anisotropic Thiele moduli. Varying the Thiele modulus had a very large effect on the optimal beta. Values of beta ranging from 1.14 to 1.922 proved to be optimal for solving the problem with different values of the parameters. During subsequent use of the program it was discovered that convergent solutions could be obtained for larger values of the Thiele moduli if the relaxation parameter was allowed to take on values less than one. This method is no longer a successive overrelaxation procedure, but an iterative underrelaxation technique.

An important result was that the optimal beta was not appreciably altered by a change in the mesh size. Thus the somewhat time-consuming procedure of locating an optimal beta was accelerated greatly by searching with the coarse mesh. The optimal beta found in this manner could then be used in the fine mesh to give quantitative solutions.

A curious mathematical result was that the axial profiles appeared to be somewhat more sensitive to changes in the Thiele modulus than were the radial profiles. Fluxes calculated from the axial and radial faces of the tablet confirm this result. It is likely that this is an artifact of the nondimensionalization procedure, which yielded a slightly asymmetric definition of the Thiele moduli (the axial modulus had an extra factor of 2).

The program was used to generate a master plot of the total flux of selenium from the axial and radial faces of the tablet as a

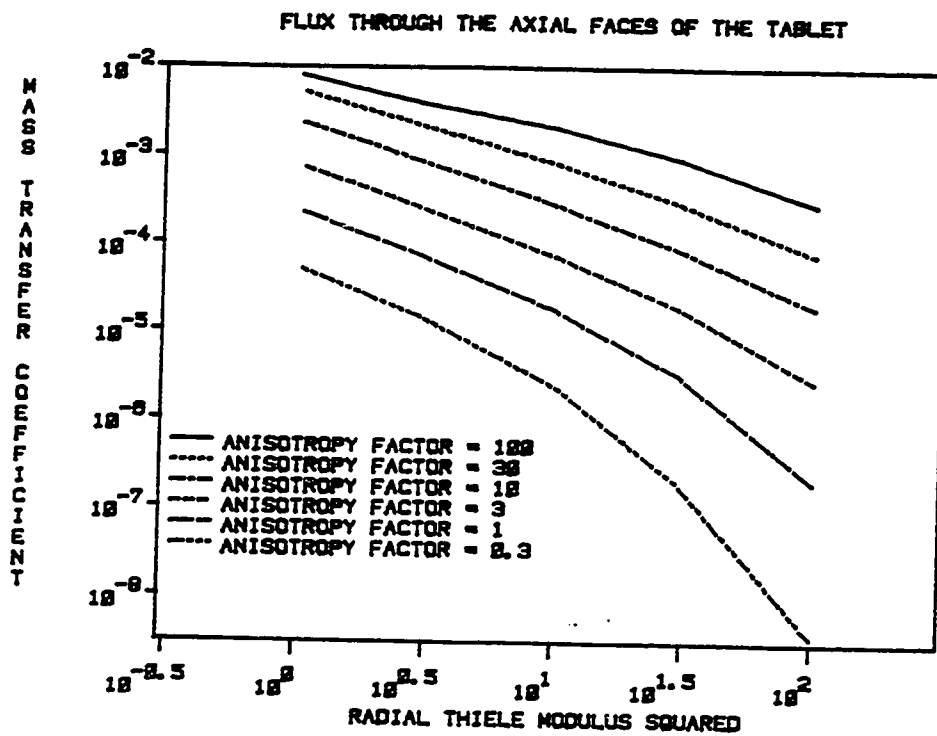


Figure 33. Mass Transfer from the Axial Tablet Face.

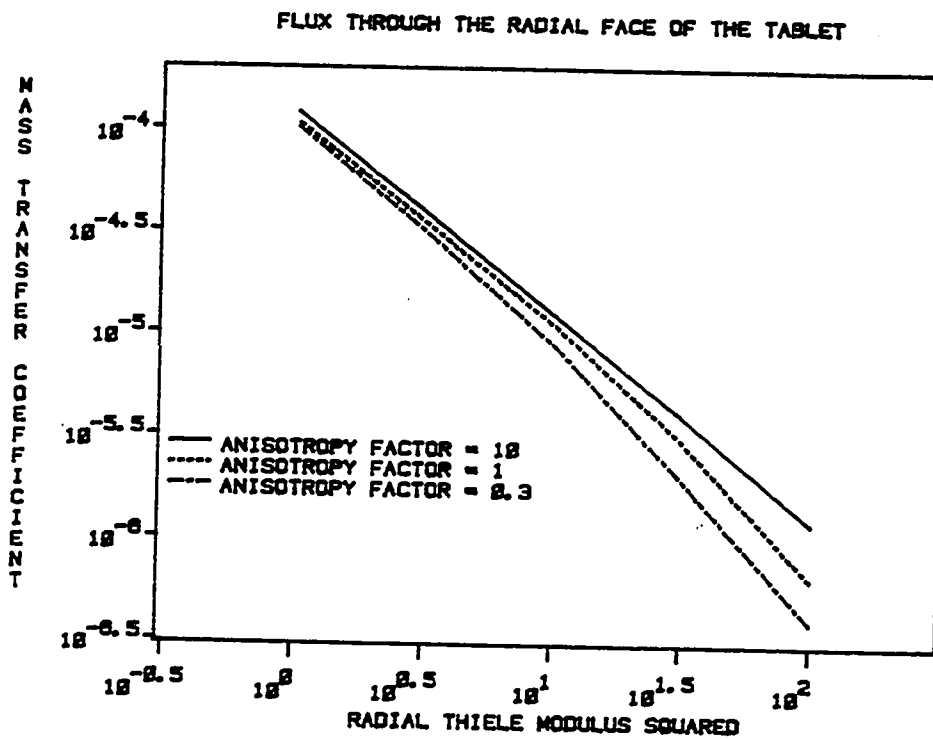


Figure 34. Mass Transfer from the Radial Tablet Face.

function of the Thiele moduli. These plots are shown in Fig's. 33 and 34. A mass transfer coefficient is defined such that the total flux from each face is obtained by multiplying the coefficient by the delivery concentration, C_t . The mass transfer coefficient so defined is plotted vs. the radial Thiele modulus squared, with the ratio of the Thiele moduli squared (denoted the anisotropy factor) as a parameter. Values of the intrinsic kinetic parameters determined experimentally could then be combined with the effective diffusivity predicted by the soil saturation model in order to find the flux from the tablet.

Section 2.2.4.3: Anisotropy in Soil Transport Properties

The amount of anisotropy present in a given soil-water situation is mainly a function of the precipitation and evaporation rates. Water movement in the vertical direction is of course enhanced whenever either of these phenomena occurs at an accelerated rate. The actual dependence of the effective diffusivity on the Peclet number is given by the following correlation:⁽⁴⁵⁾

$$\log(D_{ez}/D_{er}) = \log(Pe) \quad (2-49)$$

$$v_z L/D_o = Pe > 1$$

The data given by Dullien (p. 344) agree well with this relationship, and it can be used, together with the solution to the soil-water equations obtained with the similarity transformation, to calculate a value for the anisotropy ratio, D_{ez}/D_{er} .

Section 2.2.4.4: Efficiency of Selenium Absorption

The overall rate of selenium absorption by the seedling can be related to the flux from the tablet by a simple mass balance. Under the steady state approximation, the soil solution does not accumulate any selenium, thus the flux must equal the rate of absorption plus the rate of deactivation. The fraction which is absorbed may be calculated by integrating the kinetic expressions for both absorption and deactivation over the domain $0 < C < 1$, summing and dividing into the integrated absorption expression. Mathematically, this yields the following expression:

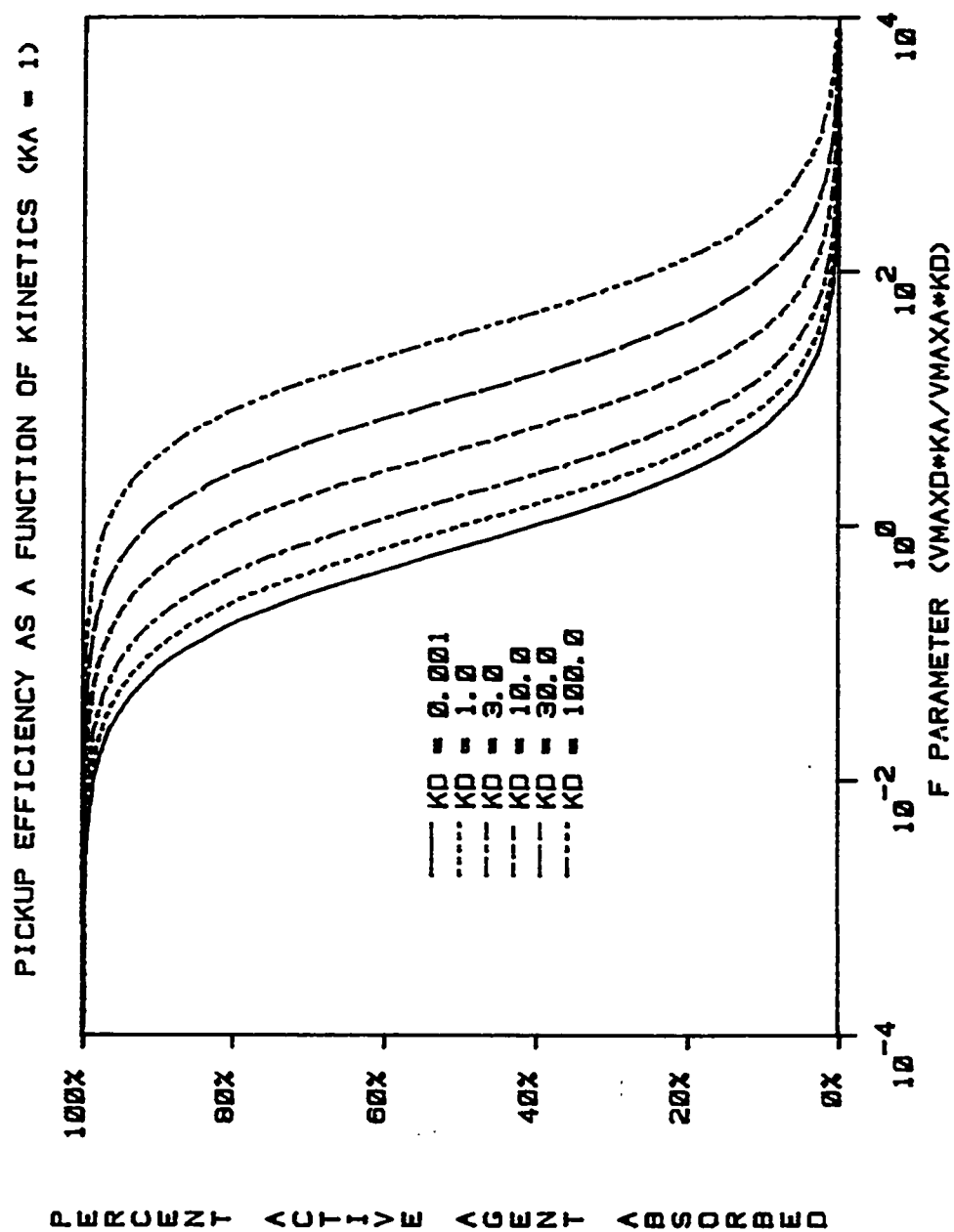
$$\text{pickup efficiency} = \frac{1}{1 + \frac{f \left(\frac{1}{k_d} - \frac{\ln(1+k_d)}{k_d^2} \right)}{\left(\frac{1}{k_a} - \frac{\ln(1+k_a)}{k_a^2} \right)}} \quad (2-50)$$

This equation may be represented by a plot of the absorbed fraction of delivered selenium as a function of f , with the dimensionless saturation kinetic constants (the k 's) as parameters. Such a plot is shown in Fig. 35. As expected, the efficiency of pickup falls off sharply as f changes from small to large values. The effect of the kinetic saturation parameters is noticeable, but secondary relative to the value of f .

Section 2.2.5: Modeling the Rate of Water Flow Through the Tree

The problem of water movement through Douglas-fir seedlings is one which has been studied in detail by Farnum. The following discussion is mainly based on his work, although an attempt has been

Figure 35. Efficiency of Selenium Pickup as a Function of the Kinetic Model Parameters.



made to translate the discussion into the language of chemical engineers.

Farnum identifies the soil-plant-atmosphere continuum (SPAC) as the system of interest. Liquid water moves through the SPAC in response to gradients in the water's potential energy. Thermodynamically speaking, this potential is just the chemical potential of water, which could be written as:

$$\mu_w - \mu_w^0 = \bar{\Psi}_w = \frac{\partial \bar{\Psi}_w}{\partial P} \Delta P + \sum_j \frac{\partial \bar{\Psi}_w}{\partial n_j} \Delta n_j + \frac{\partial \bar{\Psi}_w}{\partial n_w} \Delta n_w \quad (2-51)$$

The water potential has been denoted by $\bar{\Psi}_w$; the chemical potentials of water at the point of interest and at the reference state are given by μ_w and μ_w^0 , respectively; P is simply the pressure; T is the temperature; the n_w and n_j are the mole fractions of water and any solutes; and the overbar indicates the mean value of a variable. If the entire equation is divided by the partial molar volume of water, v_w , then the resulting terms all have units of pressure, which is the standard way in which the potential is expressed.

This definition of the water potential has been made for isothermal systems only. Including the effects of temperature gradients would necessitate an additional term for the partial molar entropy.

The total potential of the system is defined as the sum of the water and gravitational potentials, where the gravitational potential

is simply the hydrostatic head at the point of interest. The total potential, ϕ , can then be written as the sum of four terms:

$$\phi = \psi_P + \psi_O + \psi_M + \psi_G \quad (2-52)$$

The pressure potential, ψ_P , is merely the thermodynamic pressure at which the water was found. The osmotic potential, ψ_O , is related to the concentration of dissolved solutes in the water solution. The matric potential, ψ_M , is due to the action of surface tension forces, which serve to lower the pressure on the convex side of curved air-water interfaces. The gravitational potential, ψ_G is just $\rho_w g z$, where z is the height of liquid water above the reference pool.

Rose gives a relationship between the relative humidity and the sum of the matric and osmotic potentials as:

$$\psi_M + \psi_O = \frac{\rho_w R T}{M W_{\text{water}}} \ln(P_o / P_{\text{vap}}) \quad (2-53)$$

The vapor pressure of water at the system conditions and the saturated vapor pressure at system conditions are denoted by P_o and P_{vap} respectively.

Farnum goes on to relate the rate of water transport through the SPAC to conditions within each of the different regions. He makes the following assumptions in his analysis:

1. Water in the system is isotropic and chemically and

physically homogeneous.

2. Isothermal vapor movement is lumped with liquid movement.
3. Soil structural properties (i.e., saturation vs. capillary pressure and hydraulic conductivity vs. capillary pressure relationships) are constant in time and unaffected by liquid movement.
4. Gas pressure caused by entrapped air does not affect the flow.
5. Soil properties may vary spatially but are isotropic at any given point.
6. Temperature may alter the value of the hydraulic coefficients at a given point but the temperature gradients themselves do not induce a flow (i.e., thermodiffusion is ignored).
7. The osmotic potential does not contribute to flow in wet soils.
8. No hysteresis is allowed in the soil properties, which means both wetting and drying conductivities and saturation curves are identical.

The use of these assumptions allowed Farnum to develop a series of nonlinear, coupled equations for the rate of water transport through the SPAC. He employed a Galerkin finite element method to discretize the space domain around the roots, and the temporal response was handled with a semi-implicit Runge Kutta scheme. The model was tested against both field data and carefully controlled

laboratory seedlings, with quite reasonable predictions of the observed transpiration rates. Examination of his results indicates that acceptable order of magnitude estimates of the transpiration rates may be obtained by a gross simplification, in which the transpiration is recognized to be due to the pressure difference between the soil and the intercellular regions at the leaf stomata. The flow rate observed in response to this pressure drop can be modeled by an equation as simple as the Hagen-Poiseuille law:

$$Q = \frac{\pi \Delta P R^4}{8 \mu L} \quad (2-54)$$

All that is required in order to apply this relationship is an effective length over which the pressure drop is applied, and an effective radius of the tube. Both may be obtained through the performance of a simple linear regression on Farnum's results. Such an analysis yields an effective length of 100 cm, and an effective radius of 10 microns. Substitution of the appropriate pressures and a value for the viscosity of water then gives the desired result: the volumetric flowrate of water through the seedling. A method for estimating the pressure in the needles from the atmospheric demand is presented in Chapter IV as the model is tested.

Section 2.2.6: Modeling the Rate of Selenium

Transport Through the Seedling

The tree itself is modeled as a simple two compartment system.

The concentration of selenium in the root compartment is given by C_r , and the concentration in the foliage compartment is given by C_f . The absorption rate feeds the root compartment which is then emptied at a volumetric flow rate, Q , as modeled by Farnum. Since the concentration of selenium is equal throughout the compartment (the stirred tank model), the concentration of selenium in the water leaving the compartment is equal to its averaged value throughout the compartment. The foliage compartment is filled by this Q term and loses its selenium through first order volatilization. Mathematically, this yields the following mass balance on the root compartment:

$$V_r \frac{dC_r}{dt} = R_a - QC_r \quad (2-55)$$

This equation is nondimensionalized through division of the concentration by the Michaelis constant for absorption and multiplication of the time variable by the effective first order rate constant for absorption ($v_{\max}^a$ divided by K_m^a). Such a procedure yields the following equation for the concentration of selenium in the root compartment:

$$\frac{dC_r}{dt} = d - q_r C_r \quad (2-56)$$

Two dimensionless parameters have been defined in writing down this form of eq. (2-55):

$$d = \frac{R_a}{V_r v_{\max}^a} \quad (2-57)$$

$$q_r = \frac{Q K_m^a}{V_r v_{\max}^a} \quad (2-58)$$

The first is denoted by d because it quantitatively expresses the amount of dilution which the selenium experiences upon absorption into the root compartment. The second, q_r , is a ratio of the time constant for emptying the compartment to the time constant for filling the root compartment.

For time-invariant values of the two dimensionless parameters in this equation, a simple exponential solution is obtained:

$$\underline{C}_r = \frac{d}{q_r} + (\underline{C}_r(0) - \frac{d}{q_r}) \exp(-q_r \underline{t}) \quad (2-59)$$

Of more interest, however, is the concentration of selenium in the foliage, and this variable is governed by the following differential equation:

$$V_f \frac{dC_f}{dt} = Q \underline{C}_r - k_v C_f V_f \quad (2-60)$$

Nondimensionalizing as before yields:

$$\frac{dC_f}{dt} = q_r \underline{C}_r - v \underline{C}_f \quad (2-61)$$

in which the following definitions have been made:

$$q_f = \frac{Q K_m^a}{V_f v_{\max}^a} \quad (2-62)$$

$$v = \frac{k_v K_m^a}{v_{\max}^a} \quad (2-63)$$

The physical interpretation of these parameters is similar to the ones characterizing the root compartment. The first, q_f , is a ratio of the time constant for filling the foliage compartment to the time constant for absorption. The other, given as v , is the ratio of the rate of volatilization to the rate of absorption.

If it is again assumed that the two new nondimensional parameters are constant in time, then this equation is easily solved through the method of integrating factors to yield a solution which is a sum of exponentials:

$$\begin{aligned} C_f = & \frac{dq_f}{vq_r} + (C_f(0) - \frac{dq_f}{vq_r}) \exp(-vt) \\ & + q_f \frac{(C_f(0) - (d/q_r))}{(q_r - v)} (\exp(-q_r t) - \exp(-vt)) \end{aligned} \quad (2-64)$$

This expression thus gives the desired result, which was simply the selenium concentration in the foliage as a function of time.

Section 2.3: Summary

Actual use of the model to compare predictions with field results will require additional information about discretization of the time domain and incorporation of the experimental results, and these will

be addressed in Chapter IV as the model is tested.

Chapter III: Experimental Method

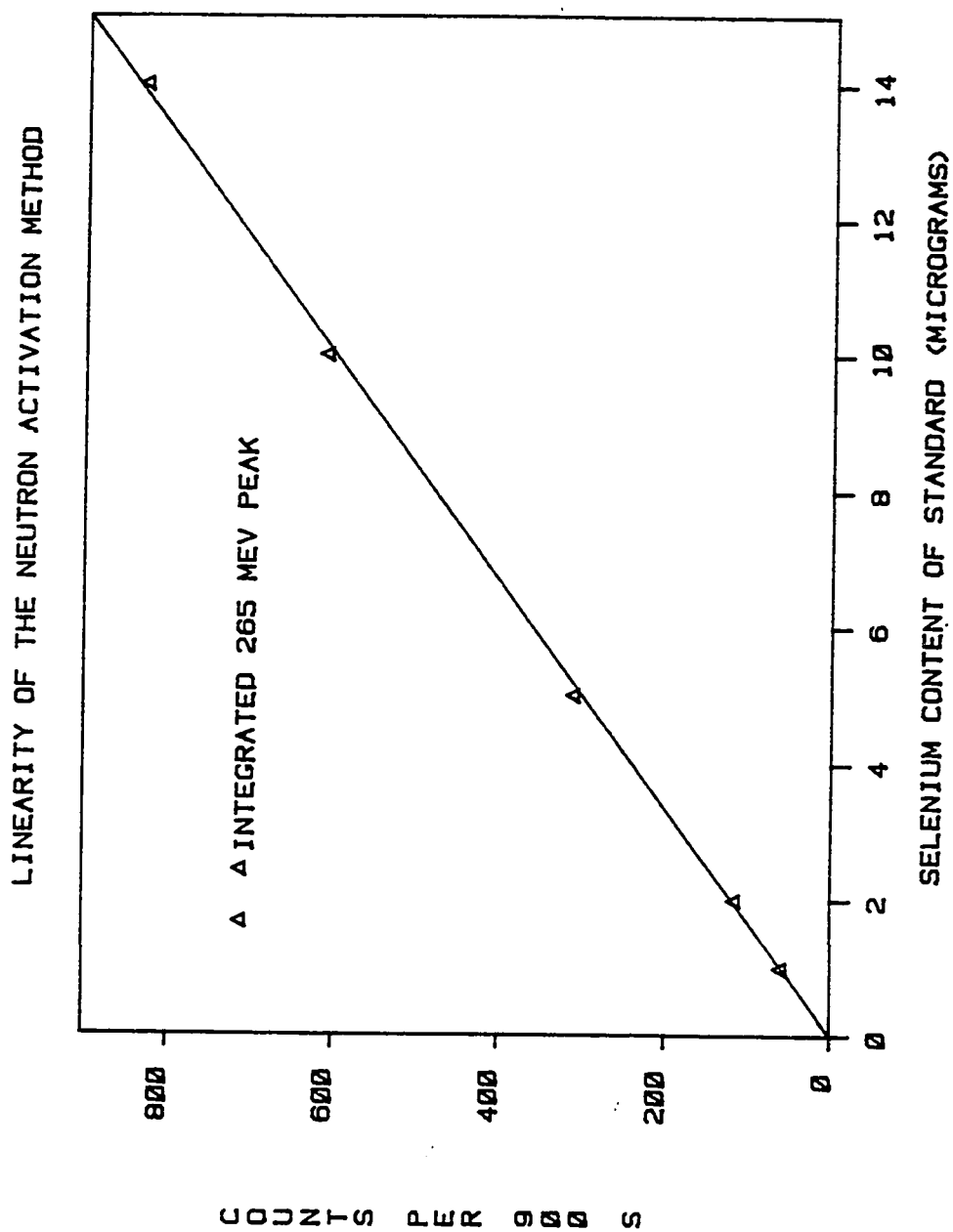
Section 3.1: Neutron Activation Analysis

Except when otherwise noted, all selenium determinations were carried out at the University of Washington Nuclear Reactor Lab. Samples to be analyzed were placed in plastic vials (2/5 dram Polyvial, Olympic Plastics Co., Los Angeles, CA) and irradiated with a neutron flux (10^{12} n⁰/cm²s) for 2 h. The samples were then allowed to cool for 10-14 days so that interfering isotopes of short half-life could decay. Activity of the samples was determined by integrating the area underneath the 265 MeV photopeak of ⁷⁵Se using a multichannel analyzer. The selenium content was calculated by comparing the number of counts produced by the sample in a known time (900 s) to the number of counts produced by each of a set of standards during an equivalent time interval. The number of counts increased linearly with selenium content in the range of interest, as confirmed by the data shown in Fig. 36. Foliage samples were not dried before analysis, as this procedure will often result in a significant loss of selenium.⁽⁵⁷⁾

Section 3.2: Dimelamine Selenite Dihydrate

A stirred solution of melamine (20 g) in distilled water (400 mL) at 100°C was treated with selenium dioxide (8.7978 g), added portionwise (~1 g) during 1 min, after which the heating and stirring were discontinued. The crystals which separated were recrystallized from water to yield dimelamine selenite dihydrate as white needles

Figure 36. Activity of Selenium Standards in Neutron Activation.



(27.0313 g) m.p. 269-270°C (d. to a pink solid). A series of elemental analyses on the crystals were carried out by Ray McLain at the University of Washington College of Fisheries, and the results were the following: C, $17.80 \pm 0.87\%$, N, $39.33 \pm 1.54\%$; and H, $5.15 \pm 1.51\%$; The molecular formula $C_6H_{14}N_{12}O_3Se(H_2O)_2$ requires: C, 17.27%; N, 40.29%; and H, 4.35%. The solubility of the dihydrate is ~ 1 g/100 g H_2O at 20°C, and the saturated solution has a pH of 5.05.

Solubility of the newly synthesized salt as a function of temperature was studied in more detail by the use of a constant temperature water bath (Model TV40, Neslab Inst. Co., Portsmouth, NH) equipped with a bath cooler (Model PBC-2). Purified dimelamine selenite crystals (2 g) were placed in a beaker containing deionized water (100 mL). The beaker was then placed in the constant temperature bath and allowed to come to chemical and thermal equilibrium at a number of temperatures (5°, 10°, 15°, 20° and 25°C). This generally required a period of many hours, nearly a day at the lowest temperature (5°). Samples of the solution in equilibrium with the crystals were then removed and placed in preweighed aluminum dishes. The weights of the dishes before and after the water had evaporated from the dish were each recorded, and the solubility was thus determined by the difference. Values obtained in this manner were confirmed by neutron activation analyses of some of the samples.

Section 3.3: Absorption of Dimelamine Selenite

From Soil by Douglas-fir Seedlings

Containerized (2-0) Douglas-fir seedlings (27) provided by the Georgia-Pacific Corporation (Bellingham, Washington) were transplanted into pots (diameter, 25 cm) which were then sunk into a nursery bed. Various amounts of dimelamine selenite (50, 100, 500 and 1000 mg salt) were mixed with the upper surface of the soil in 24 of the pots. In half of these pots (12), and in the three remaining pots, melamine/urea fertilizer prills (Super-60TM, Melamine Chemicals Inc., Donaldsonville, LA) were applied (112 kg/ha).

Foliage samples (~300 mg) were collected monthly from the uppermost lateral branches, and after digestion in aqueous nitric acid and hydrogen peroxide, their selenium content was determined with a Perkin Elmer 305B atomic absorption spectrophotometer. Phytotoxic effects were determined both quantitatively, by measuring the heights of the seedlings at weekly intervals, and qualitatively, by daily observations.

Section 3.4: Absorption of Potassium Selenate

From Soil by Douglas-fir Seedlings

Eight Douglas-fir seedlings of the same origin as those used in the above study were placed in pots and sunk into a nursery bed exactly as before. In this case, however, various amounts of

potassium selenate (25, 50, 250 and 500 mg salt) were mixed with the upper surface of the soil. Foliar samples were collected and analyzed for selenium by atomic absorption. The trees were observed daily, and any visible phytotoxic reactions to the treatment were recorded. Heights were measured weekly and recorded.

Section 3.5: Preparation of Sustained Release Selenium

Tablets for Use in Field Trial Studies

Powdered dimelamine selenite (~1g) was moistened with a 37% aqueous formaldehyde solution (0.73 mL), formed into a pellet (diameter 12.7 mm, height ~7 mm) by the use of a standard hand pellet press (Parr Instrument Co., Moline, IL) and then heated at 100°C for 15 min. To ensure subsequent safe handling, the tablets were then placed on a screen and immersed in a 1% solids solution of chitosan in 1% acetic acid. The solution was allowed to dry, forming a thin, biodegradable film of chitosan acetate.

Section 3.6: Investigation of other Possible Timed

Delivery Systems for the Release of Selenium

Other sustained release systems were synthesized as possible devices for the delivery of selenium over extended periods of time. Some of these are described below.

Section 3.6.1: Fibrous Dimelamine Selenite Pellets

These tablets were prepared with the same materials in roughly the same proportions as had been used in the pellets described above, except that disks of cheesecloth were cut and placed at various positions within the pellet mixture just before they were pressed. Mechanical integrity of the tablets was evaluated, and any other observations about their potential usefulness were recorded.

Section 3.6.2: Monolithic Erodible Polymer- Selenium Combinations

Several disks were synthesized which were comprised of either dimelamine selenite or melamine and selenium dioxide dispersed in a polymer matrix (various mixtures of poly(oxyethylene glycol) and poly(vinyl acetate)). Mechanical integrity of the devices was evaluated and they were observed daily for chemical stability; this merely involved an evaluation as to whether a pink color had appeared in the device. The appearance of such a color would have indicated the undesirable formation of elemental selenium within the matrix.

Section 3.6.3: "Tea-Bag" Delivery Systems Filled with Selenium

Various mixtures of free melamine and selenium dioxide were placed in pieces of paper that were then folded and glued together. The bags were then observed for chemical stability.

Section 3.6.4: Selenium Impregnated Cardboard Strips

A hot solution (90°) of dimelamine selenite (0.0959 M) was poured over a cardboard disk that had been formed with melamine and recycled newspaper pulp. Samples of the cardboard strip were submitted for selenium determination. Visual observations of the chemical stability of the device were recorded. The release characteristics of the cardboard were determined by placing a disk (diameter, ~ 9 cm; mass, 3.930 g) of the material into a 1 L beaker filled with 200 mL deionized water. The beaker was provided with a magnetic stirrer (1000 rpm), and samples of the solution were removed at various times (5, 10, 15, 20, 25, 30 min) and submitted for selenium analysis by neutron activation.

Section 3.6.5: Selenium Impregnated Toothpicks

Standard round (length, 65 mm; radius, 1 mm) toothpicks (Diamond International Co., New York, NY) were placed in a hot (100°) dimelamine selenite solution (0.0959 M) and removed after various periods of time (30 s, 1 min, 2 min, 5 min and 10 min). The selenium content of one toothpick from each equilibration time was determined and the release rate determined as with the cardboard strips, except that the volume of water used was reduced to 150 mL and the magnetic stirrer operated slightly faster (1030 rpm). Visual observation of the chemical stability was recorded.

Section 3.6.6: Selenium Impregnated "Popsicle Sticks"

Several dozen "popsicle" sticks (length, 110 mm; width 10 mm) were prepared for impregnation by placement in a flask equipped with a Buchner funnel. A vacuum was pulled on the flask and boiling water was poured through the funnel until all the sticks were completely immersed. Bubbles of air, presumably from the pores of the sticks, could be seen appearing on the stick surfaces. The saturated sticks were then placed in a 1 L flask filled with ~300 mL of a dimelamine selenite solution (0.0554 M) such that the lower halves of the sticks were in the solution. One third of the sticks were removed at each of various times (15, 30 and 55 min).

Samples of the sticks were submitted for selenium analysis. The release rate characteristics were determined as with the cardboard and the toothpicks, except that the volume of water used was increased to 400 mL.

Section 3.6.7: INCO Plastic Devices for Selenium Delivery

These devices were produced at INCO through the following technique. Mixtures of selenium dioxide (1.3 g), earth (6.0 g) and sodium silicate (8.0 g) were compression molded (550 psi) and encapsulated in a polyester resin (resin thickness ~1 cm). A hole (either 0.16 or 0.32 cm) was then drilled through the polyester to the molded matrix, allowing delivery to proceed through the portal. Several of the devices were placed in individual beakers of distilled water, and samples of the solution were taken at a number of times for

selenium analysis.

The performance of the devices in vivo was determined by placing them in the planting soil of Douglas-fir seedlings that were potted and sunk into nursery beds. Foliage samples were collected at monthly intervals and analyzed for selenium. Visual observations of the appearance of the seedlings were recorded.

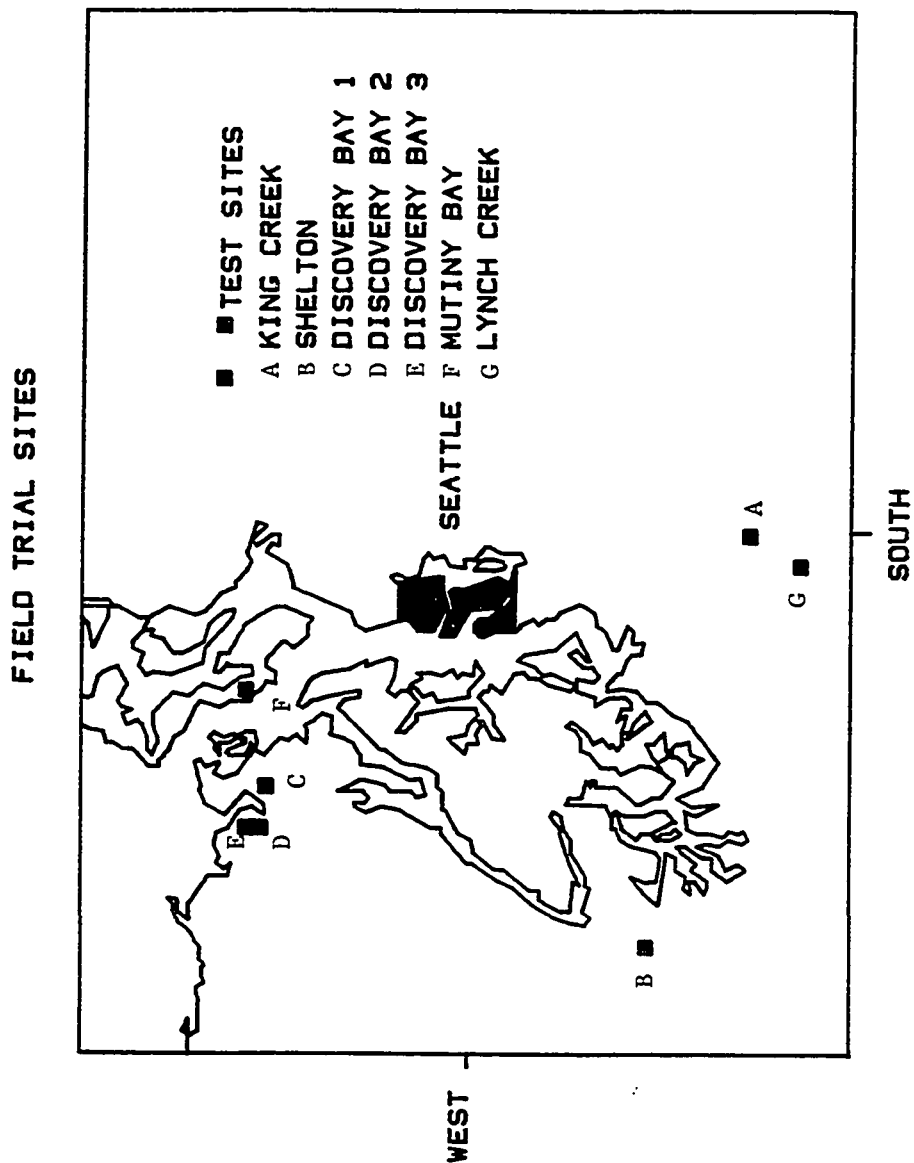
Section 3.6.8: MCI Selenized Granules

As reported by Mac Crews, Product Development Engineer, MCI used the following procedures to produce 0.5% Se (by weight) melamine/urea granules. Urea prills were ground to a fine powder and mixed with a melamine powder in a 80:20 weight ratio (melamine:urea). That powder was then mixed with the proper amount of SeO_2 required to yield 0.5% Se. A urea/formaldehyde resin was formed by mixing a 2:1 molar formaldehyde:urea solution in a beaker. The solution was heated to boiling and held until a cloud point was reached. As the powder mixture was fed into a 16" pan granulator the urea/formaldehyde resin solution was applied as a spray. The granules were then heated for two hours in a 180°F oven. The product was screened (-4 and +12 mesh) to remove dust and oversized particles.

Section 3.7: Field Trial Tests of the Selenium Tablets

Seven field trials were established at sites in western Washington historically notorious for heavy deer browsing pressure on

Figure 37. Field Trial Test Sites in Western Washington Established to Test the Effectiveness of The Repellent Tablets.



tree seedlings (Fig. 37). At all sites the trees were sequentially numbered, flagged, measured and inspected for previous browse damage. The trees were generally divided into three groups: in Group I all trees were treated with tablets; in Group II the even numbered trees received tablets; and Group III served as control. The King Creek site included a fourth group in which $3/4$ of the trees were given tablets.

Site properties varied widely at the different field trial locations. The soil types at five of the seven field trials are reported in the series of soil surveys published by the United States Department of Agriculture Soil Conservation Service in cooperation with the Washington Agricultural Experiment Station. The soil at the King Creek site is described as Barnestone gravelly coarse sandy loam. It is described as "suitable to the production of Douglas-fir...annually [yielding] 135 cubic feet/acre." The Lynch Creek site is approximately twenty miles south of this field test area, and the soil there is described as Scamman silt loam which is "well suited to the production of Douglas-fir...producing annually 160 cubic feet/acre." The three Discovery Bay sites are within just a few miles of each other, but there are fairly wide variations in the soil type at each. Discovery Bay I has soil described as Alderwood gravelly sandy loam, Discovery Bay II has Hyopus gravelly sandy loam, and Discovery Bay III has Tukey gravelly loam. Further details on the description of each soil type can be found in the Soil Survey series itself. The Mutiny Bay site was not covered by the Soil Survey series

in Washington, but a survey was carried out by Georgia Pacific which measured it as a site class III. The area was harvested in 1979, and it yielded 11,100 board feet per acre.

Tablets were placed 2 cm deep at a distance 3-5 cm from the stem at all sites except for Mutiny Bay. At this particular site the trees (Styro-8's) were given tablets on the same day they were planted, and the tablets were placed near the top of the planting hole in intimate contact with the root ball.

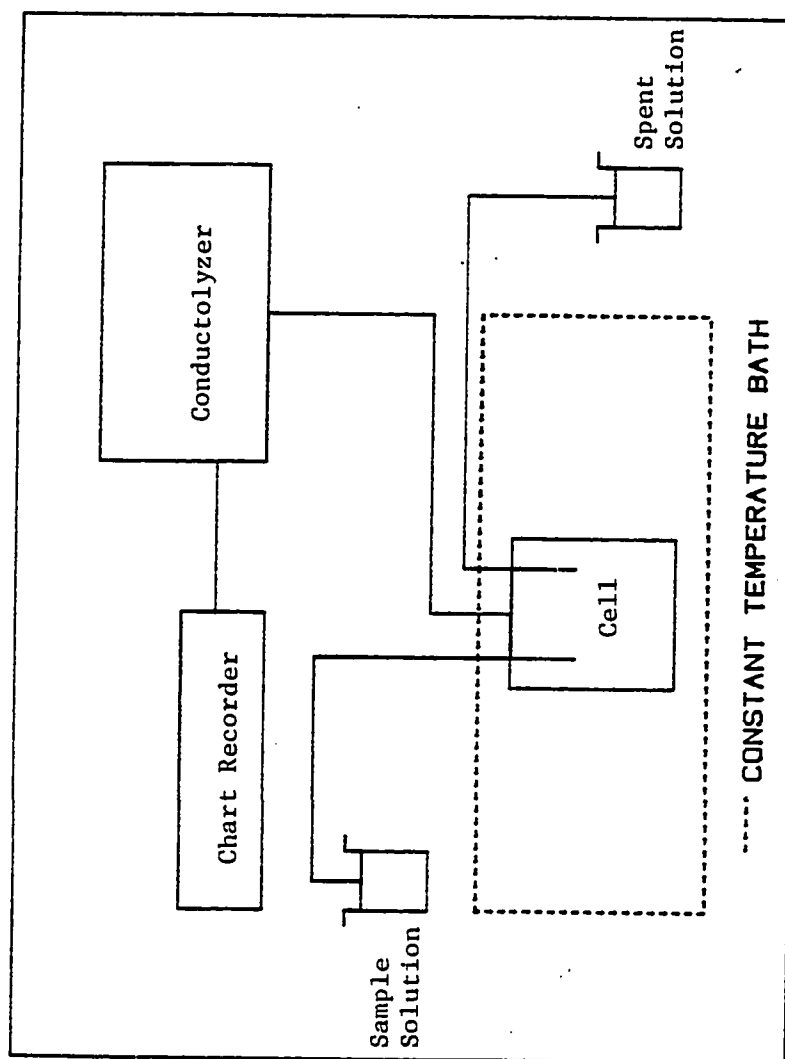
Foliage samples (300-500 mg) were collected from the uppermost lateral branches of the seedlings at monthly intervals. In addition, soil samples at various positions below and to the side of the tablets were collected for selenium analysis. During budburst, samples of both new and old foliage from the same tree were collected. The stems of seedlings which had apparently died due to a toxic response were also submitted for Se determination. Weather data, comprising precipitation, temperature, and (rarely available) evaporation rate were collected for each of the sites. Heights were measured at the end of each growing season. Browse results were tabulated if a period of extensive browse appeared to have occurred between the monthly visits. Severity of browse was not recorded; it was simply noted whether or not the leader had been eaten.

Precipitation and temperature data are available from a number of weather stations throughout the state in the NOAA reports. These reports are routinely accessible at various libraries, and they provided the climactic data for each of the field trial sites.

Section 3.8: Determination of Selenite Ion Diffusivity in Water

A series of aqueous selenious acid solutions was prepared by adding various known amounts of selenium dioxide to deionized water (resistance $> 1.44 \times 10^3$ ohms/cm). The conductivity of each of these solutions was determined on a LKB 5300A Conductolyzer (LKB-Produkter, Stockholm, Sweden). A schematic of the apparatus appears in Fig. 38. The cell constant was calculated by measuring the conductivity of various standard solutions (KCl, NaF and others) for which numerous determinations of the conductivity have been reported in the literature. Examples of the curves used to determine the cell constant are shown in Fig's. 39 and 40 for KCl and NaF, respectively. Several selenious acid solutions were then prepared and their resistances measured with the device. In order to calculate the true ionic concentration, a value for the dissociation constant of selenious acid was required. This was obtained from Pourbaix's Atlas of Electrochemical Constants,⁽¹²⁰⁾ which reported $K_1 = 2.57 \times 10^{-3}$ M. The data found there also indicate that the doubly charged ion, SeO_3^{2-} , is present only at $\text{pH} > 8$, conditions which were never investigated experimentally and are not found in western Washington planting soils. Values of the molar conductivity were then extrapolated back to zero concentration in order to obtain a value for the molar conductivity of the hydrogen selenite ion at infinite dilution. This value can be theoretically related to the diffusion coefficient of the ion through the Einstein equation.⁽⁶⁶⁾

Figure 38. Apparatus for Determining Solution Conductivity.



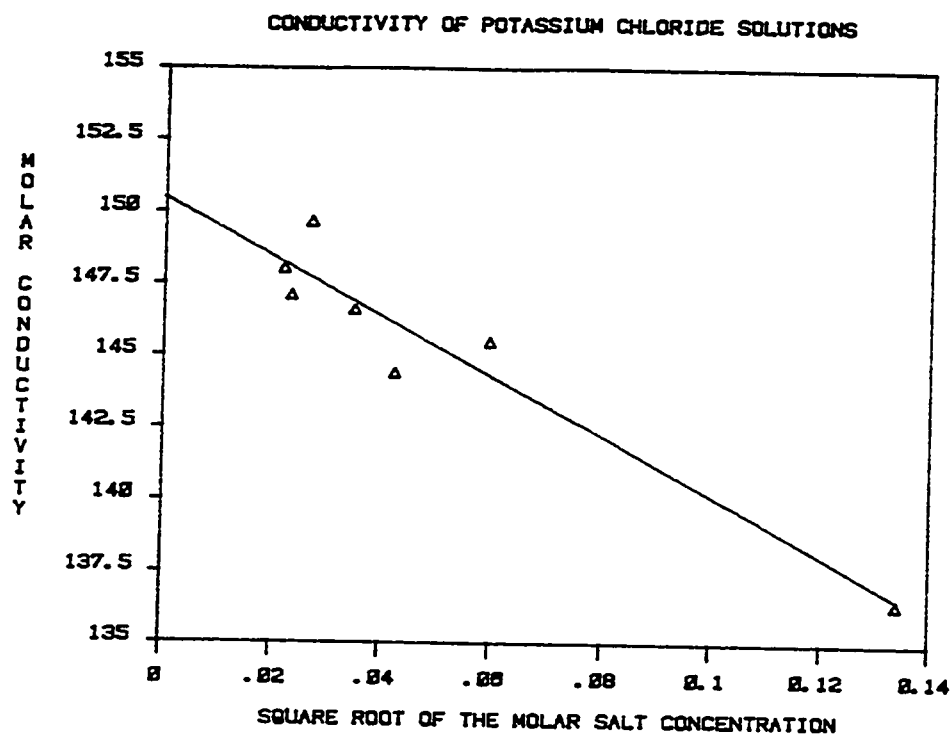


Figure 39. Conductivity of Potassium Chloride Solutions.

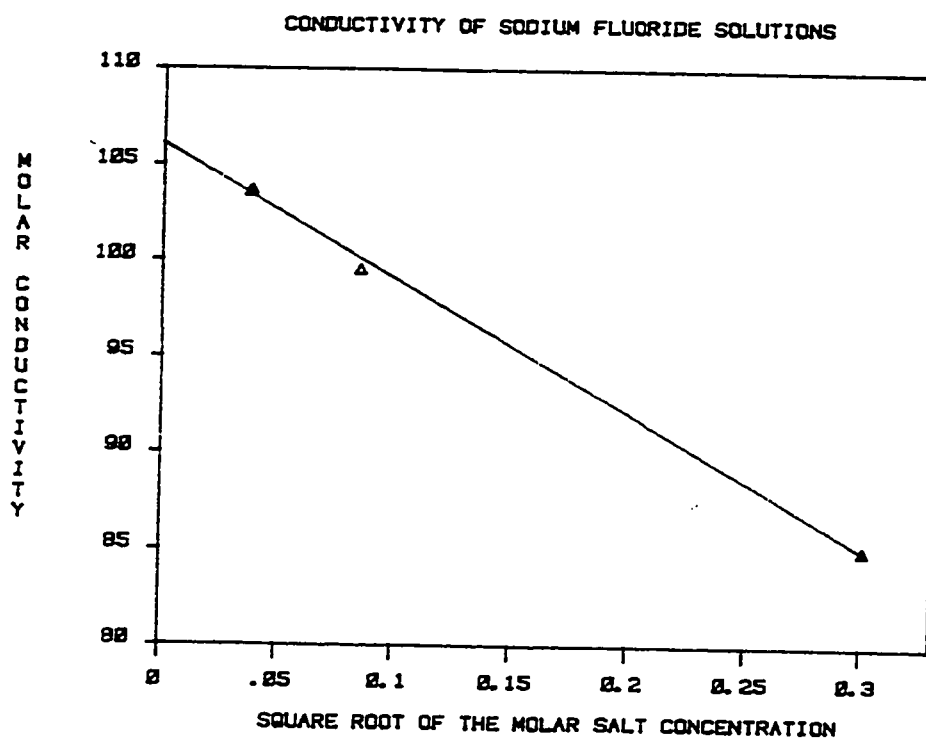


Figure 40. Conductivity of Sodium Fluoride Solutions.

Section 3.9: Accelerated Dissolution Studies

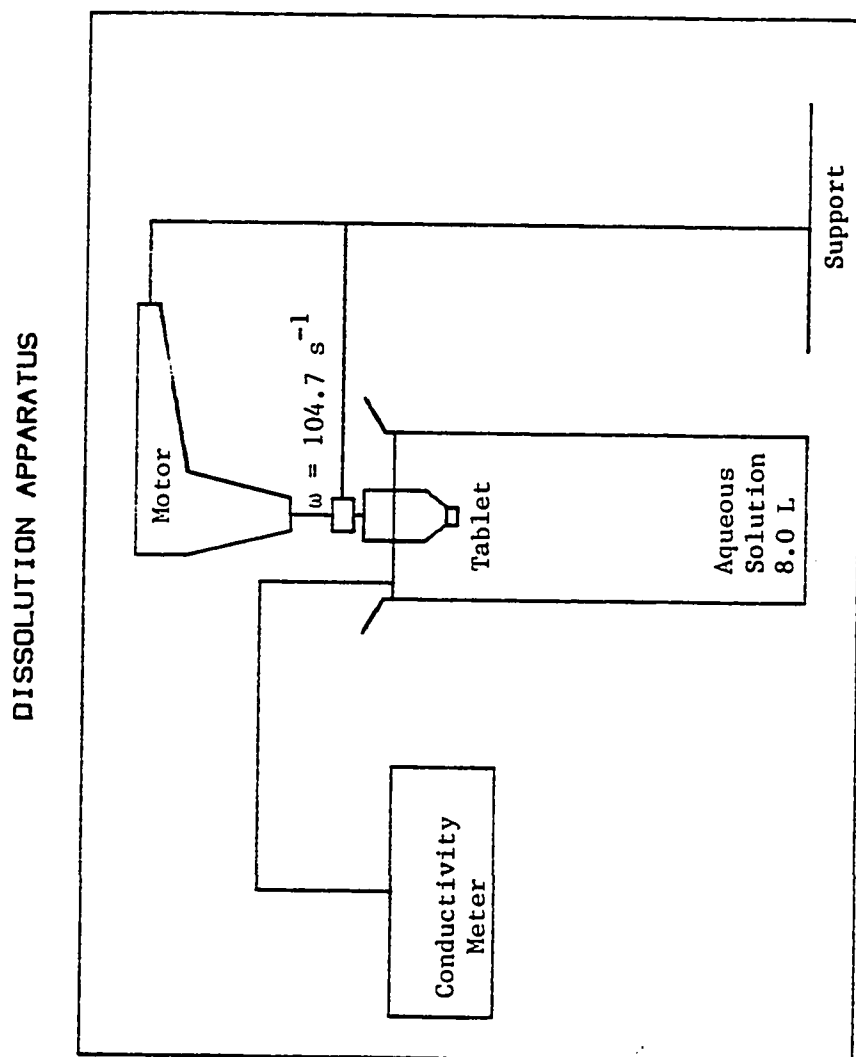
A rotating dissolution apparatus was constructed from a variable speed motor (Model E60, Heidolph Elektro Kg, Munich, West Germany) and various supportive materials (see Fig. 41). The motor was capable of continuous operation from speeds of 220 to 1600 rpm. A platform was lathed from polyethylene (HDPE obtained from General Plastics Co., Seattle, WA) and placed at the end of a rod inserted in the motor jaws. Various aqueous solutions of different ionic strength (from 0 to 0.75 M) were employed during the dissolution experiments, which simply involved gluing (Silicone sealant, Dow Corning, Midland, MI) a tablet to the polyethylene platform and operating the motor at 1000 rpm ($=104.7 \text{ s}^{-1}$). Selenium concentrations in the dissolution solution were determined by analysis of samples taken at known times from the apparatus. Some samples were analyzed by neutron activation and others were acidified to 1.4% nitric acid concentration for atomic absorption analysis.

Section 3.10: Mechanical Preparation of Slightly

Soluble Selenium Tablets by INCO

As reported by Dr. Douglas Brown of INCO, dimelamine selenite crystals were ground to a 20 mesh screen size in preparation for formulation in a V-cone blender. Dimelamine selenite (72% by weight) and CymelTM 405 (American Cyanamide) (27% by weight) were charged into the V-cone. The contents were tumbled for 15 to 30 minutes, and

Figure 41. Accelerated Dissolution Apparatus.



Acrawax^(TM) (Glyco Chemicals) (1% by weight) was added, followed by another 15 minutes of mixing. A measured amount of this mixture (2.1 g) was compression molded in a highly polished cylindrical die (0.625 inches diameter) to a thickness of 0.380 inches. The tablets were then cured in a forced air convection oven (105°C) for 24 hours.

The tablets were then coated at the University of Washington through the following procedure. A coating solution was prepared by mixing one part polymer PolyoxTM (Union Carbide WSRN-3000) with approximately 100 parts distilled, deionized water. Heating and stirring were used to facilitate dissolution. A plastic screen (250 squares per inch) was placed in a plexiglass trough (18 x 24 inches), and the screen was then covered with approximately 1000 of the cured tablets. The coating solution was poured over the tablets repeatedly (about 10 times), with the tablets rearranged intermittently to assure uniform coating. The tablets were then dried under a hood.

Section 3.11: Absorption of Selenium as Dimelamine

Selenite by Other Plant Species

Both as an animal repellent and as an insecticide, selenium has sufficient potential to be of interest as a bioactive systemic material in other plant species. A number of investigations were initiated to study the toxic and therapeutic levels of selenium in these other plants.

Section 3.11.1: Tropical Cedar

Several tropical cedar (Cedrela sp.) trees were grown in pots (diameter 25 cm) in the University of Washington greenhouse. After they were well-established and had attained a height of nearly 1 m, powdered dimelamine selenite was mixed with the surface of the planting soil. The seedlings were watered as usual and after 3 months foliar samples were taken and submitted for selenium analysis. Observations were also recorded concerning their overall appearance.

Section 3.11.2: Fruit Trees

Fruit trees (25) provided by the May Nursery Co., Yakima, WA, were planted on University of Washington Urban Horticulture land near Union Bay. The trees included five each of peaches (Prunus persica), pears (Pyrus communis), cherries (Prunus sp.) and two types of apples (Malus sp.). On the same day as they were planted they were treated with dimelamine selenite tablets (INCO Research and Development, Sloatsvurg, NY) at the rate of 1, 2, 3, 4 and 5 per seedling. The trees were watered during periods of relative drought and foliar samples were collected at monthly intervals for selenium analysis. Qualitative observations concerning their appearance were recorded.

Section 3.11.3: Cottonwood

Cottonwood (Populus deltoides) shoots were sprouted from cuttings of mature trees. Samples were grown in the greenhouse for a period of 4 months and were then treated with aqueous dimelamine selenite

solutions (~2 g Se per 5 seedlings). Foliar samples were taken monthly for selenium determination, and the trees were observed every few days for signs of phytotoxicity.

Section 3.11.4: Rhododendron

A mature rhododendron (Rhododendron sp.) plant at the University of Washington arboretum was treated with approximately 4 g dimelamine selenite spread on the soil around its stem. Foliar samples were collected and observations recorded as above.

Section 3.11.5: Grasses

A mixed stock of grass species (Shady Area^R, Scott, Seattle, WA) was seeded into 20 pots. The grass was allowed to establish for a period of a month, and was then treated with various amounts of two types of melamine granules (see Section 3.6.8) sprinkled on the surface of the soil. Both the granule types contained 0.5% selenium dioxide. The first granules were prepared by mixing this SeO_2 with Super-60TM, and they became quite discolored (pink) indicating extensive reduction to elemental selenium. The second preparation utilized 80 parts melamine and 19.5 parts Cymel (American Cyanamid, Stamford, CT) resin with the SeO_2 . These second granules were not as discolored.

After 6 weeks of growth the grass was cut to pot level, and the clippings from 7 of the pots were submitted for selenium analysis. Clippings were subsequently collected and analyzed every 6 weeks, and

qualitative observations of the appearance of the grass were recorded.

Section 3.12: Determination of the Intrinsic Kinetics
Of Selenite Ion Absorption by Douglas-fir

Bare-root (2-0) Douglas-fir seedlings (20) provided by the Georgia-Pacific Corp., Bellingham, WA, were placed in jars (2 L) containing Hoaglands solution (Hoagland and Arnon, 1950) and oxygenated with a continuous airstream. The trees were grown in the University of Washington greenhouse. The trees were established for 3 weeks and were then treated with various amounts of selenium (1, 2, 5, 10 and 20 mg Se) as selenious acid. Samples of the solution and roots at each treatment level were collected at several times (1, 3, 5, 10 and 15 d) following treatment and submitted for selenium analysis. Root samples were extensively rinsed with warm water before being placed in the sampling vials. Foliar sample were taken (3, 10, 40 and 70 d) after treatment for Se determination. The trees were watered every other day, and any apparently toxic reactions to the treatment were recorded. Data analysis was then performed to fit the data to a Michaelis-Menten kinetic expression.

Section 3.13: Determination of the Rates of Adsorption
And Deactivation of Selenium by Test Site Soils

Samples of soil (~1 kg) from each of the field trial sites were collected. A weighed amount of the soil (~10 g) was placed in a 1 L beaker. At time = 0 a selenious acid solution of known concentration (2.0, 10.0, 20.0, 100.0 or 999.0 ppm Se) was placed in the beaker and the resulting slurry was stirred. Samples of the aqueous solution were withdrawn with a syringe of narrow diameter (0.1 mm) at various times (1, 6, 11, 22, 33, 66, and 99 min) during the experiment. These samples were submitted for selenium determination by neutron activation analysis. Data analysis was then performed to fit a kinetic expression to the results.

Section 3.14: Determination of the Rate of Volatilization
Of Selenium from the Foliage of Douglas-fir

Seedlings containing known amounts of selenium in their foliage were placed in a plastic chamber. A pump then recirculated the chamber gases through a liquid nitrogen cold trap for a measured period of time. The condensed gases were collected and analyzed for selenium by atomic absorption analysis.

Section 3.15: Determination of Soil Properties

The particle size distribution of the Mutiny Bay soil was determined by taking a dried sample of the soil and passing it through a number of screens, with the mass of soil retained on each screen recorded. Water (deionized) was allowed to come to equilibrium with the soil, passed through glass wool, and then submitted to a conductivity determination as for the selenious acid solutions. Soil pH was determined with a specially designed kit (Hellige-Truog Soil Reaction (pH) Tester, Hellige Inc., Garden City, NY).

The dependence of the hydraulic conductivity and saturation of the soil as a function of pressure (also called the suction or tension since these are negative pressures) was determined as suggested by Hillel.⁽⁷⁰⁾ A column containing a weighed amount of the oven dried soil was wetted with deionized water and elevated above 2 reference beakers to a known height. The flowrate through the column was measured until steady state had been established (this generally required several days). The mass of the column was then determined before and after drying, and the water content given by difference.

Section 3.16: Establishment of Other Field Trial

Tests of the INCO Tablet

A number of field trials were established with the tablets prepared by INCO. These field trials are listed in Table 5.

Table 5. Field Trials Established to Evaluate
The X-BrowSe Animal Repellent Tablets

COATING	QUANTITY	DELIVERED TO	TREE TYPE
<u>First Shipment</u> (February 11, 1983)			
1/3 each PEG,PVA,Chitosan		Rick Iverson International Paper 34937 Tennessee Road Lebanon, OR 97335	Douglas-fir (503) 259-2651
1/2 each PEG,PVA	~5000	Rick Iverson	Douglas-fir
1/2 each PEG,PVA	~900	Rick Iverson	Douglas-fir
1/2 each PEG,PVA	~700	Art Schick Naval Submarine Base Bangor Code 86: Public Wrks Eng. Div. Bremerton, WA 98315 (206) 396-4192	Douglas-fir
1/2 each PEG,PVA	120	Doug Brown, INCO Research and Development	
1/2 each PEG, PVA	~100	Returned by Dan Bochner	
<u>Second Shipment</u> (March 25, 1983)			
PEG (WSR-N-750) (same as above)	200	Bob Klapptap Ont. Min. Nat. Res.	Black Spruce
PEG (WSR-N-750)	200	Ron McGlaughlin MacMillan-Bloedel 65 Front Street Nanaimo, BC V9R5H9 (604) 753-1112	Douglas-fir Cedar
PEG (WSR-N-750)	20	Doug Brown, INCO Research and Development	
PEG (WSR-N-750)	~300	Art Schick, Navy	
PEG (WSR-N-750)	600	Tharon O'Dell Champion P.O. Box 849 1600 Valley River Drive	Douglas-fir

		Eugene, OR 97440	(503) 392-0881
PEG (WSR-N-750)	30	Cass Kowaleski 1240 Bubb Road Cupertino, CA 95014 (408) 255-8515	Wine grapes
PEG (WSR-N-750)	22	Donald Merkeley 2928 Eastlake Ave E Seattle, WA 98102	Fruit trees (206) 323-7331
PEG (WSR-N-750)	100	Sylvia Tufte Ketron Island Box 580 Steilacoom, WA 98399 (206) 588-7254	Garden plants
PEG (WSR-N-750)	300	Al Rasmussen Wash. State Dept. of Game 600 N Capitol Way Olympia, WA 98504 (206) 753-5740	Fruit Trees
PEG (WSR-N-750)	500	Gene Slonicker Mt. St. Helens Nat. Volcanic Monument Route 1 Box 369 Amboy, WA 98601	Douglas-fir (206) 247-5473
PEG (WSR-N-750)	1000	Don Cady Cady Tree Farm c/o Reid Realty Belfair, WA 98528 (206) 625-0273	Douglas-fir True Firs
PEG (WSR-N-750)	500	Howard Grabhorn Route 1 Box 849 Beaverton, OR 97007 (503) 628-1866	Douglas-fir
PEG (WSR-N-750)	~100	Ron McGlaughlin, MacMillan Bloedel	

Third Shipment (March 29, 1983)

PEG (WSR-N-750)	2100	Ron McGlaughlin, MacMillan Bloedel
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Fourth Shipment (April 14, 1983)

PEG (WSR-N-3000)	1500	Spencer Bruskin U.S. For. Service P.O. Box 232 Cedro Wooley, WA 98284 (206) 856-1324	Douglas-fir
PEG (WSR-N-3000)	100	Craig Regert Washington County Courthouse Extension Hillsborough, OR 97123 (503) 648-8772	Fruit Trees
PEG (WSR-N-3000)	11	I.Z. Lopez 11015 196th SE Snohomish, WA 98292	Douglas-fir
PEG (WSR-N-3000)	500	Howard Grabhorn	
PEG (WSR-N-3000)	75	David Gustafson Fruit Tree Study	
PEG (WSR-N-3000)	~1200	Doug Brown	
PEG (WSR-N-3000)	~1000	Doug Morrison McLaren Ind. Buckingham, Quebec J8L2X3	Black Spruce
PEG (WSR-N-3000)	12	Devra Daniels Number 2 Tenaya Lane Englewood, CO 80110 (303) 771-2000	Lilacs
PEG (WSR-N-3000)	~600	Greg Lyle 3400 Swede Hill Road Clinton, WA 98236 (206) 221-7505	Douglas-fir
PEG (WSR-N-3000)	~1000	Dan Fowler 4801 Crestway Austin, TX 78731 (512) 454-8822	Pecans
PEG (WSR-N-3000)	53	David Gustafson Film Thickness Study, and then 10 were sent	

to Dr. Ernest Ball Sequoia
University of California
at Santa Cruz
Division of Natural Sciences
Applied Sciences Bldg. 273
Santa Cruz, CA 95064

PEG (WSR-N-3000)	~300	Stan Pasin Douglas-fir North Bend Ranger Station 42404 SE North Bend Way North Bend, WA 98045
PEG (WSR-N-3000)	550	Back to INCO, from Wolff/Ishakson and Gordon Schatz

Fifth Shipment, (April 28, 1983)

PEG (WSR-N-3000)	~500	Ron McGlughlin
PEG (WSR-N-3000)	~500	Scott McCoy Myrtle Lakeway Co. No. 1 World of Tennis Square Austin, TX 78734 (512) 261-6630
PEG (WSR-N-3000)	~500	Carl Lundberg Douglas-fir Walking L Tree Farm 960 E Astor Colville, WA 99114 (509) 684-6317
PEG (WSR-N-3000)	~2000 many of these were returned	Al Rasmussen

Sixth Shipment (May 5, 1983)

PEG (WSR-N-3000)	~1200	Doug Brown
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remainder (~6300) returned to INCO (Doug Brown)

Chapter IV: Results and Discussion

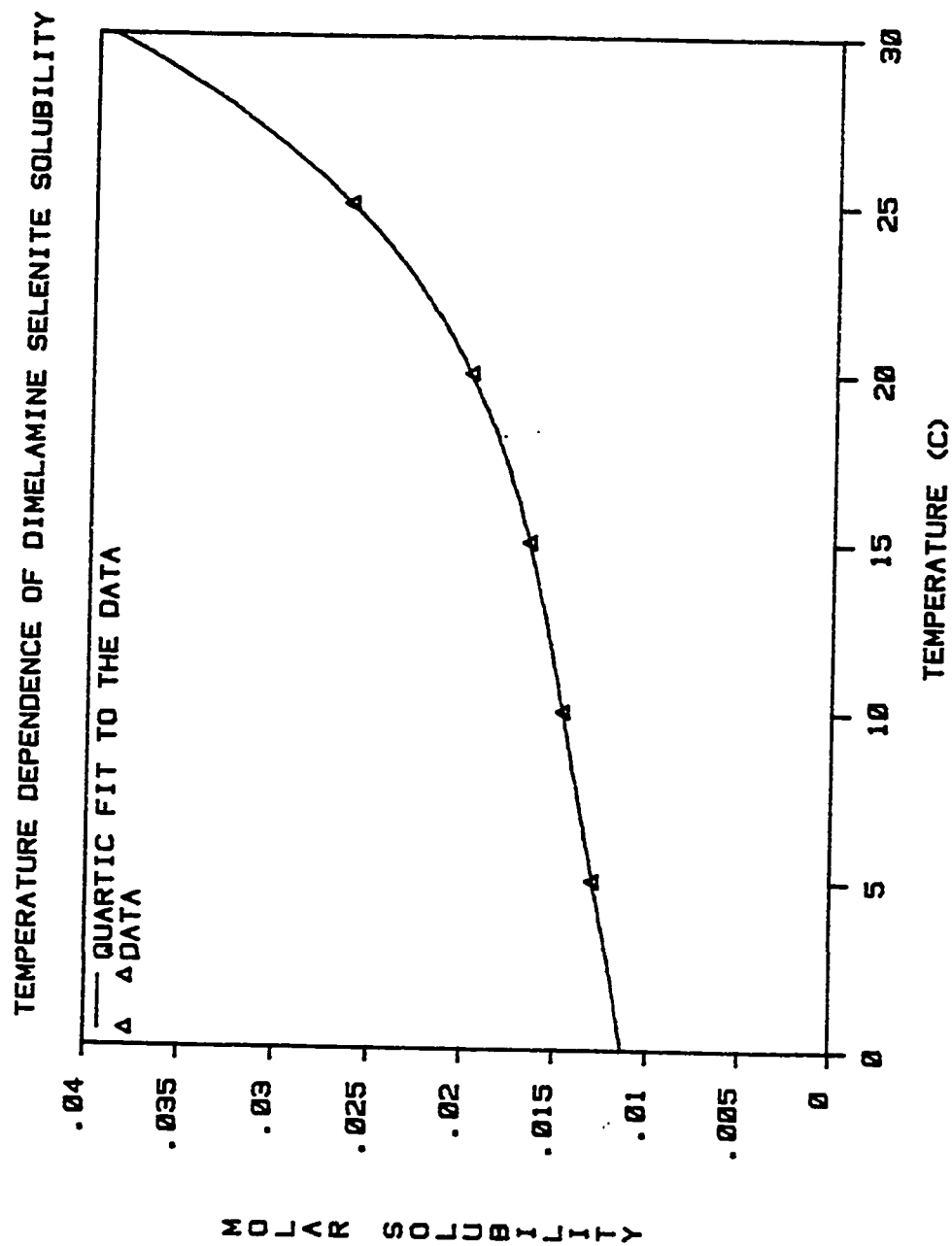
Section 4.1: Characterization of Dimelamine Selenite

The raw filtrate of white needles was recrystallized from water three times, and the resultant purified crystals were dried over CaCl_2 . A small amount of the purified salt was ground in a mortar and pestle to enhance the accuracy of a melting point determination. The salt decomposed to a pink color without melting in the range $269^\circ\text{--}271^\circ$. The pink color is characteristic of a redox reaction involving the selenite moiety, a strong oxidant. Melamine appeared to be indefinitely inert to this oxidation reaction at room temperatures, however, and this property is of supreme importance to any sustained selenite ion delivery system.

The detailed solubility determination of the newly synthesized salt reveals a predictable dependence on temperature in the range of interest ($5^\circ\text{--}25^\circ$). The data shown in Fig. 42 demonstrate that a quartic polynomial in T is capable of representing the data quite well. The equation was fit through a standard forward difference interpolation procedure,⁽⁵¹⁾ which gave the following result:

$$\begin{aligned} C_s (\text{mol/L}) = & 1.1263 \times 10^{-2} + 3.0391 \times 10^{-4} T \\ & + 1.2574 \times 10^{-5} T^2 - 1.4763 \times 10^{-6} T^3 + 5.8325 \times 10^{-8} T^4 \end{aligned} \quad \begin{matrix} (4-1) \\ T(^{\circ}\text{C}) \end{matrix}$$

Figure 42. Solubility of Dimelamine Selenite in Water as a Function of Solution Temperature.



Section 4.2: Absorption of Dimelamine Selenite

From Soil by Douglas-fir Seedlings

The atomic absorption analyses of the foliar samples demonstrated that selenium, when applied as dimelamine selenite, was translocated to the foliage by the Douglas-fir seedlings (see Fig. 43). There is also indirect evidence that selenium was volatilized from the foliage, as indicated by the decrease in the foliar concentration after about two months and the intense, garlic odor noticed around the trees. This is not entirely unambiguous because it is possible for "growth dilution" to decrease the foliar concentration of trace materials. The odor could have been due mainly to volatilization from the soil, which has been reported in the literature and observed by the author in the field. Growth dilution has in fact been invoked by certain researchers to explain selenium foliar results.⁽¹⁴¹⁾ In the current study, however, the needles that were submitted for analysis had already attained their largest size after about two weeks, thus the effect of growth dilution must have been negligible during the period (8-12 weeks after treatment) when the decrease was observed. Subsequent quantitative confirmation of the volatilization of selenium from the foliage (see Section 4.9) demonstrated conclusively that Se was indeed given off by the tree needles. Thus the dimelamine selenite proved to be a suitable carrier for the delivery of selenium to the seedling.

The effect of the dimelamine selenite on the seedlings' health

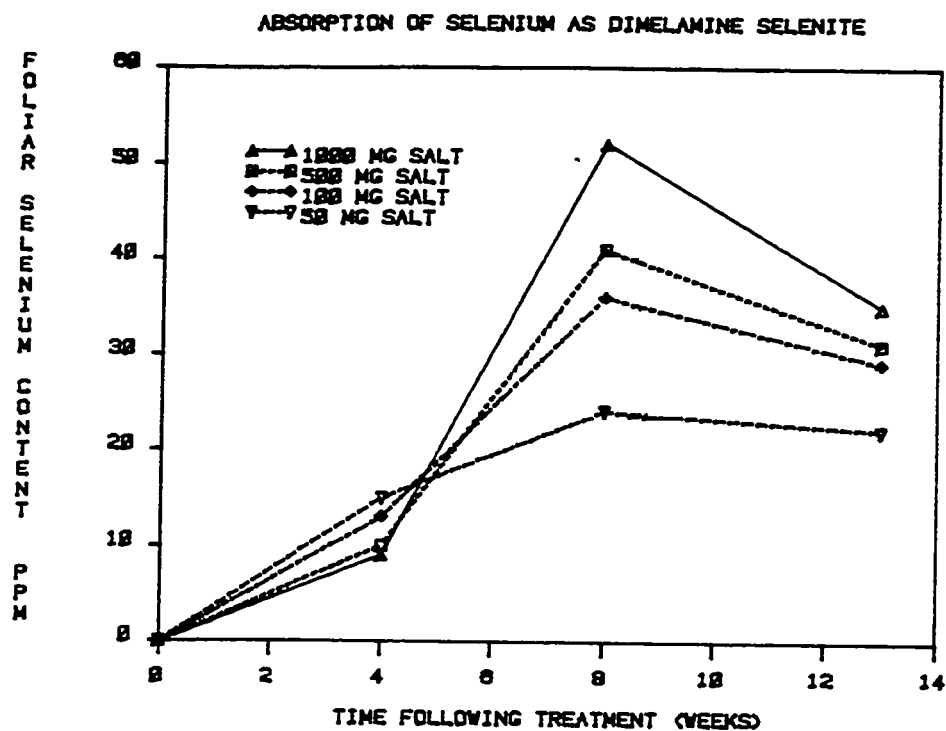


Figure 43. Pickup of Se as Dimelamine Selenite by Douglas-fir.

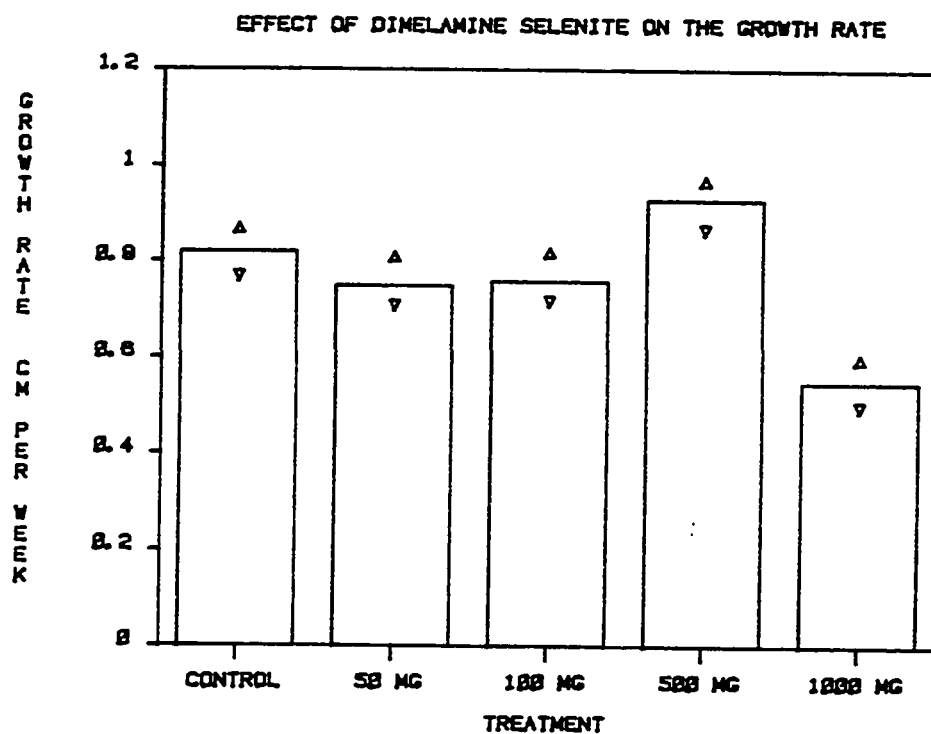


Figure 44. Effect of Dimelamine Selenite on the Growth Rate.

was apparently limited to a slight (~30%) deceleration of the growth rate at the highest treatment level (1000 mg/tree), as shown by the data in Fig. 44. The appearance of those seedlings treated with selenium was indistinguishable from the untreated controls. It should also be noted that no effect was detected due to the presence of the Super-60TM prills in half of the pots, thus the data for trees both with and without prills have been combined to form Figures 43 and 44.

These results encouraged the development of a controlled release device based on the dimelamine selenite, because even at the lowest treatment level (50 mg/tree), enough selenium had been transported to the foliage (>20 ppm) to exceed the minimally effective repellency level (10 ppm) determined by earlier workers with selenite ion.⁽¹¹¹⁾

Section 4.3: Absorption of Potassium Selenate

From Soil by Douglas-fir Seedlings

Although originally considered by Rediske and Lawrence⁽¹²⁶⁾ to be the most likely candidate for a systemic animal repellent, the selenate species proved to be highly toxic to the Douglas-fir seedlings. The treatment levels used in these pick-up studies were adjusted so that they would be equivalent, on a total selenium basis, to the dimelamine selenite experiments.

The foliar concentrations of selenium were much higher for these seedlings, which may have been due to the higher solubility of the K_2SeO_4 relative to the melamine salt. Both sets of seedlings were

watered extensively, however, and it seems unlikely that even the sparingly soluble dimelamine selenite crystals would withstand the virtual torrent of water that they experienced every two to three days during the experiment. A much more plausible explanation of the results is that the well-documented⁽⁹⁸⁾ difficulty which plants experience upon attempting to reduce the more highly oxidized selenate compound is responsible for the toxic accumulation of selenium in the foliage.

The severe effect which the selenium treatment had on the growth rate is documented by the data given in Fig. 45. The appearance of nearly every seedling was visibly altered by the treatment, with a discoloration of the foliage becoming discernible within two weeks. By the end of the test, after four months, three out of the four seedlings treated with the largest amount of potassium selenate (500 mg/tree) were apparently dead.

Section 4.4: Evaluation of Controlled Release Devices

The field tests of the slow release selenium tablets are discussed in detail below. This particular section is concerned with the lab scale determination of the performance of the sustained delivery systems described in section 3.6.

Section 4.4.1: Dimelamine Selenite/Formaldehyde Tablets

The accelerated dissolution of these tablets demonstrated that

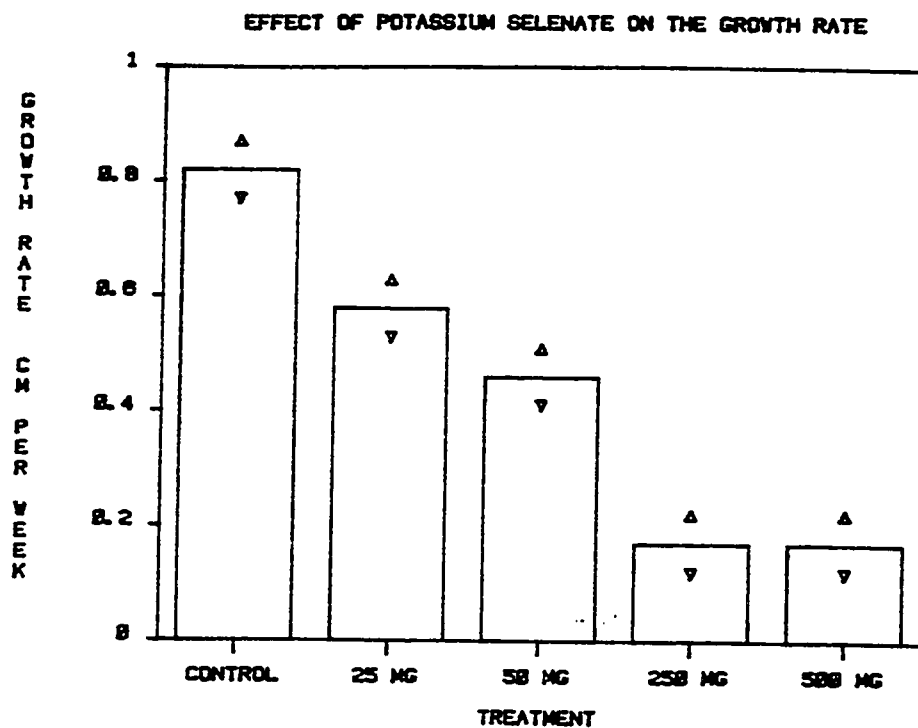


Figure 45. Effect of Potassium Selenate on the Growth Rate.

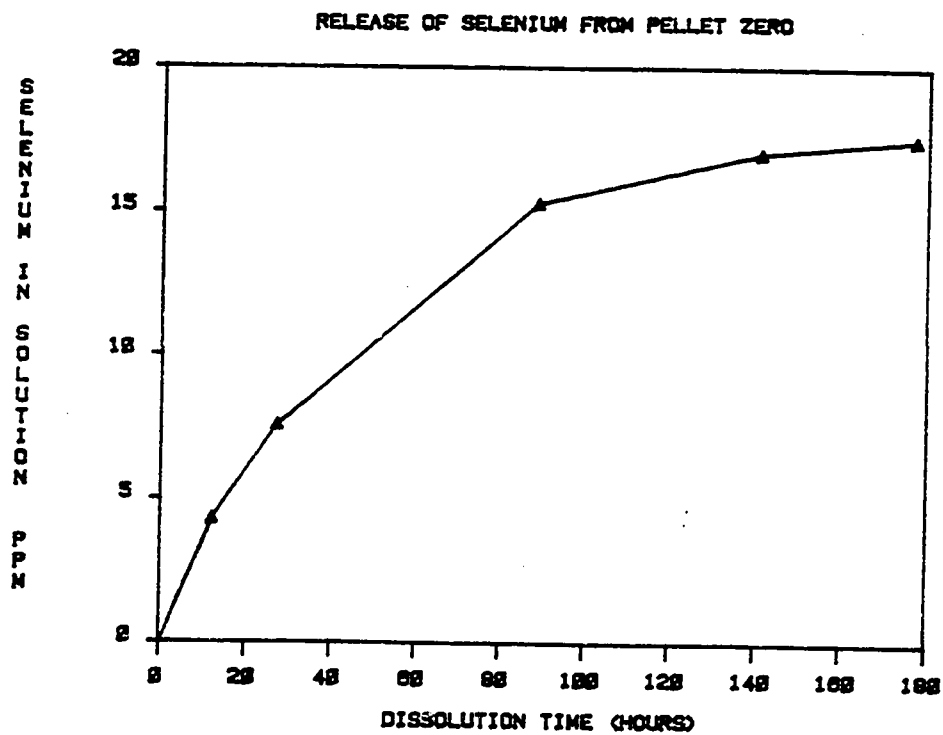


Figure 46. Release of Selenium from Pellet Zero (KCl = 0.001 M).

they would provide a selenium flux for a very long period of time (possibly 5 years) under field conditions. As seen in Fig. 46, the selenium concentration in the dissolution apparatus continued to rise more than 100 hours after the pellet had been placed in the device. Since the external mass transfer coefficient in the accelerator is at least 2-3 orders of magnitude higher than what is observed in the field (1.4×10^{-3} cm/s vs. $\sim 1 \times 10^{-6}$ cm/s), the release data indicate that field delivery should proceed for 10^4 to 10^5 hours (1.1 to 11 yrs).

The release rate is not maintained at a constant level, however, and the data indicate a quite good fit to both the Higuchi analysis and the exponential decay model, as shown in Fig's. 47-48. The exponential type behavior is preferable to the square root behavior for several reasons, both mathematical and aesthetic. Mathematically, the exponential dependence makes for simple derivatives and thus gives simple expressions for the flux that are well behaved over the entire t domain, while the Higuchi analysis predicts an unrealistic infinite flux at $t = 0$. The exponential model simply states that the total release of selenium is given by:

$$M = M_0 (1 - e^{-k_0 t}) \quad (4-2)$$

The releaseable selenium is M_0 and the rate constant for release is k_0 . This simple expression is a first order approximation to the analysis developed in Section 2.2.3. This may be shown by ignoring the final term in the brackets on the the right hand side of equation

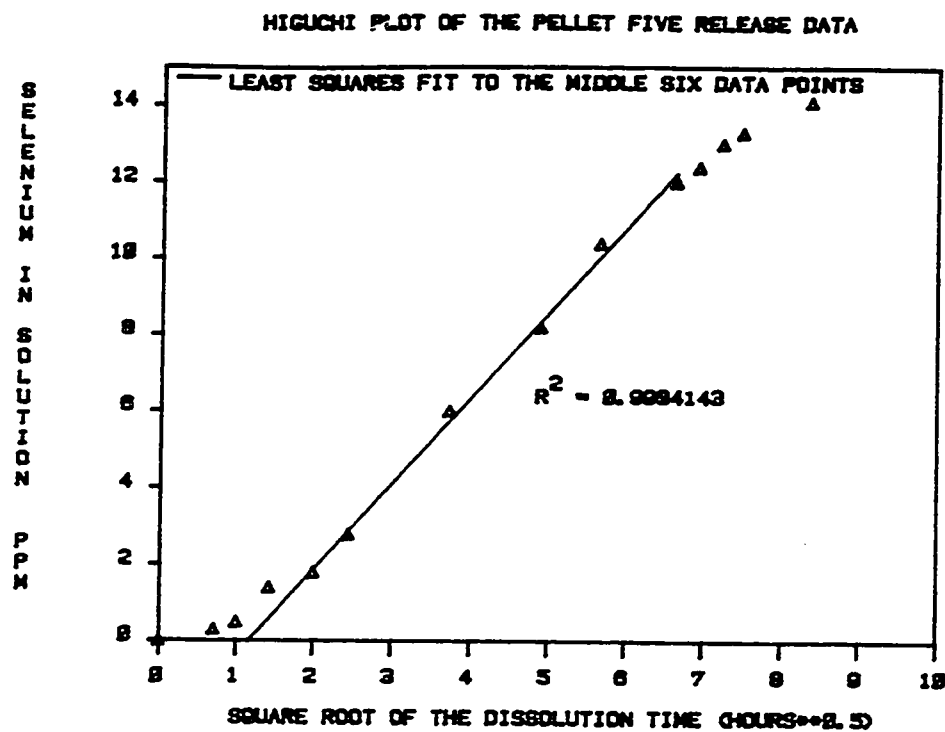


Figure 47. Higuchi Plot of the Pellet Five Release Data.

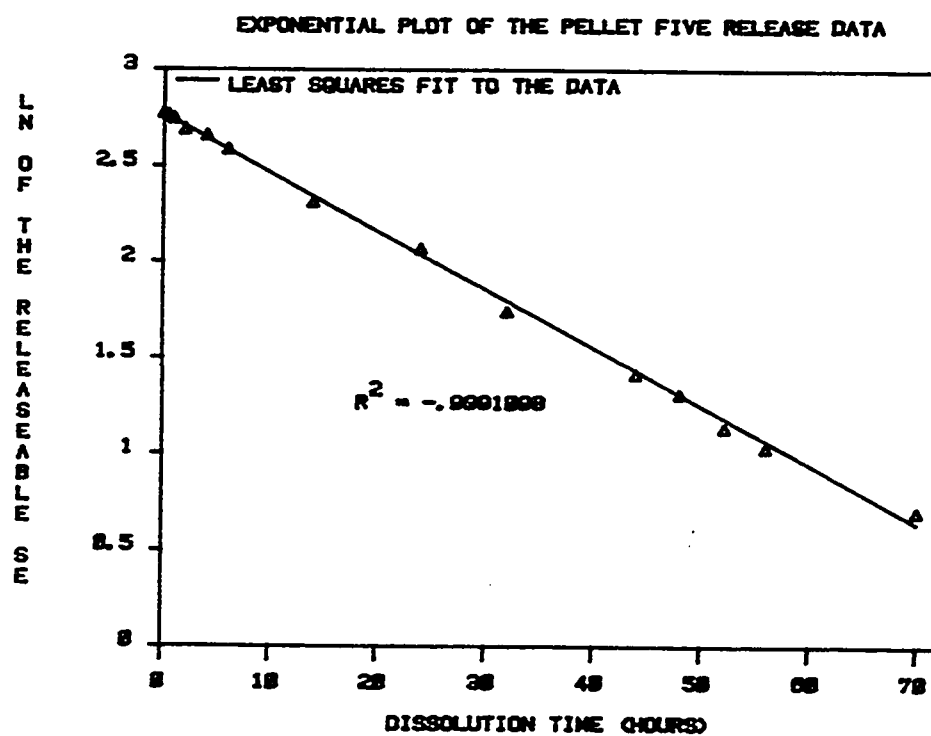


Figure 48. Exponential Plot of the Pellet Five Release Data.

(2-29). An exponential relationship of the form given in eq. (4-2) then results. The fit is better to the exponential relationship as indicated by the correlation coefficients. The Higuchi plot appears to indicate a lag period that might be attributed to the chitosan film. Diffusion through this film should be governed by eq. (1-10) with the film thickness, L , given by eq. (1-4), except that only one side of the chitosan is exposed, changing the 2 in eq. (1-4) to a 1. Thus the initial period (3-4 hr in diss. app., 30-40 days in soil) of diffusion from the tablet is governed by the following equation:

$$J = \frac{D(C_s - C_t)}{L - k_e t} \quad (4-3)$$

The release profiles observed from the tablets for various concentrations of potassium chloride in solution are summarized in Fig. 49. Assuming a simple exponential fit to these data (eq. (4-2)), the effect of ion exchange may be investigated by plotting the releaseable selenium and the effective rate constant for release as a function of ionic strength. These functions are shown in Fig. 50. It can be seen that an increase in the KCl level slightly increased the releaseable selenium, M_0 , while the rate constant of the release, k_0 , fell with increasing KCl concentration.

Section 4.4.2: Fibrous Pellets

These pellets were made with a number of different proportions of the ingredients used in the field pellets, but none of the tablets

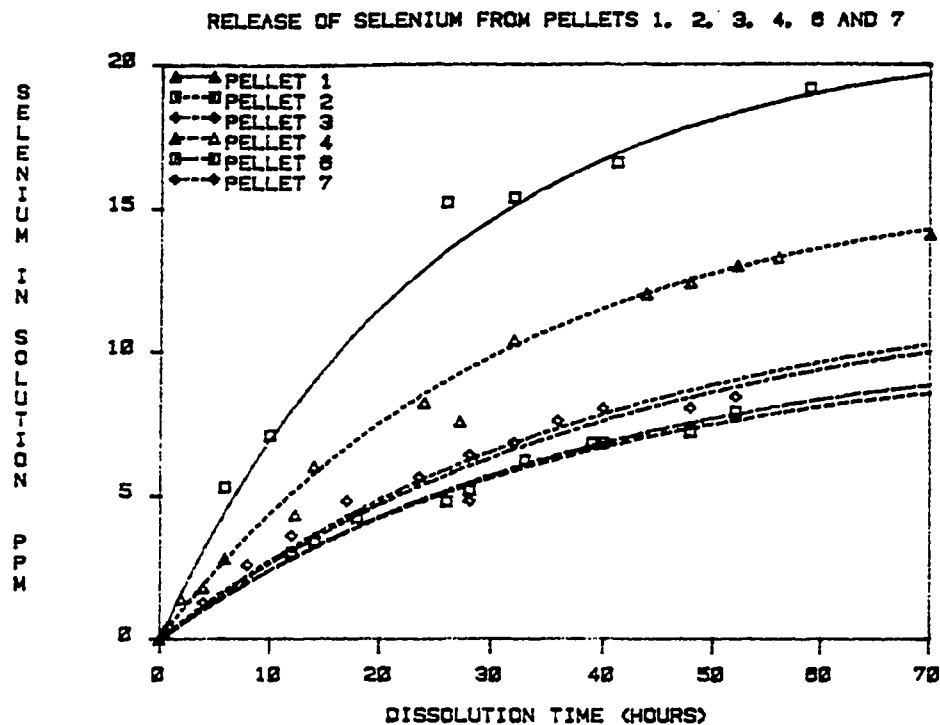


Figure 49. Release of Selenium from Pellets 1, 2, 3, 4, 6 and 7.

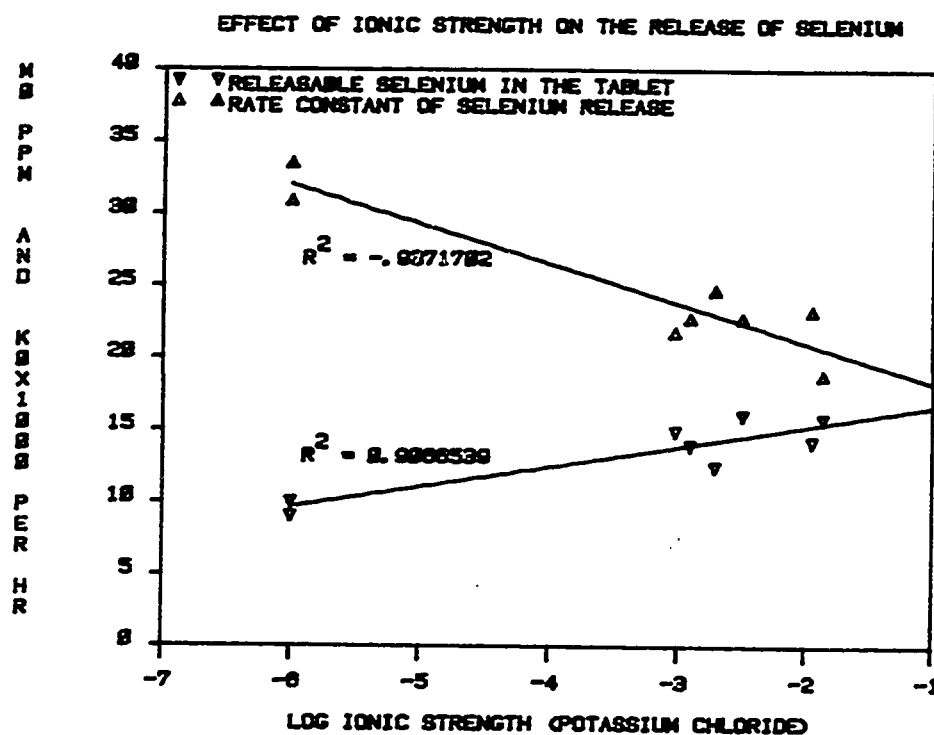


Figure 50. Effect of Ionic Strength on the Release of Selenium.

retained mechanical integrity. The fibers apparently absorbed a large portion of the aqueous formaldehyde that had been added to the pellet mixture. It is also possible that adhesion of the pellet mixture was somehow disrupted by the presence of the fibers; at any rate, the tablets never showed enough promise to warrant further consideration.

Section 4.4.3: Monolithic Erodible Systems

None of these devices appeared to be suitable as delivery systems. The SeO_2 attacked the polymer matrices in every case and a quite pink color was evident in each in a matter of days.

Section 4.4.4: "Tea-Bag" Delivery Systems

Pink colors appeared on the surface of the selenium containing paper packets within hours after they were synthesized. The hydrophilic nature of both the SeO_2 and the cellulose combined to accelerate the rate of water deposition, which appeared to catalyze the redox reactions between the selenium dioxide and the reactive groups within the paper.

Section 4.4.5: Impregnated Cardboard Strips

The selenium content of the cardboard strip sample was 237.7 ppm. The release rate characteristics of the device are shown in Fig. 51. It can be seen that the release rate fell slightly with time, and a plot of the data with the time coordinate raised to the one-half power (see Fig. 52) indicates linear behavior, as predicted by the Higuchi

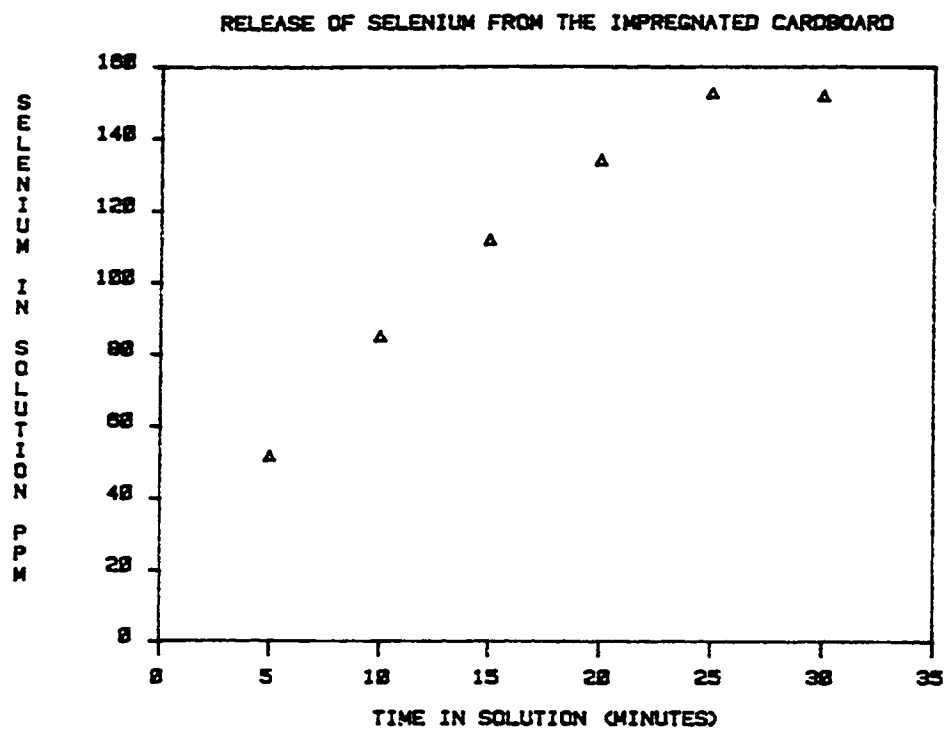


Figure 51. Release Rate from the Impregnated Cardboard Strip.

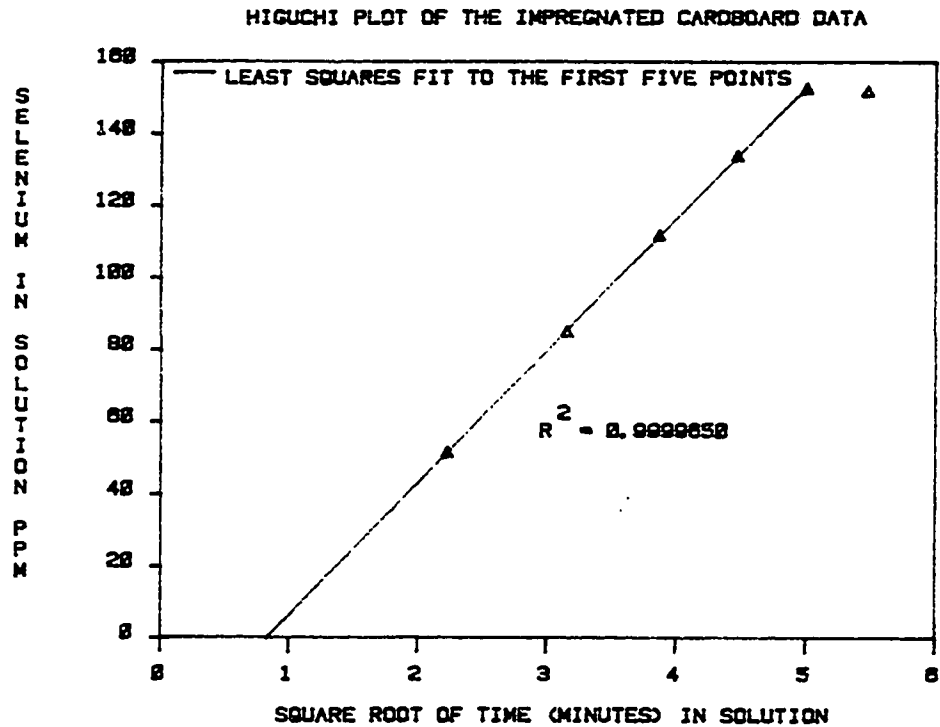


Figure 52. Higuchi Plot of the Cardboard Release Data.

analysis. This indicates that selenium penetrated the entire sheet in a fairly uniform manner.

Section 4.4.6: Impregnated Toothpicks

Curiously, the selenium content of the impregnated toothpicks was not increased by leaving them in the dimelamine selenite solution for a longer time. The results found for the toothpicks are shown in Table 7. The toothpick with the highest selenium content was the one that had been left in the solution for only 1 min. The toothpick left in for 10 min had the smallest amount of selenium. It was not clear why this was the case, but the samples may have been contaminated at the Nuclear Reactor Lab. The toothpicks did not show enough promise to warrant further consideration anyway, so the matter was not further studied.

The release from the sticks is shown in Fig. 53. It can be seen that the Higuchi analysis again describes the release from the devices quite accurately (see Fig. 54).

Section 4.4.7: Impregnated Popsicle Sticks

Pulling a vacuum on the sticks appears to have increased the available surface area of the wood, thus increasing the Se holding capacity. The selenium content of the sticks are listed in Table 8, and indicate much more consistent behavior than had been observed with the toothpicks.

The release rates observed from these devices are shown in Fig.

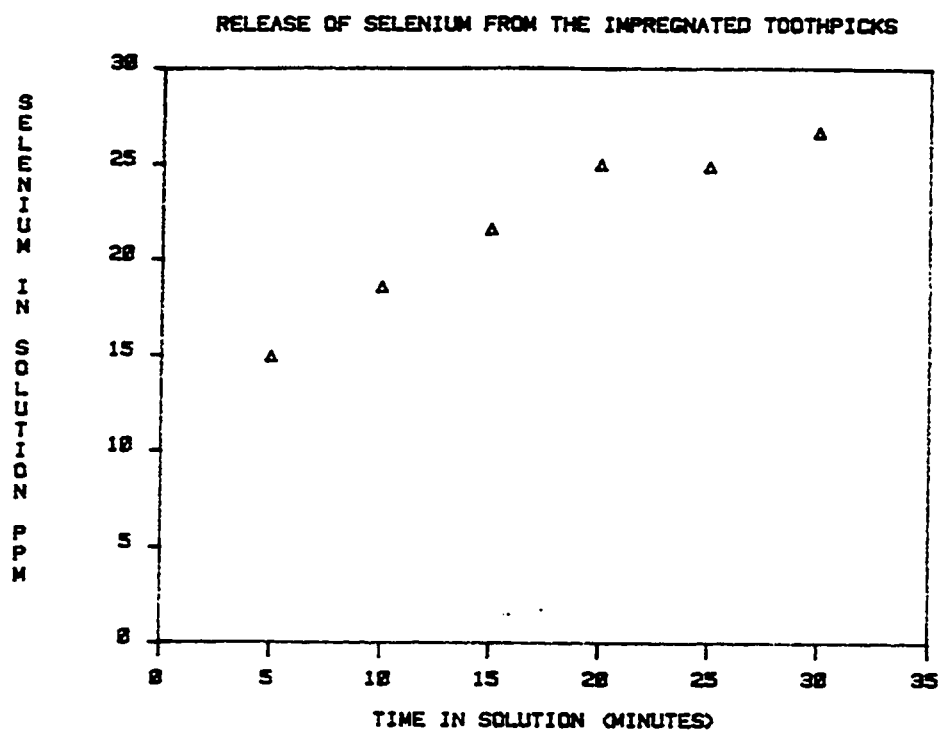


Figure 53. Release Rate from the Impregnated Toothpicks.

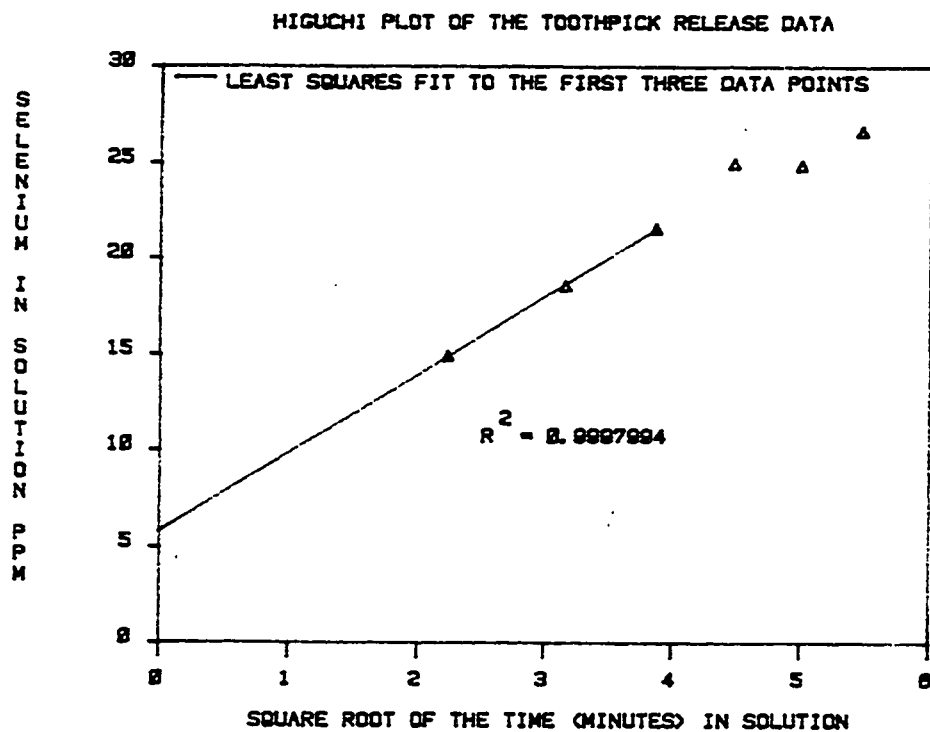


Figure 54. Higuchi Plot of the Toothpick Release Data.

Table 6. Foliar Selenium Content of Douglas-fir Seedlings
Treated with Powdered Potassium Selenate

AMOUNT OF K_2SeO_4 ADDED TO SOIL	SELENIUM CONTENT ppm OF FOLIAGE AFTER (time)
25 mg	16.0 (4 weeks)
	225.6 (8 weeks)
50 mg	31.5 (4 weeks)
	582.0 (8 weeks)
100 mg	30.7 (4 weeks)
	450.0 (8 weeks)
250 mg	33.3 (4 weeks)
	160.0 (8 weeks)

Table 7. Selenium Content of Impregnated Toothpicks

TIME TOOTHPICK LEFT IN SOLUTION	SELENIUM CONTENT (PPM)
0.5 min	16.85
1.0 min	19.28
2.0 min	4.06
5.0 min	13.06
10.0 min	3.86

Table 8. Selenium Content of Impregnated Popsicle Sticks

TIME POPSICLE STICK LEFT IN SOLUTION	SELENIUM CONTENT (PPM)
15 min	2095
30 min	2511
55 min	3285

55. The Higuchi analysis (Fig. 56) once again proved ideal as a description of the release pattern from the device. Selenium became reversibly adsorbed uniformly throughout the matrix.

Section 4.4.8: Summary of the Performance of the Various
Selenium Delivery Systems Synthesized

The relative capabilities of the systems as delivery devices are summarized by the data listed in Table 9, which gives the average flux observed from each over the period of the experiment. It can be seen that both the toothpicks and the cardboard systems gave significantly lower fluxes than either the popsicle sticks or the dimelamine selenite/formaldehyde tablets. The popsicle sticks are thought to have performed better than the toothpicks because of the vacuum impregnation technique used. The tablets certainly had more loading capacity than the popsicle sticks, as they were able to maintain their release for around 100 times as long. For short term applications, however, such as the selenizing of small seedlings in a greenhouse situation, the popsicle sticks might be ideal.

Section 4.4.9: INCO Plastic Delivery Devices

The release characteristics of these devices in aqueous solution were determined by INCO, and the results are shown in Fig. 57. It can be seen that the devices gave sustained, zero-order release for a period of over a month in distilled water. The flux from the device increased proportionately with the surface area of the hole that had

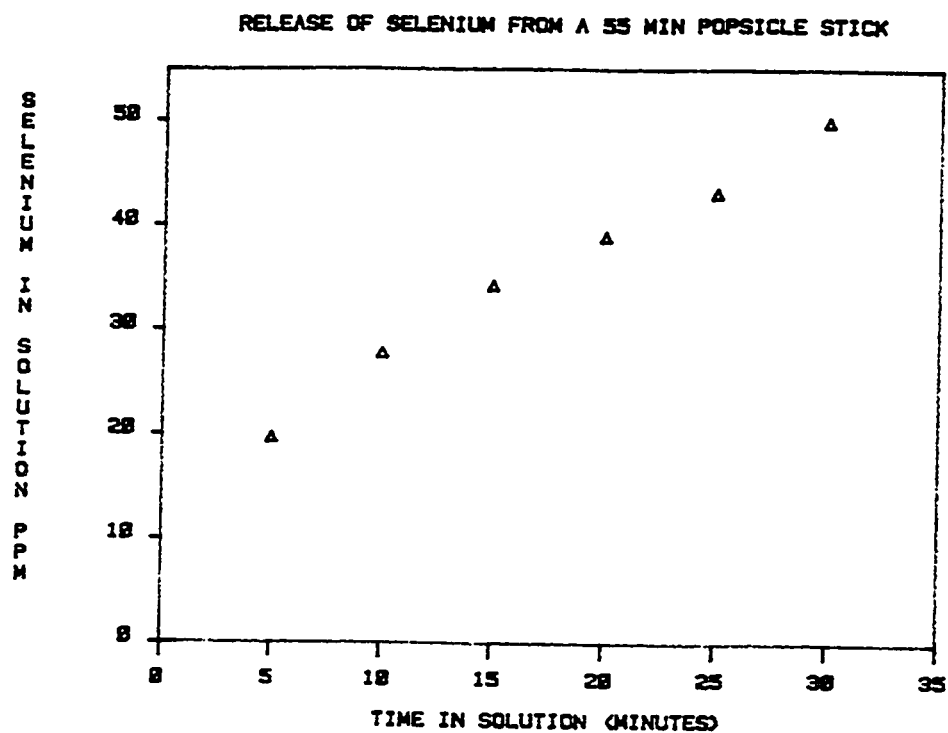


Figure 55. Release Rate from the Impregnated Popsicle Sticks.

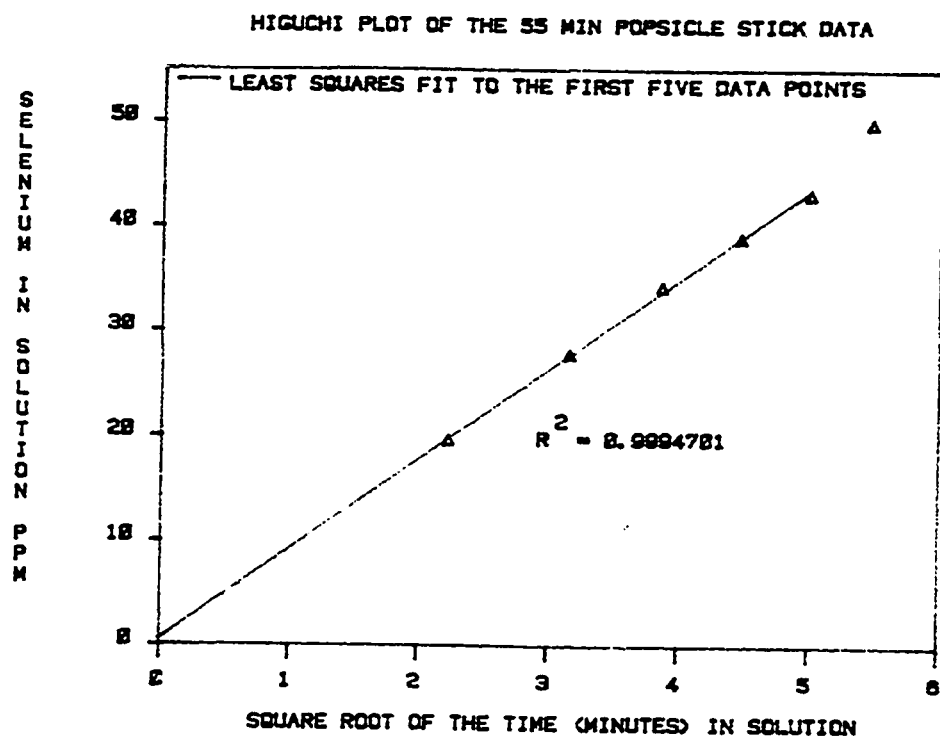


Figure 56. Higuchi Plot of the Popsicle Stick Release Data.

been drilled through the resin, conforming to intuitively held notions about the expected release characteristics.

The performance of these devices in the potted test studies is summarized by the data in Fig. 58. The devices appeared capable of delivering roughly the same amount of selenium as the simple tablets produced at the University of Washington. The relative expense of the devices, coupled with the lack of any striking advantages over the simple tablets eliminated them from further consideration in the study.

Section 4.4.10: MCI Granules

The selenium content of grasses grown in the presence of these granules are listed in Table 10. The release from the Super-60TM type granules appeared to be much slower than that from the resin granules. This seems to confirm the visual observation that the Super-60TM mixture underwent extensive oxidation. The reduced form of selenium left in the granule was apparently not available for absorption, conforming to the generally accepted notions about plant extraction of selenium from soils.⁽⁷⁾

Section 4.5: Field Trial Tests of the Selenium Tablets

Selenium analyses of the foliar samples collected at the sites are summarized in Fig. 59. Results from all areas except for the Mutiny Bay site are quite consistent, demonstrating that the tablets

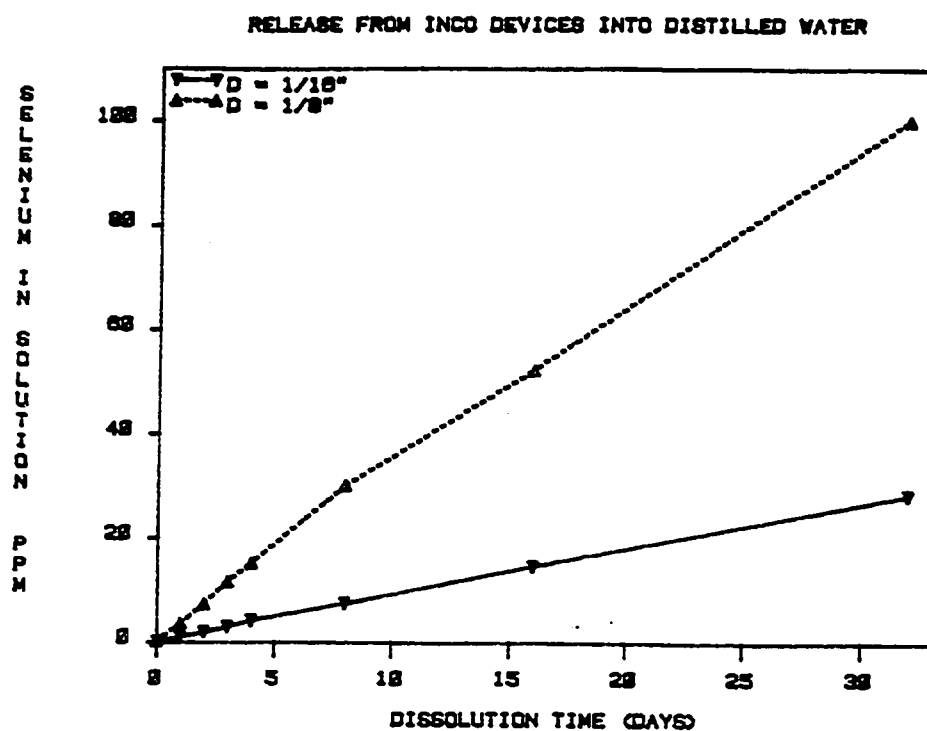


Figure 57. Release of Selenium from INCO Devices Placed in Water.

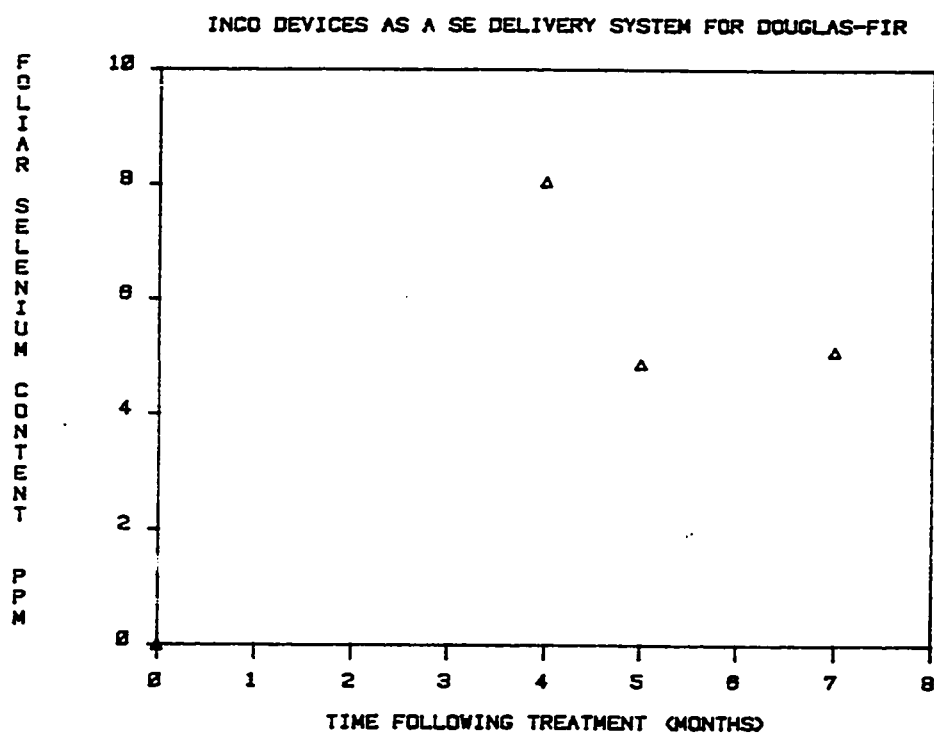


Figure 58. Pickup of Selenium by Douglas-fir from INCO Devices.

Table 9. Average Selenium Flux From Various Delivery Systems

TYPE OF DELIVERY SYSTEM	AVERAGE FLUX (micrograms Se/cm ² s)
Impregnated Cardboard	0.17
Impregnated Toothpicks	0.16
15 minute Popsicle Stick	0.43
30 minute Popsicle Stick	0.46
55 minute Popsicle Stick	0.48
Tablet Number Five	0.40

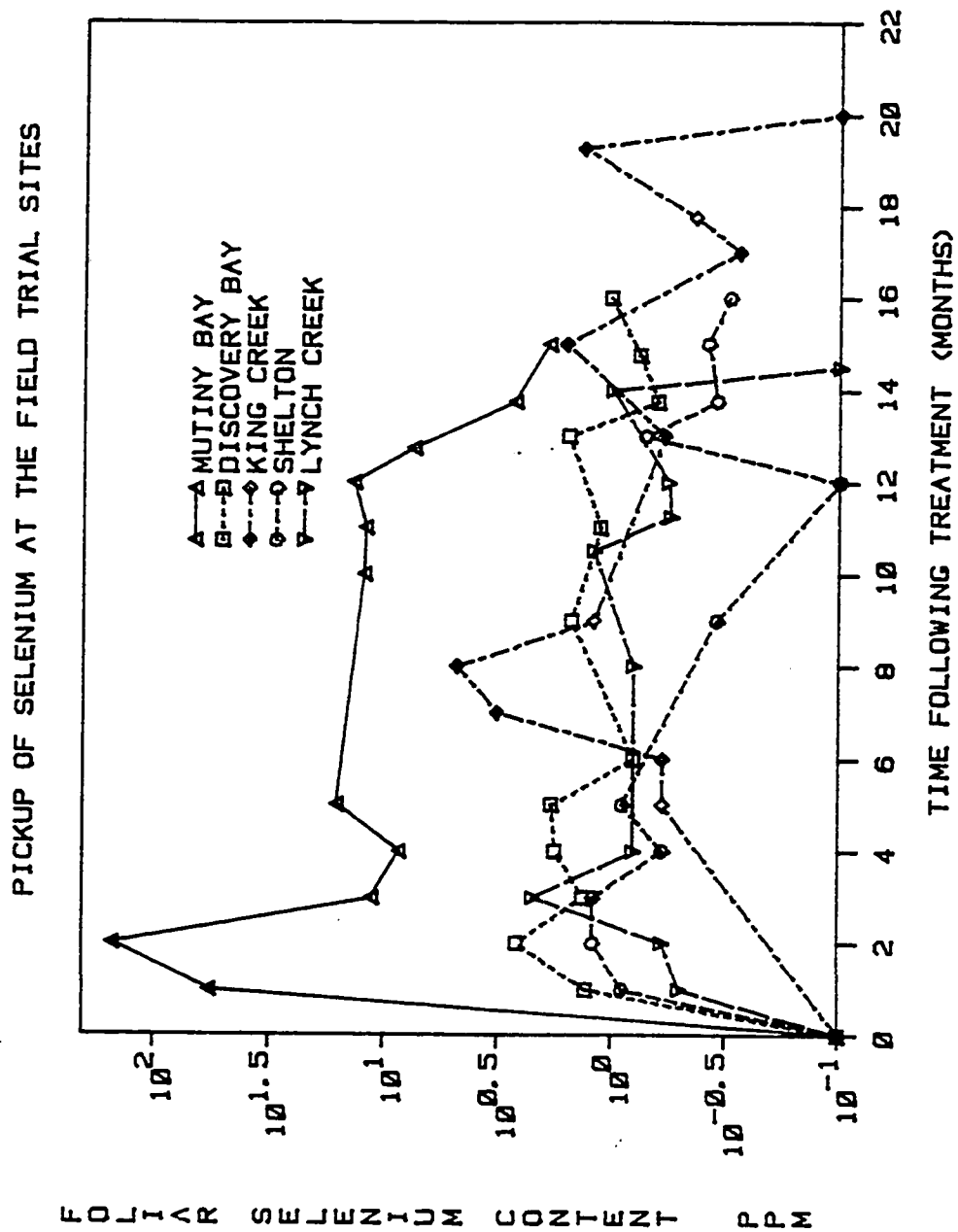
Table 10. Selenium Content of Grasses Treated With Selenized Granules Prepared by MCI

GRANULE TYPE USED	AMOUNT OF GRANULE ADDED (mg)	SELENIUM CONTENT OF GRASS ppm AFTER (time)
Cymel Resin	95	4.96 (12 weeks)
Cymel Resin	146	12.34 (6 weeks)
Cymel Resin	155	29.64 (6 weeks)
Cymel Resin	159	38.23 (6 weeks)
Cymel Resin	217	20.05 (18 weeks)
Cymel Resin	279	25.49 (6 weeks)
Super-60 TM	40	3.69 (12 weeks)
Super-60 TM	41	5.25 (6 weeks)
Super-60 TM	136	8.83 (6 weeks)
Super-60 TM	159	10.43 (6 weeks)
Super-60 TM	213	28.39 (18 weeks)

Table 11. Comparison of the Selenium Content of Old and New Foliage at Mutiny Bay

CODE NUMBER OF TREE	DATE FOLIAGE SAMPLED	SELENIUM CONTENT OF (old foliage) (new foliage)	
3	April 9, 1983	16.31 ppm	3.18 ppm
66	April 9, 1983	17.50 ppm	2.18 ppm
67	April 9, 1983	10.87 ppm	2.60 ppm
81	April 9, 1983	17.53 ppm	5.27 ppm
Average of samples collected on April 9		15.55 ppm	3.31 ppm
1	April 30, 1983	4.36 ppm	1.58 ppm
2	April 30, 1983	5.15 ppm	3.47 ppm
3	April 30, 1983	19.07 ppm	3.46 ppm
81	April 30, 1983	19.52 ppm	2.94 ppm
Average of samples collected on April 30		12.03 ppm	2.86 ppm

Figure 59. Summary of Se Foliar Content at the Field Trials.



planted in holes adjacent to the two-year old seedlings were able to maintain foliar concentrations of selenium at around 1-2 ppm for one and a half years. At the Mutiny Bay site the results were quite different, almost certainly because of the different manner by which the trees were treated with the tablets.

The higher selenium foliar concentrations at Mutiny Bay had a significantly detrimental effect on the seedlings' health. In fact, several of the seedlings appeared to be near death only one month after treatment. After one year many of these seedlings recovered, but some still appeared quite brown and others simply withered away and died (14 out of 150). The data shown in Fig. 60 demonstrate that the seedlings treated with the tablets experienced a severe deceleration of the growth rate. These data are uncorrected for the browse effect. As will be discussed later, the presence of selenium in the foliage apparently reduced the amount of browse damage to the treated seedlings. This benefit, however, was not seen in the overall height gain of the seedlings, with the phytotoxic effect overwhelming the browse reduction effect.

At all of the other sites (see Fig's. 61-64) there was no significant effect of the treatment on the height gain of the seedlings during the first year. This was true even though the treated seedlings were generally browsed somewhat less than the untreated controls. One would not expect any phytotoxic effect due to the levels of selenium found in the trees at these other sites, and there were certainly none of the visible harmful effects that had been

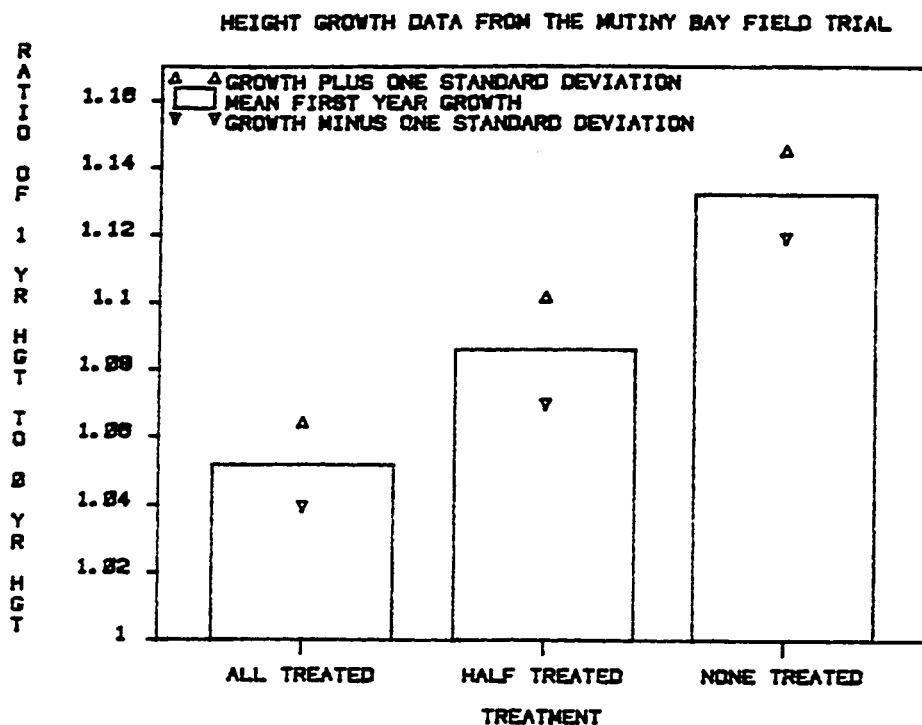


Figure 60. Effect of Tablets on Growth at Mutiny Bay.

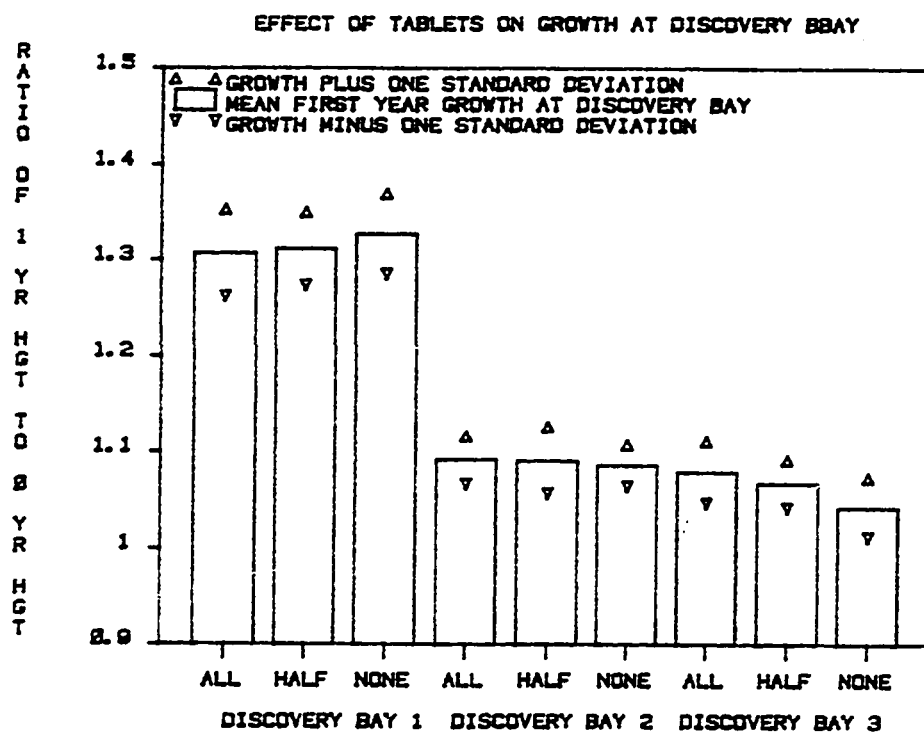


Figure 61. Effect of Tablets on Growth at Discovery Bay.

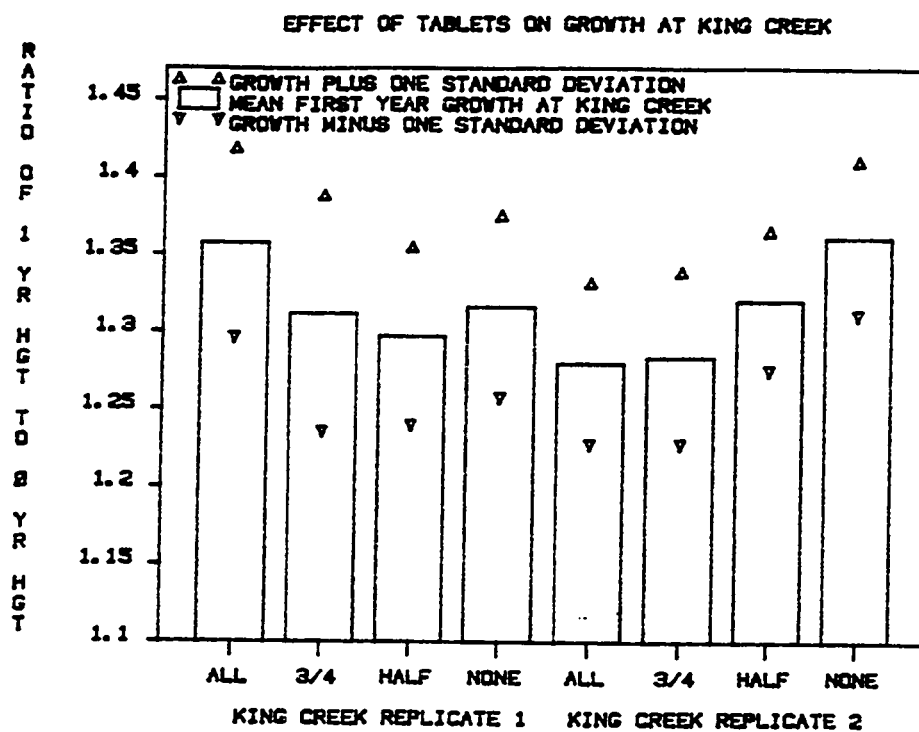


Figure 62. Effect of Tablets on Growth at King Creek.

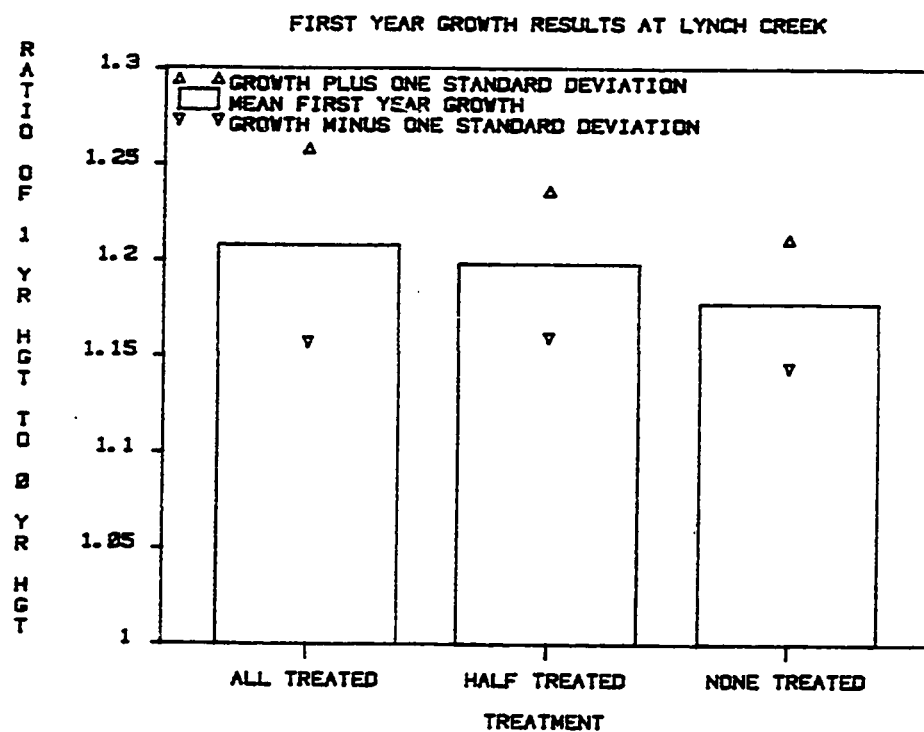


Figure 63. Effect of Tablets on Growth at Lynch Creek.

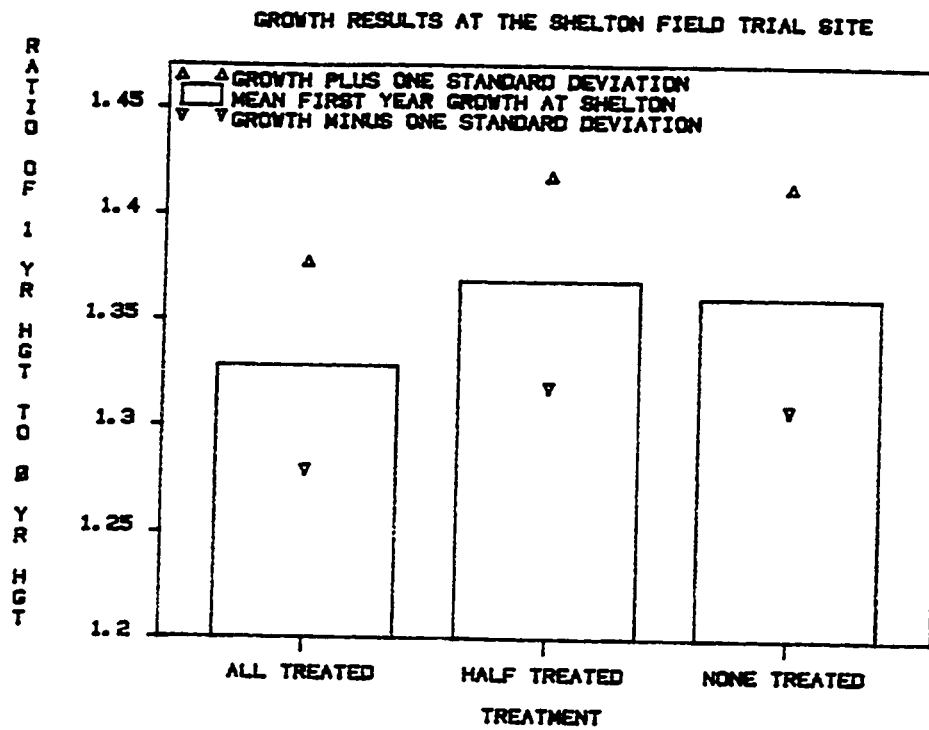


Figure 64. Effect of Tablets on Growth at Shelton.

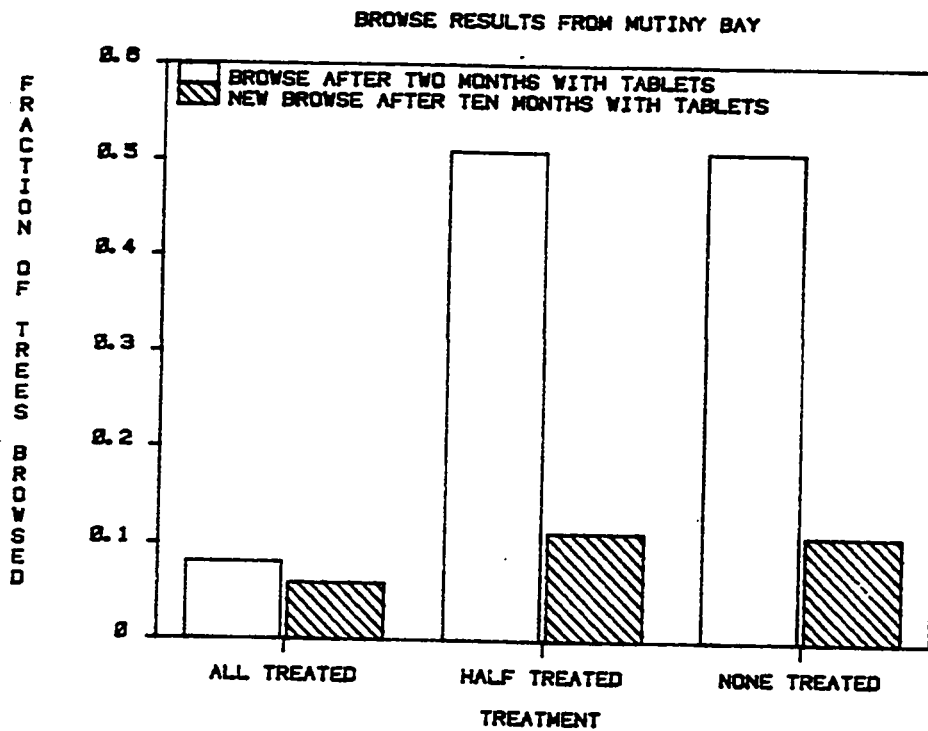


Figure 65. Browse Reduction Results at Mutiny Bay.

observed at Mutiny Bay.

The effect of the treatment on browse frequency at Mutiny Bay was encouraging, as indicated by the data shown in Fig. 65. In the first browse period (two months after treatment) only some 10% of the living treated trees in Group I had been browsed, while well over half of the living trees in both Group II and in Group III had been browsed. Selenium levels in the foliage of treated seedlings at the time of this browse were approximately 100 ppm. In a second attack by the deer (winter browse, ten months after treatment) about half as many trees in Group I were browsed than were browsed in Group II and Group III. The relative ineffectiveness of treating every other seedling (as Group II had been treated) is a result that was repeated at the other field trials. The selenium content of the foliage was only about 10 ppm by the time this second period of browse occurred at Mutiny Bay. This trend of less browse reduction at the lower selenium foliar concentrations is also a pattern which was confirmed by the data collected at the other field trial sites.

An interesting observation at the Mutiny Bay site was the consistent disparity between the selenium levels in new and old foliage during the spring of 1983. These data are listed in Table 11, and indicate that some of the selenium may have been incorporated as protein in the old foliage, as those Se concentrations remained higher than the levels in the presumably more metabolically active new foliage. This again points out the desirability of an increasing delivery rate from the tablet. Both the modeling work and the field

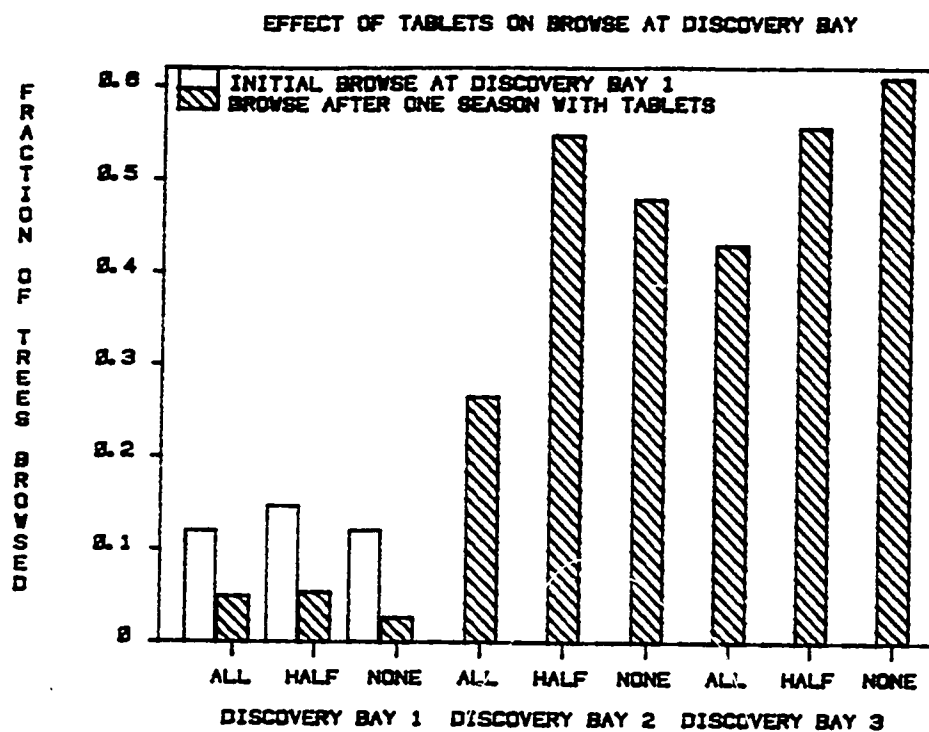


Figure 66. Browse Reduction Results at Discovery Bay.

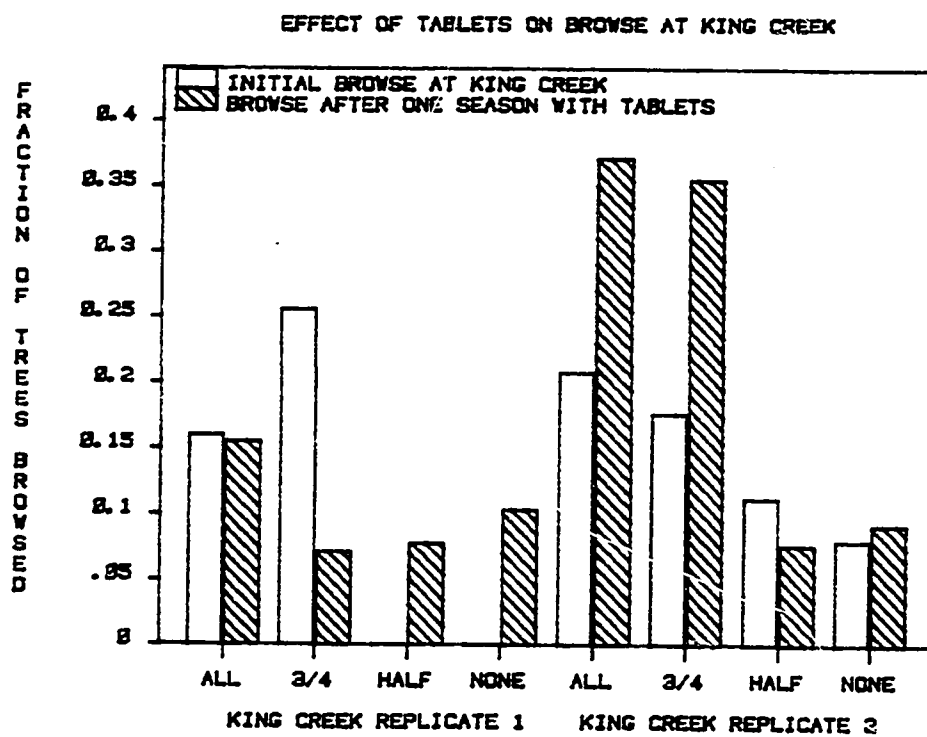


Figure 67. Browse Reduction Results at Lynch Creek.

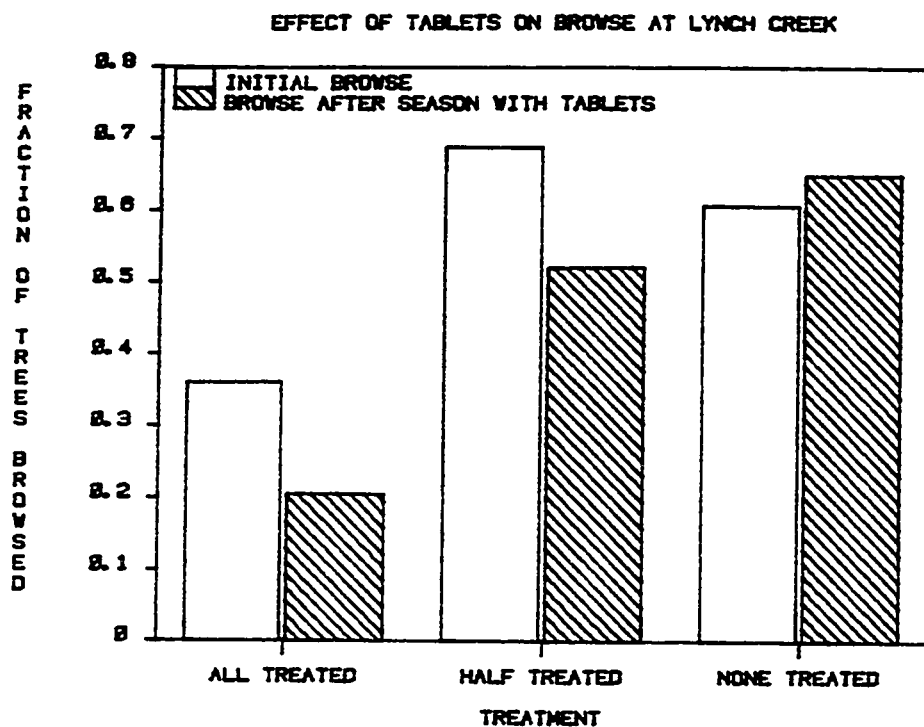


Figure 68. Browse Reduction Results at Lynch Creek.

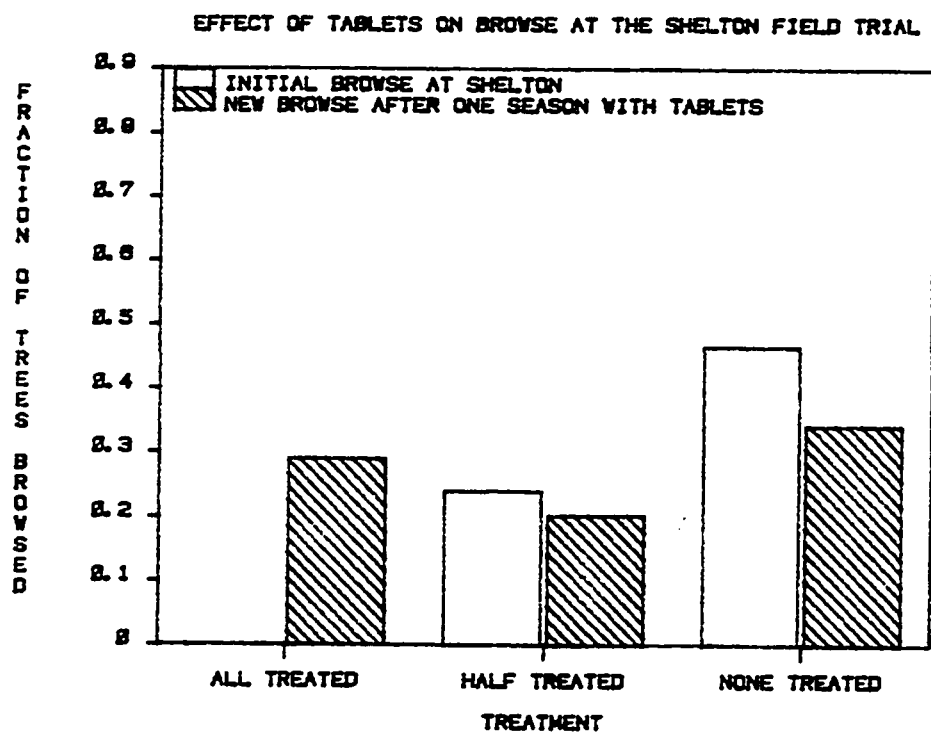


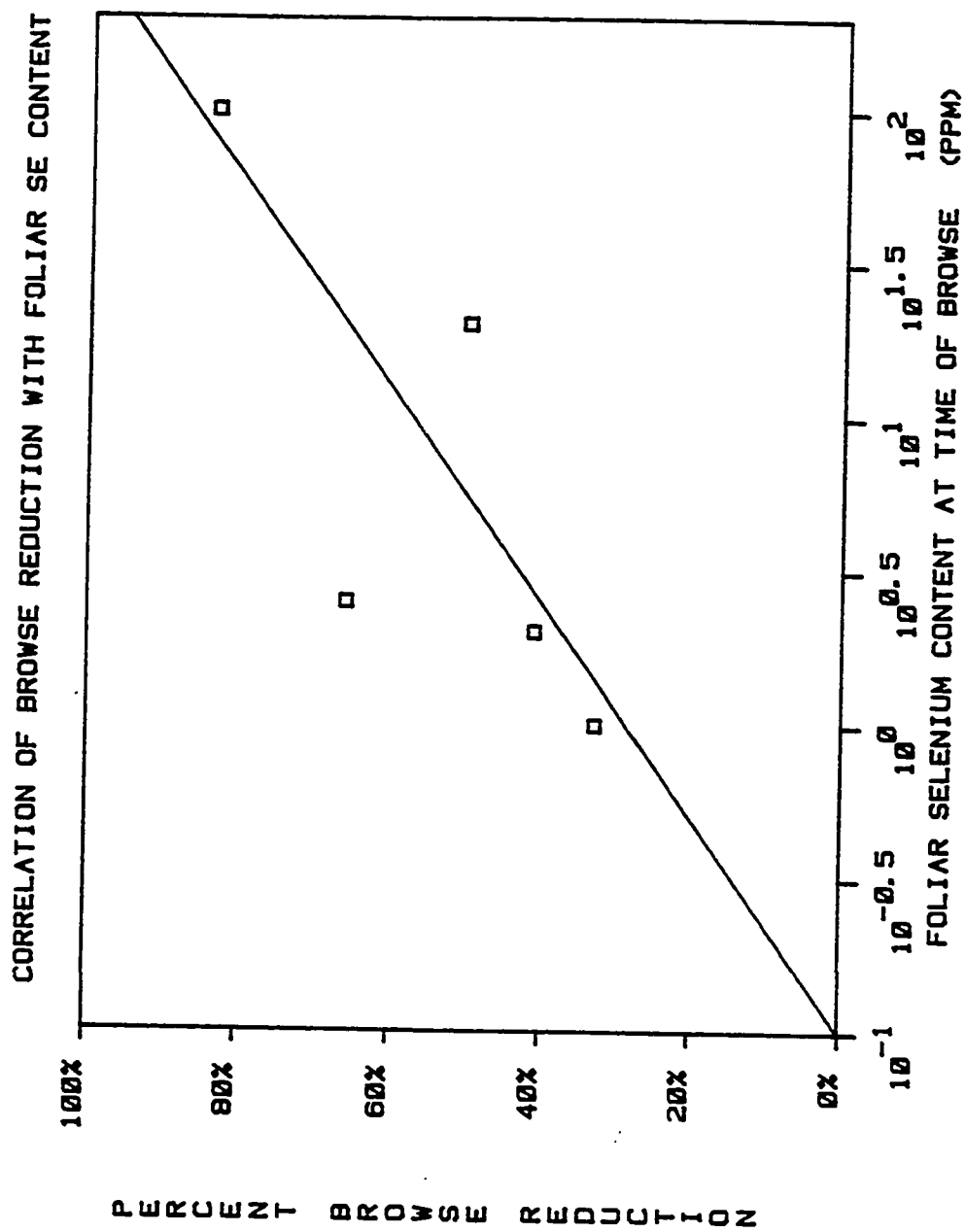
Figure 69. Browse Reduction Results at Shelton.

data indicated that the dimelamine selenite/formaldehyde tablet was not capable of sustaining such as increasing release rate after the initial burst.

The browse reduction results for the other field trials are given in Fig's. 66-69. These field trials were fairly consistent in yielding a browse reduction of about 50% for the trees in Group I relative to the seedlings in Group II and Group III. This trend is best summarized by the plot given in Fig. 70, which shows the amount of browse reduction observed in Group I relative to the controls as a function of the approximate selenium foliar content at the time of browse. Two important facts should be noted. First, 100% browse reduction with the selenium treatment is obviously not attainable, as the 80% reduction achieved at Mutiny Bay was only at the expense of several seedlings' lives. Of course, the foliar levels could be brought up to 200 ppm Se in order to completely eliminate browse activity. Unfortunately, the tree would also be eliminated. Secondly, the amount of browse reduction appears to fall to zero as the selenium returns to its natural level (in the range 0.01 to 0.1 ppm). If the correlation did anything else suspicions would be aroused about the validity of the results, but the increase in browse reduction with levels above the natural concentrations seems to confirm the positive results obtained with the tablets.

This correlation also points out the desirability of being able to predict the response of the trees to treatment with a soil-applied slow release system, as there appears to be an optimal range at which

Figure 70. Correlation of Browse Reduction with Foliar Se Content.



the Se foliar levels ought to be. A priori prediction of the pellet properties which would give concentrations in this range was not possible when the work began, but the model developed in this study should bring the state of the art to that point very soon. A test of the model is discussed later, in section 4.14.

Section 4.6: Determination of the Intrinsic Kinetics

Of Selenite Ion Absorption by Douglas-fir

The selenium concentrations of the root samples are summarized in Table 12. A Michaelis-Menten expression for the rate of selenite ion absorption was hypothesized. The standard method for the verification of such kinetics is to form either a Lineweaver-Burke or an Eadie plot. Such plots involve various combinations of the initial rate of reaction and the initial concentration of substrate. In this case, the reaction rate is the moles of selenium absorbed per gram of root tissue per unit time, and the substrate concentration is the selenium concentration on the solution side of the root/solution interface. The initial substrate concentration is easy to obtain, as this was specified through the experimental method. The initial rate of reaction is a bit more difficult to obtain, but the following procedure gave consistent results.

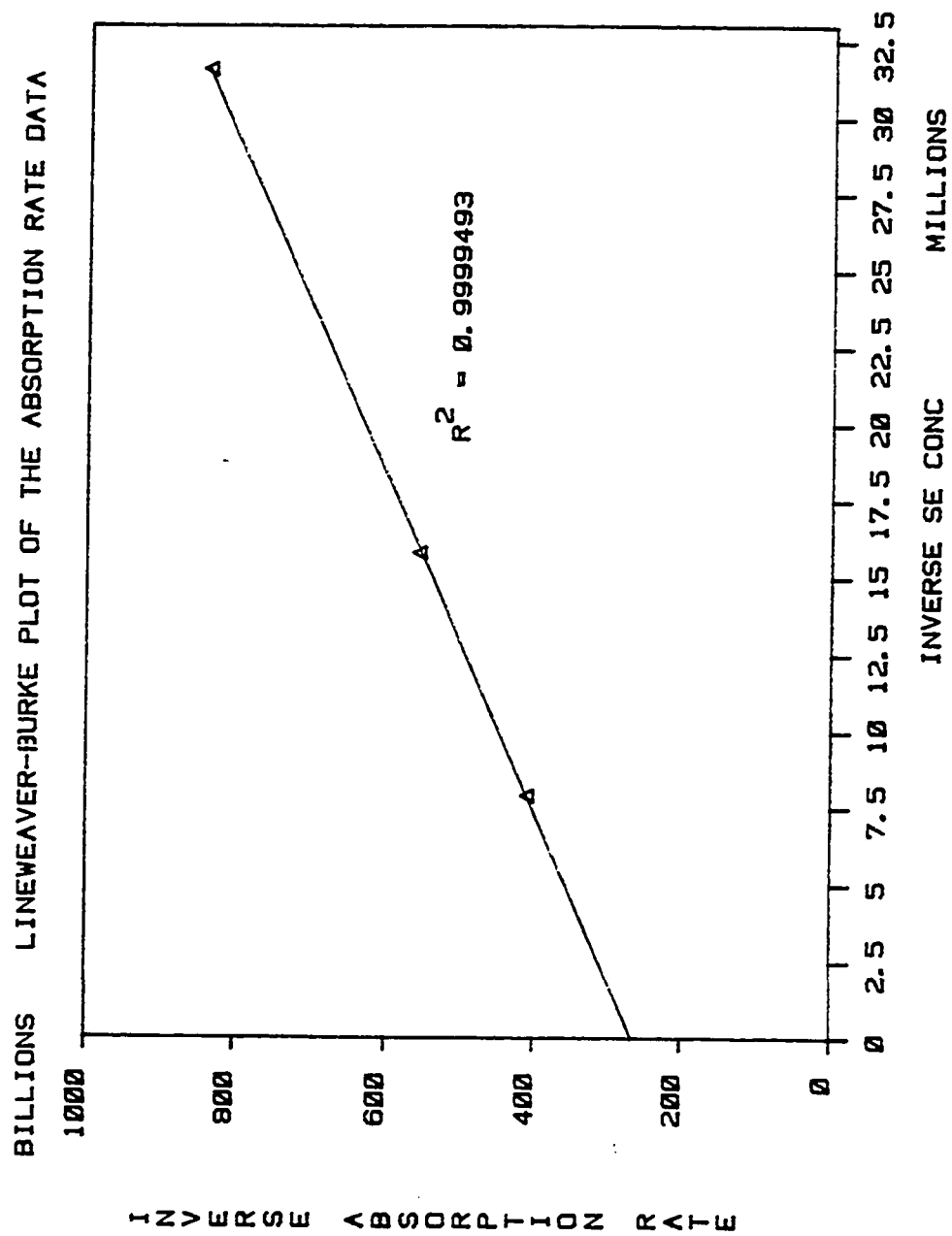
An n th order Taylor's series expression for the selenium concentration in the root tissue about time $t=0$ (actually a MacLaurin series) could be written for each time at which the data were collected:

$$C_r(t) = C_r(0) + tC_r'(0) + \frac{t^2}{2}C_r''(0) + \frac{t^3}{6}C_r'''(0) + \frac{t^4}{24}C_r''''(0) + \dots \quad (4-4)$$

If as many terms are retained in these series as there are equations for C_r , then the entire set may be solved simultaneously for the unknowns, which are simply the first and higher order derivatives of the root concentration of selenium as a function of time. It is only the first derivative which is of interest, however, since this is the initial rate of reaction. Use of this technique gave the data which were then plotted in the forms traditionally used to analyze for Michaelis-Menten kinetics. The inverse of the initial rate is plotted vs. the inverse of the initial substrate concentration in order to generate Fig. 71 (a Lineweaver-Burke plot). The initial reaction rate is plotted vs. the ratio of the initial rate to the initial substrate concentration in order to generate Fig. 72 (an Eadie plot). The ratio of the initial substrate concentration to the initial rate is plotted vs. the initial substrate concentration in order to generate Fig. 73 (a Hanes plot). Each one of these plots is obviously quite linear, and appears to confirm that a Michaelis-Menten expression adequately describes the rate of selenium pickup by Douglas-fir seedling roots.

From the slopes and intercepts of these graphs it is possible to extract values for the maximum rate of absorption and for the Michaelis constant. As each graphical method weights the data slightly differently, each gives different results. The higher concentration results are thought to correspond most closely to the results observed in the field, so it is the Lineweaver-Burke plot

Figure 71. Lineweaver-Burke Plot of the Absorption Rate Data.



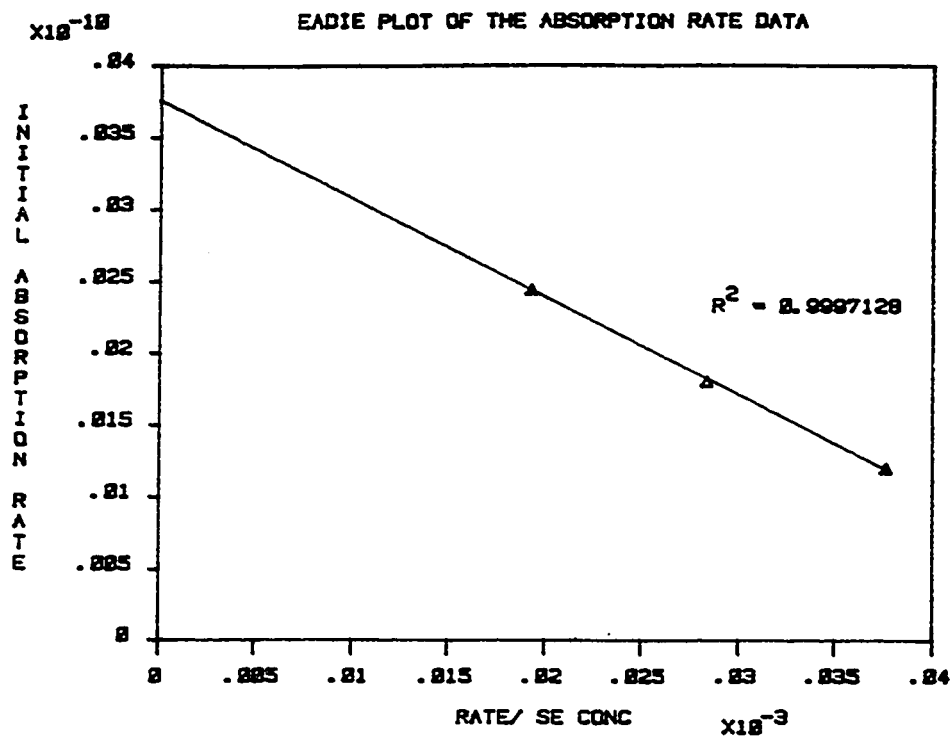


Figure 72. Eadie Plot of the Absorption Rate Data.

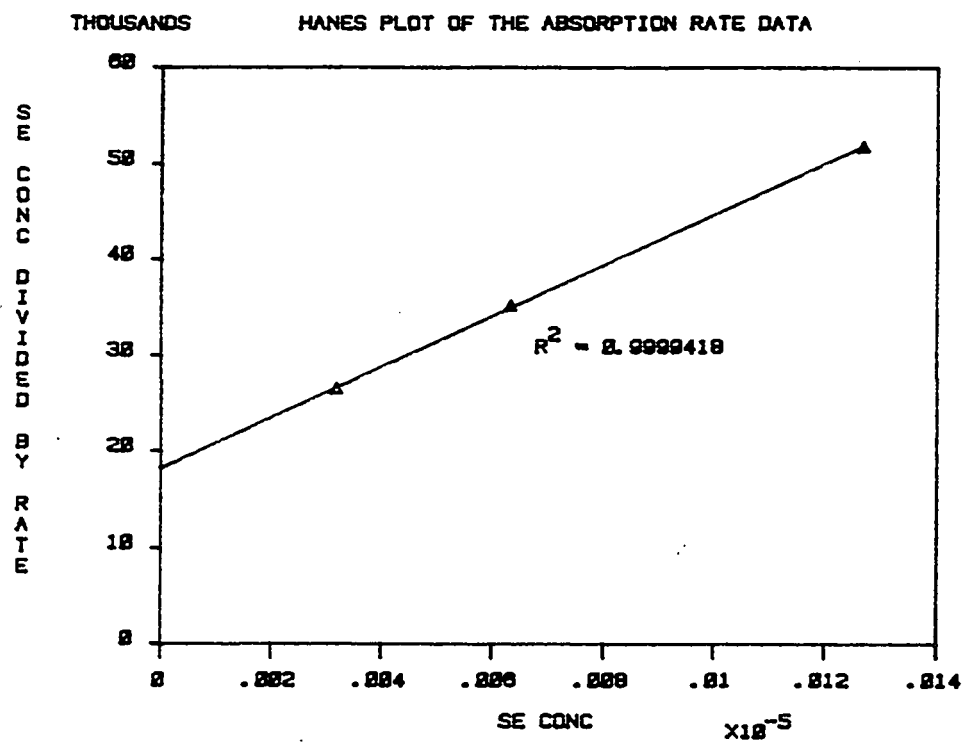


Figure 73. Eadie Plot of the Absorption Rate Data.

results that are used throughout the remainder of the analysis. The values of the parameters suggested by the data in Fig. 71 are:

$$v_{\max}^a = 3.754 \times 10^{-12} \frac{\text{mol Se}}{\text{s g}_{\text{root}}} \quad K_m^a = 6.878 \times 10^{-8} \frac{\text{mol Se}}{\text{cm}^3}$$

Section 4.7: Results of the Rate of Volatilization Studies

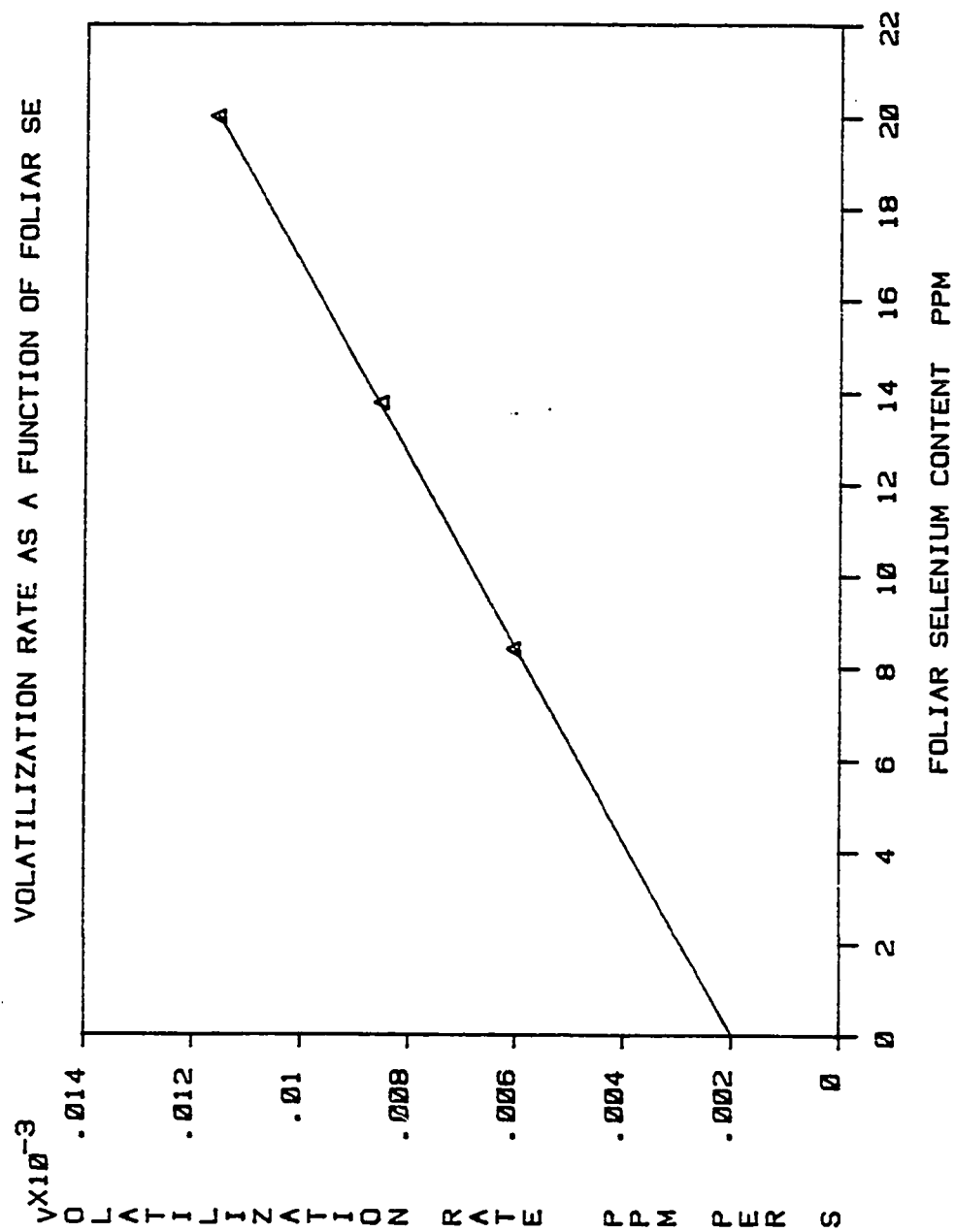
The rate of volatilization of Se from Douglas-fir seedlings is shown as a function of foliar selenium content in Fig. 74. An estimate of total needle mass was made by counting needles and weighing a known number of them. The roughly linear relationship of Fig. 74 suggests that the first order removal assumption is acceptable, and the rate constant suggested by the least squares fit to the data is $6.4 \times 10^{-7} \text{ s}^{-1}$.

Section 4.8: Results of the Soil Adsorption Studies

The adsorption studies with the Mutiny Bay soil revealed that the Michaelis-Menten kinetics quite adequately described the removal of selenium from solution by soil particles. Though not an enzymatic process, the adsorption process would be expected to reach a saturation level at which all of the available surface sites are occupied, and no increase in the rate of deactivation would be observed upon increasing the amount of selenium in solution any further. The Lineweaver-Burke plot of the Mutiny Bay soil adsorption results shown in Fig. 75 demonstrates this graphically. The kinetic parameters suggested by these data are the following:

$$v_{\max}^d = 2.4643 \times 10^{-9} \frac{\text{mol Se}}{\text{s g}_{\text{soil}}} \quad K_m^d = 9.483 \times 10^{-7} \frac{\text{mol Se}}{\text{cm}^3}$$

Figure 74. Volatilization Rate as a Function of Foliar Se Content.



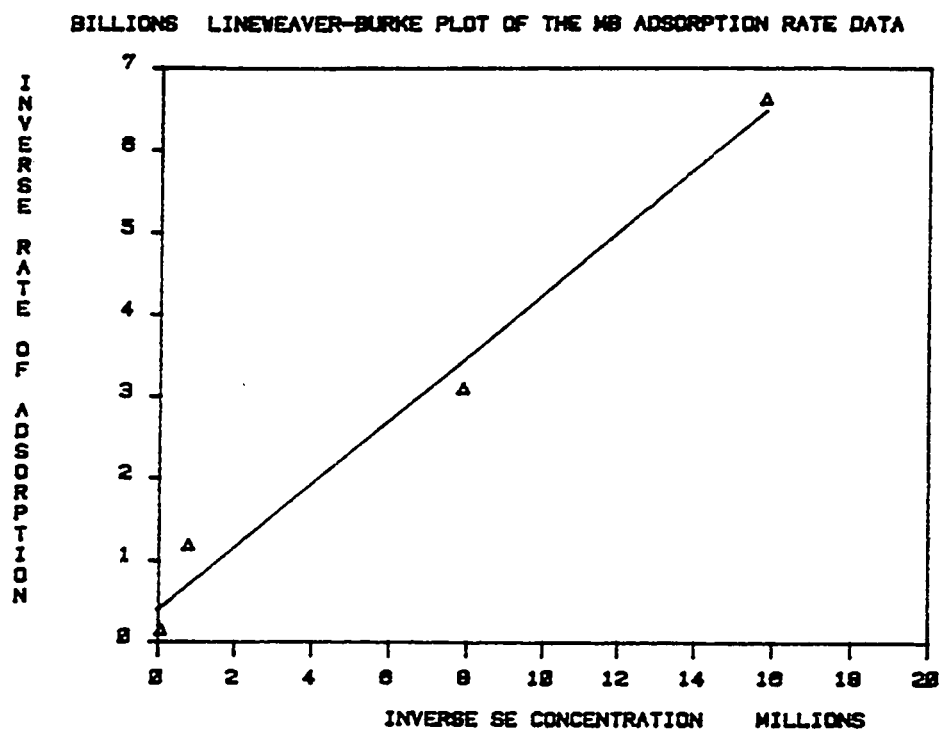


Figure 75. Lineweaver-Burke Plot of the MB Soil Adsorption Data.

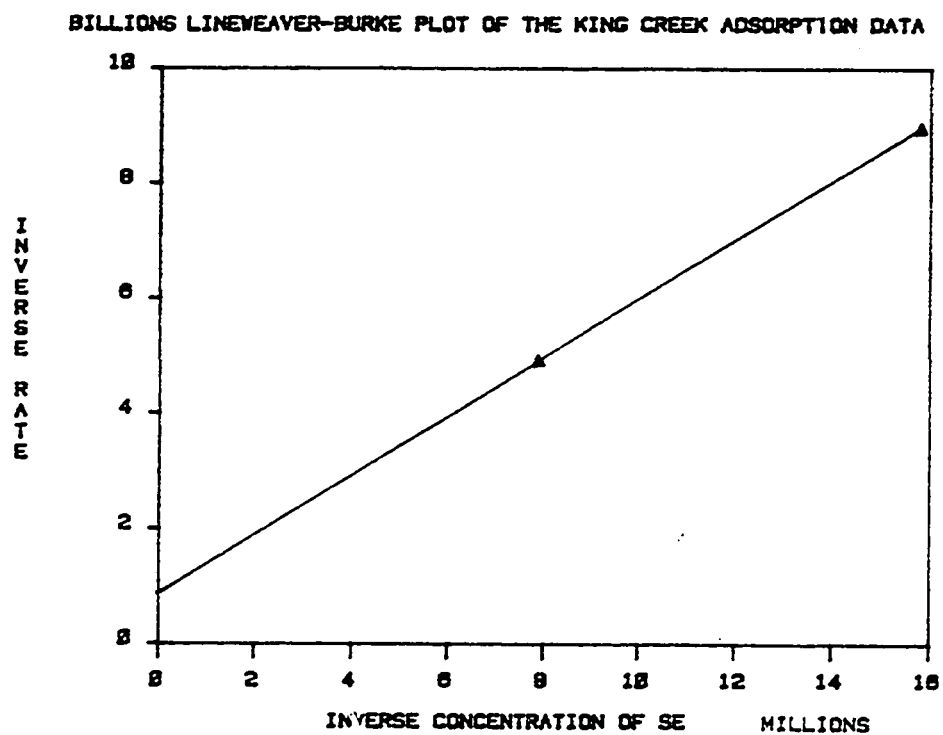


Figure 76. Lineweaver-Burke Plot of the KC Soil Adsorption Data.

The King Creek soil appeared to pickup the selenium a bit more slowly, as shown by the data in Fig. 76. As will be proved later, the King Creek foliar data were not significant statistically, so that no effort was made to model those results. Thus the kinetic parameters found for this soil were not of further use, but the data indicated the following values:

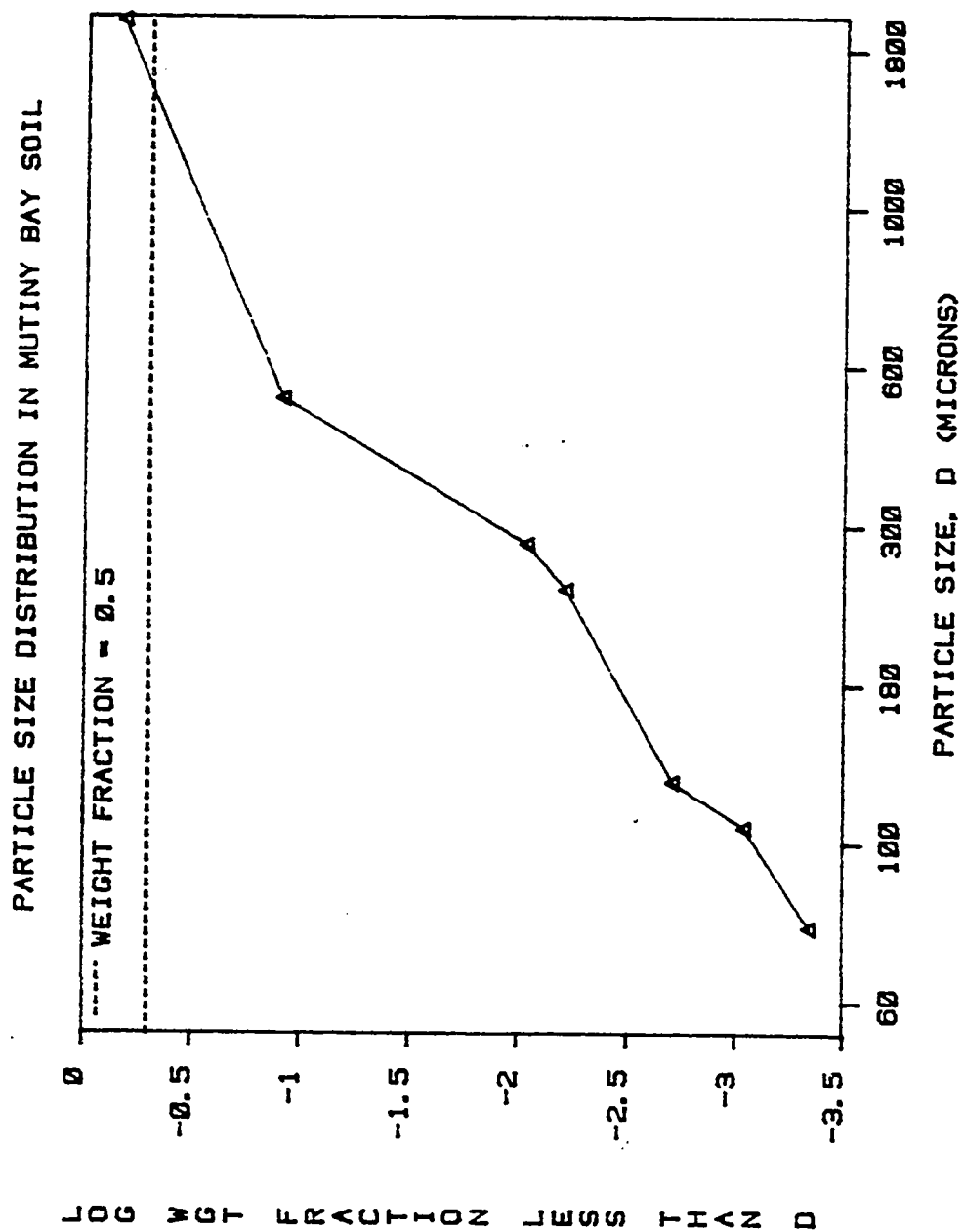
$$v_{\max}^d = 1.1203 \times 10^{-9} \frac{\text{mol Se}}{\text{s g}_{\text{soil}}} \quad K_m^d = 5.738 \times 10^{-7} \frac{\text{mol Se}}{\text{cm}^3}$$

Section 4.9: Results of the Soil Property Determinations

The particle size distribution of the Mutiny Bay soil sample is shown in Fig. 77, and indicates that the mass averaged particle size is approximately 0.15 cm, with 80% of the particles falling within 0.05 cm to 0.2 cm. The bulk density was approximately 1.12 g/cm³. The electrical conductivity measurements failed to yield a measureable amount of ions in solution. One can only conclude from this failure that the resistance of the solution in equilibrium with the soil was >6.94x10³ ohms/cm. Soil pH's fell within a narrow range for the field trial samples, from 5.5 to 6.3.

The tedium and inaccuracies inherent in the partially saturated hydraulic conductivity and water content measurements necessitated some approximation. It was decided to take a small number of measurements and compare them with more complete data reported in the literature. Data were found that gave excellent agreement with the

Figure 77. Particle Size Distribution in the Mutiny Bay Soil.



results obtained in this study, and these more complete data were fit to the empirically derived relationships, eq's. (2-3) and (2-4). The fit was accomplished by first linearizing the equations, which involved taking the logarithm of each side after rearrangement. A least squares fit to the data then gave the following parameter values:

$$\begin{aligned}\lambda &= 1.9583 & B &= 33.1018 \text{ cm} \\ \eta &= 0.7531 & A &= 223.946 \text{ cm} \\ & & L &= 10 \text{ cm}\end{aligned}$$

The hydraulic conductivity data are summarized in Fig. 78, and the saturation data for this same Geary silt loam are shown in Fig. 80. The starred data points in each indicate the data found in this study. Both empirical relationships gave excellent linear fits as indicated by the correlation coefficients and the linear appearance of each of the doubly logarithmic plots (Fig. 79 and 81).

Section 4.10: Results of the Application of Selenium To Plants Other Than Douglas-Fir Trees

These data indicated that Douglas-fir seedlings are among the hardiest plants when it comes to selenium sensitivity. No plant was found in the study that could withstand more selenium than Douglas-fir, and most experienced severe phytotoxicity at foliar concentrations of approximately 10-20 ppm. The actual levels observed in these other species are summarized in Tables 13-15.

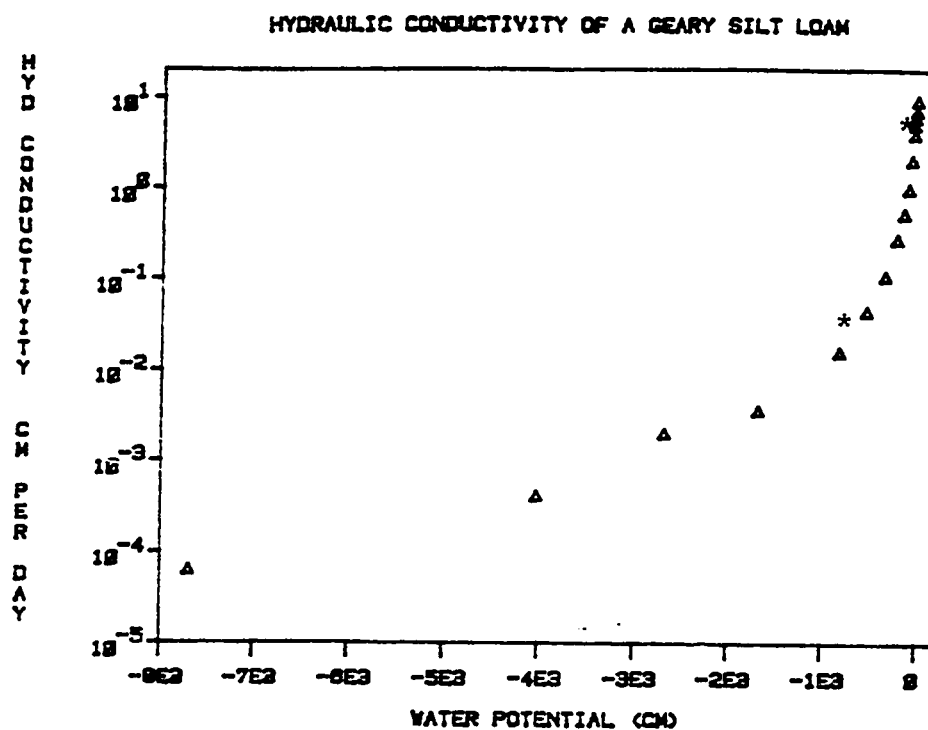


Figure 78. Hydraulic Conductivity of a Geary Silt Loam.

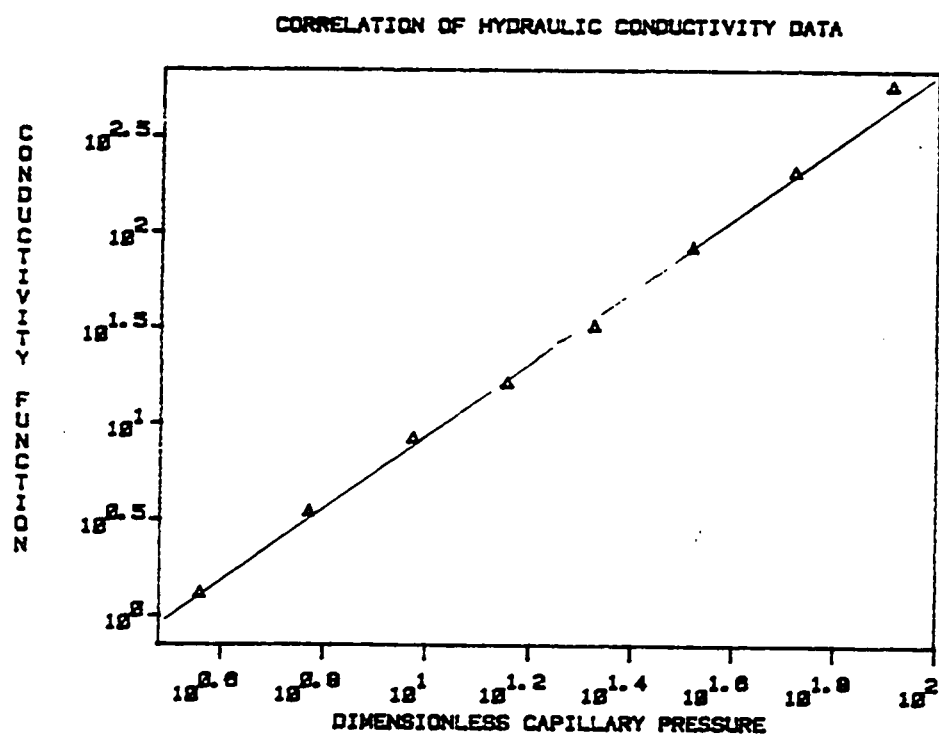


Figure 79. Correlation of Hydraulic Conductivity Data.

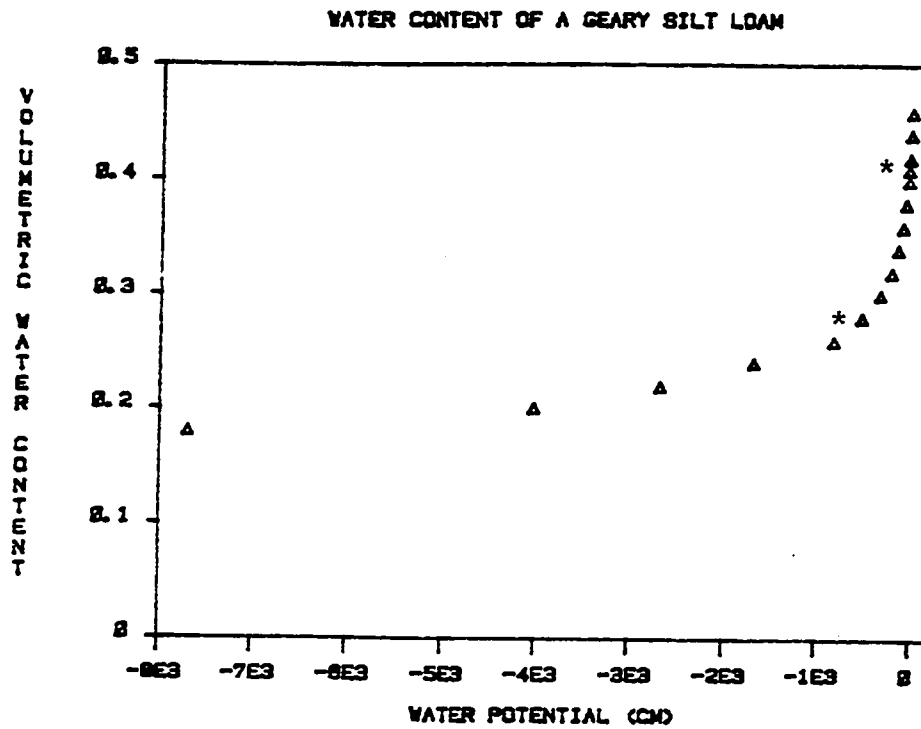


Figure 80. Fractional Saturation of a Geary Silt Loam.

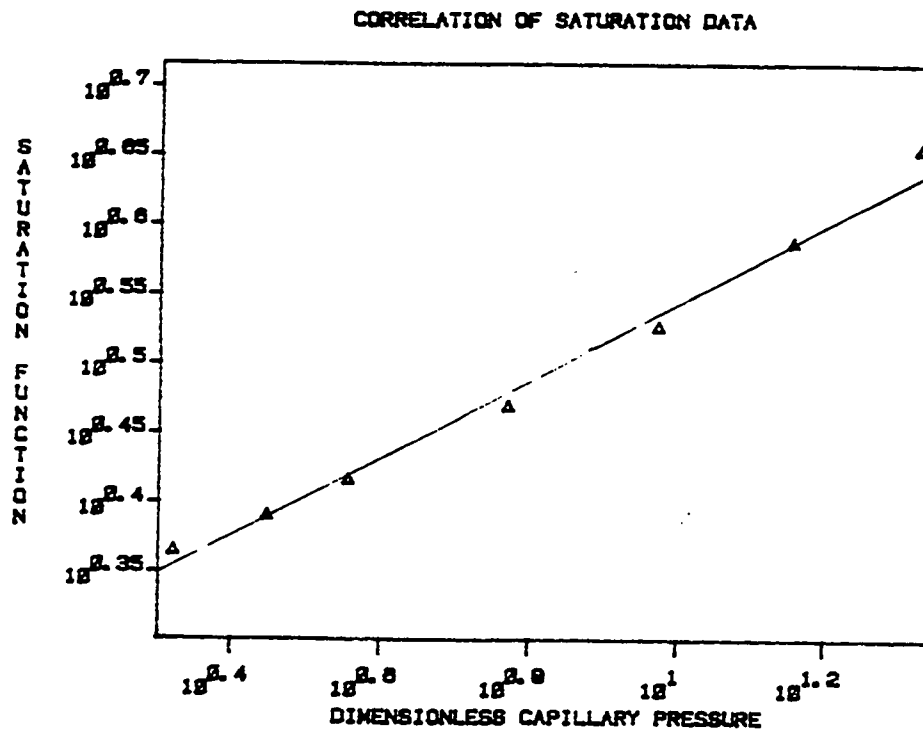


Figure 81. Correlation of the Saturation Data.

Table 12. Results of the Rate of Uptake of Selenium
By Nutrient Grown Douglas-fir Seedlings

CONCENTRATION OF SELENIOUS ACID IN SOL ^a	SELENIUM CONTENT OF THE ROOT TISSUE (PPM) AFTER				
	(22 hr)	(70 hr)	(118 hr)	(240 hr)	(360 hr)
2.5 ppm Se	5.449	10.334	13.955	25.038	26.79
5.0 ppm Se	7.977	15.551	24.086	35.832	51.05
10.0 ppm Se	13.330	33.117	45.621	67.636	117.06

a The 0.5 and 1.0 ppm Se tree samples were contaminated at the Nuclear Reactor Lab, and those data were therefore lost.

Table 13. Results of Foliar Analyses for Trees Other than
Douglas-fir Treated with Dimelamine Selenite Tablets

TREE SPECIES TREATED WITH THE TABLETS (Investigator if not UW)	NUMBER OF TABLETS INCO formulation	SELENIUM CONTENT OF FOLIAGE AFTER		
		(30 days)	(60 days)	(90 days)
Bartlett Pears	3	0.000 ppm	2.045 ppm	
	5	0.000 ppm	0.255 ppm	
Red Delicious Apple	4	0.387 ppm		
	5	1.284 ppm	0.701 ppm	
Golden Delicious Apple	4	1.329 ppm	1.264 ppm	
	5	0.935 ppm	1.224 ppm	
Bing Cherry	4	0.000 ppm	0.152 ppm	
	5	0.953 ppm	0.085 ppm	
Fruit Trees (Donald Merkeley)	1	0.365 ppm		
Lilacs (Devra Daniels)	1	1.960 ppm		
Rhododendron	1 stick		0.390 ppm	
Arailia (Sylvia Tufte)	1	1.234 ppm		
Magnolia (Sylvia Tufte)	1	1.798 ppm		
Davidi Viburnum (Sylvia Tufte)	1	0.000 ppm		
Apple (Sylvia Tufte)	1	0.000 ppm		
Pear (Sylvia Tufte)	1	2.908 ppm		
Fatshedra (Sylvia Tufte)	1	0.000 ppm		
Rose (Sylvia Tufte)	1	0.000 ppm		
China Rose (Sylvia Tufte)	1	0.000 ppm		
Chrysanthemum (Sylvia Tufte)	1	0.000 ppm		
Saxifrage (Sylvia Tufte)	1	7.155 ppm		
Petunia (Sylvia Tufte)	1	1.250 ppm		
Filbert (Sylvia Tufte)	1	5.514 ppm		
Pin Oak (Sylvia Tufte)	1	5.079 ppm		
White Pine (Ontario MNR)	1	1.054 ppm		
White Pine (Ontario MNR)	2	0.545 ppm		
White Pine (Ontario MNR)	3	0.556 ppm		

Black Spruce (Ontario MNR)	1	1.444 ppm	
Black Spruce (Ontario MNR)	2	5.927 ppm	
Black Spruce (Ontario MNR)	3	4.065 ppm	
Red Spruce (Ontario MNR)	1	1.955 ppm	
Red Spruce (Ontario MNR)	2	0.762 ppm	
Red Spruce (Ontario MNR)	3	3.601 ppm	
White Spruce (Ontario MNR)	1	0.168 ppm	
White Spruce (Ontario MNR)	2	0.607 ppm	
White Spruce (Ontario MNR)	3	0.671 ppm	
Jack Pine (Ontario MNR)	1	0.558 ppm	
Jack Pine (Ontario MNR)	2	1.103 ppm	
Jack Pine (Ontario MNR)	3	3.712 ppm	
Scotch Pine (Cady)	1	0.110 ppm	
Noble Fir (Cady)	1	0.000 ppm	
Tropical Cedar	1500 mg powder		29.00 ppm
Tropical Cedar	750 mg powder		67.80 ppm
Tropical Cedar	150 mg powder		16.60 ppm
Grasses (Georgia Pacific)	stick	2.900 ppm	10.60 ppm
Salal (Georgia Pacific)	stick		2.500 ppm
Thistle (Georgia Pacific)	stick		0.000 ppm
Vine Maple (Georgia Pac.)	stick		0.000 ppm
Oregon Grape (Georgia Pac.)	stick		0.000 ppm
Fern (Georgia Pacific)	stick		0.000 ppm
Cottonwood	1 g powder		65.29 ppm
Lemon	stick	20.66 ppm	

Table 14. Black Spruce Uptake Results

TREATMENT TYPE	CODE NUMBER OF TREE	SELENIUM IN CAMBIUM (ppm)	SELENIUM IN FOLIAGE (ppm)	TIME AFTER TREATMENT
Controls	97	0.82	0.10	2 weeks
	105	0.94	1.38	
	111	1.46	0.54	
	120	0.92	1.89	
PVA Tablet	121	68.53	19.89	2 weeks ^a
	144	53.85	18.22	
PEG Tablet	26	2.05	1.46	2 weeks
	32	0.76	1.56	
Dimelamine Selenite (300 mg)	199	121.1	37.71	2 weeks ^a
	209	139.97	80.39	
(100 mg)	52	18.56	10.42	2 weeks
	54	25.36	11.77	
	58	10.71	15.58	
	59	16.85	7.90	
(50 mg)	170	14.52	2.56	2 weeks
	179	22.69	7.57	
	187	19.58	16.40	
	189	9.21	3.62	
Sodium Selenite	1	12.32	2.22	2 weeks
	7	4.49	3.85	
	20	7.47	7.74	
	22	20.60	11.55	
(10 mg)	77	14.13	10.90	2 weeks
	83	22.36	12.39	
	84	7.96	5.05	
	87	6.73	5.09	
	93	13.91	10.71	
(5 mg)	146	1.58	1.52	2 weeks

a Phytotoxicity observed

Table 15. Eastern White Pine Uptake Results

TREATMENT TYPE	CODE NUMBER OF TREE	SELENIUM IN CAMBIUM (ppm)	SELENIUM IN FOLIAGE (ppm)	TIME AFTER TREATMENT
Controls	41	1.10	1.11	2 weeks
	44	1.29	0.99	
PVA Tablet	207	22.27	8.07	2 weeks ^a
	215	88.77	46.68	
PEG Tablet	218	5.06	2.18	2 weeks ^a
	225	3.34	1.81	
	228	0.96	1.08	
	235	1.41	1.06	
Dimelamine	100	316.15	195.33	2 weeks ^a
Selenite	102	320.45	80.99	
(300 mg)	115	245.60	50.95	
(100 mg)	127	19.88	8.68	2 weeks ^a
(50 mg)	52	9.04	3.85	2 weeks
(25 mg)	17	3.31	1.62	2 weeks
Sodium Selenite	148	70.54	33.57	2 weeks ^a
	(20 mg) 152	89.61	35.09	
(10 mg)	77	28.10	8.97	2 weeks ^a
	89	26.03	3.12	
	95	15.55	8.25	
(5 mg)	172	65.10	100.55 ^b	2 weeks ^a
	180	6.63	8.49	
	183	23.07	13.86 ^b	
	191	106.97	19.58 ^b	

a Phytotoxicity observed

b There is some doubt as to the authenticity of these figures.

Table 16. Results of Foliar Analyses of Douglas-Fir Seedlings Treated at the The New Field Trial Test Sites

NAME OF THE INVESTIGATOR	TYPE OF TREATMENT	SELENIUM CONTENT OF FOLIAGE AFTER		
		(30 days)	(60 days)	(90 days)
International Paper	PVA Large	9.728 ppm	3.084 ppm	
International Paper	PEG Large	11.38 ppm	3.756 ppm	
International Paper	PVA Small	5.603 ppm	1.132 ppm	
International Paper	PEG Small	4.575 ppm	1.895 ppm	
Howard Grabhorn	1	3.830 ppm		
Don Cady	1	0.450 ppm		
Don Cady	2	0.260 ppm		
Champion	1	1.021 ppm	1.177 ppm	
Gene Slonicker	1	5.593 ppm		

Section 4.11: Results of Field Trial Studies
Involving the INCO Tablet

The INCO tablet has thus far been quite a bit more stingy about releasing its selenium than the tablet produced here at the University of Washington. The results summarized in Table 16 indicate that the foliar concentrations of the treated seedlings were much lower, even though the tablet was much bigger (100%) than the UW version. This is apparently due to the relatively large amount of binder used during pellet formulation.

Section 4.12: Statistical Analysis of the Browse
Reduction Results Observed in the Field

The effectiveness of the selenium treatment as a browse deterrent must be verified statistically if it is to ever become widely used. The hypothesis to be tested is the following: the treatment of a seedling with a tablet does not reduce the chance that it will be browsed. The well known t statistic is used to analyze the data. The assumption of the random sampling of two populations gives the following relationship governing the difference in their means, $\bar{X}_1$ and $\bar{X}_2$:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s_{1,2} \sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \quad (4-5)$$

N_1 and N_2 are the number of members in the population and $s_{1,2}$ is the geometric mean of the two samples' average deviations. The data summarized in Fig. 82 were generated by counting each site as one member of the population. This meant that N was very small, and the t statistic must then become very large for high confidence. Positive numbers in Fig. 82 indicate browse reduction, and it can be seen that complete treatment of a group of seedlings gave browse reduction (at the 70% confidence interval) at Mutiny Bay, two of the Discovery Bay sites and at Lynch Creek. Most significantly, the total t statistic for all of the field trials confirmed browse reduction with the tablet treatment (the rightmost point in Fig. 82). The treatment of every other tree with a tablet never gave significant browse reduction.

Section 4.13: Statistical Analysis of Foliar
Samples from the Field Trials

The hypothesis to be judged in this section is the following: the selenium foliar concentrations observed in the treated seedlings at each of the field trial sites do not differ from those of the untreated seedlings. Application of the same technique used in the previous section yields the results given in Fig. 83. It can be seen that only at the Mutiny Bay field trial were the foliar concentrations consistently significantly different from the controls. The confidence criterion is slightly less for the Mutiny Bay site because twice as many samples were analyzed per visit.

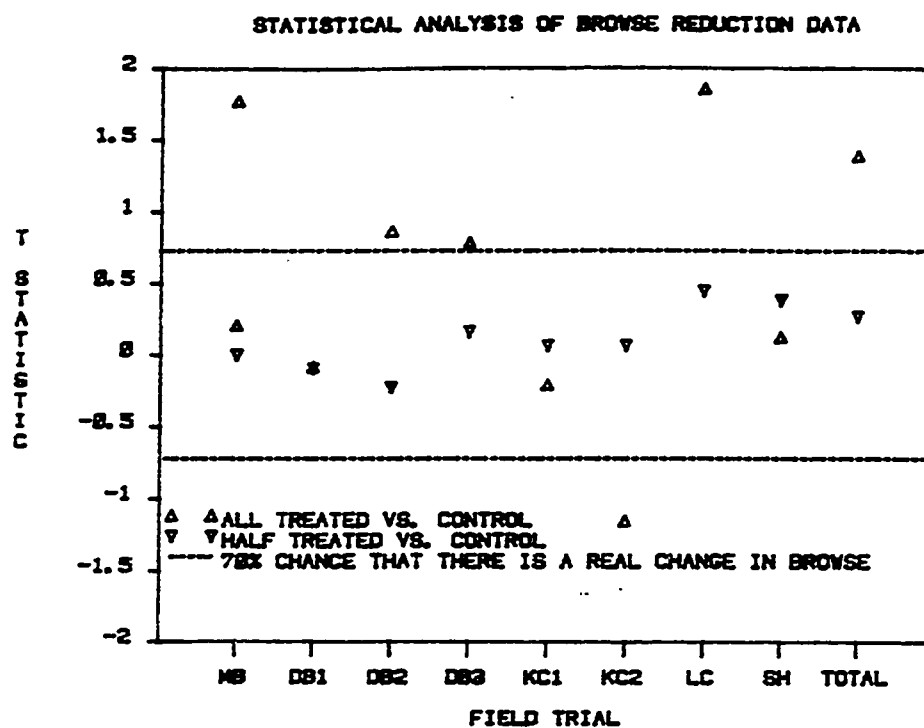


Figure 82. Statistical Analysis of Browse Reduction Results.

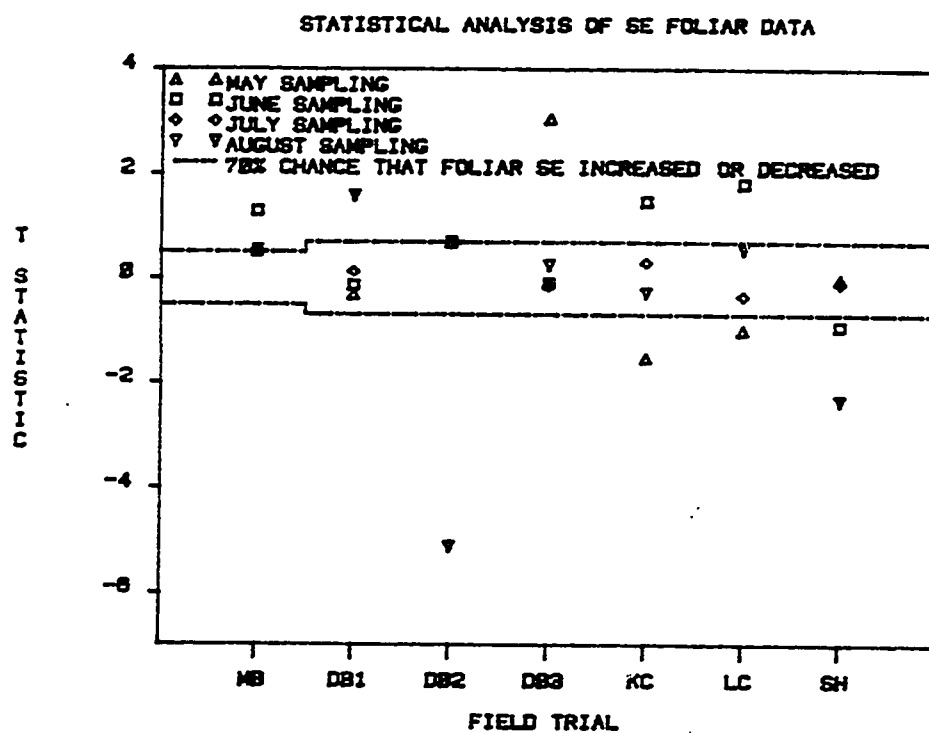


Figure 83. Statistical Analysis of Foliar Selenium Content Data.

Section 4.14: Comparison of Model Predictions

With Foliar Levels at Mutiny Bay

As shown by the previous statistical analysis, the only field results which were significant were those obtained at the Mutiny Bay site. The foliar levels observed at this site thus provided the only real test of the model's predictive capabilities. The results of such a test are reported in this section, and it is demonstrated that chemical engineering principles may be successfully applied to this complex system.

Precipitation and temperature data were collected from the NOAA reports for the three full recording stations nearest to the Mutiny Bay site. The locations of these weather stations relative to the field trial site are portrayed in Fig. 84. The climactic data for the Mutiny Bay site itself were taken to be the weighted average of the three stations' data. The weighting function was determined by the following expression:

$$W_i = 0.5 \left(1 - \frac{L_i}{L_{\text{total}}} \right) \quad (4-6)$$

The distances between the site and each of the stations (L_i) were summed to give L_{tot} . Thus this weighting function merely implied that the proximity of the station to the site was directly related to the similarity in their local climates. The precipitation data given by this weighting function for the Mutiny Bay site are summarized by the

Figure 84. Proximity of Weather Stations to Mutiny Bay.

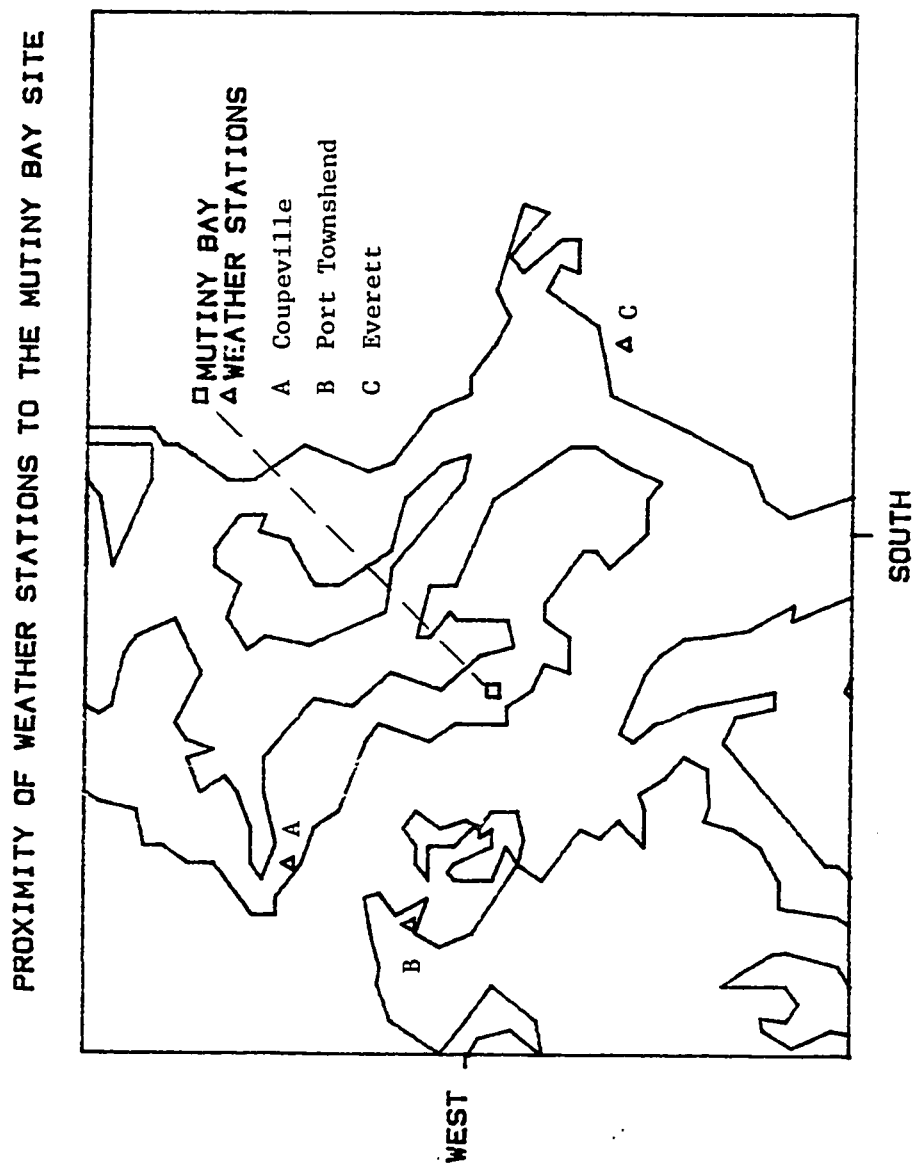
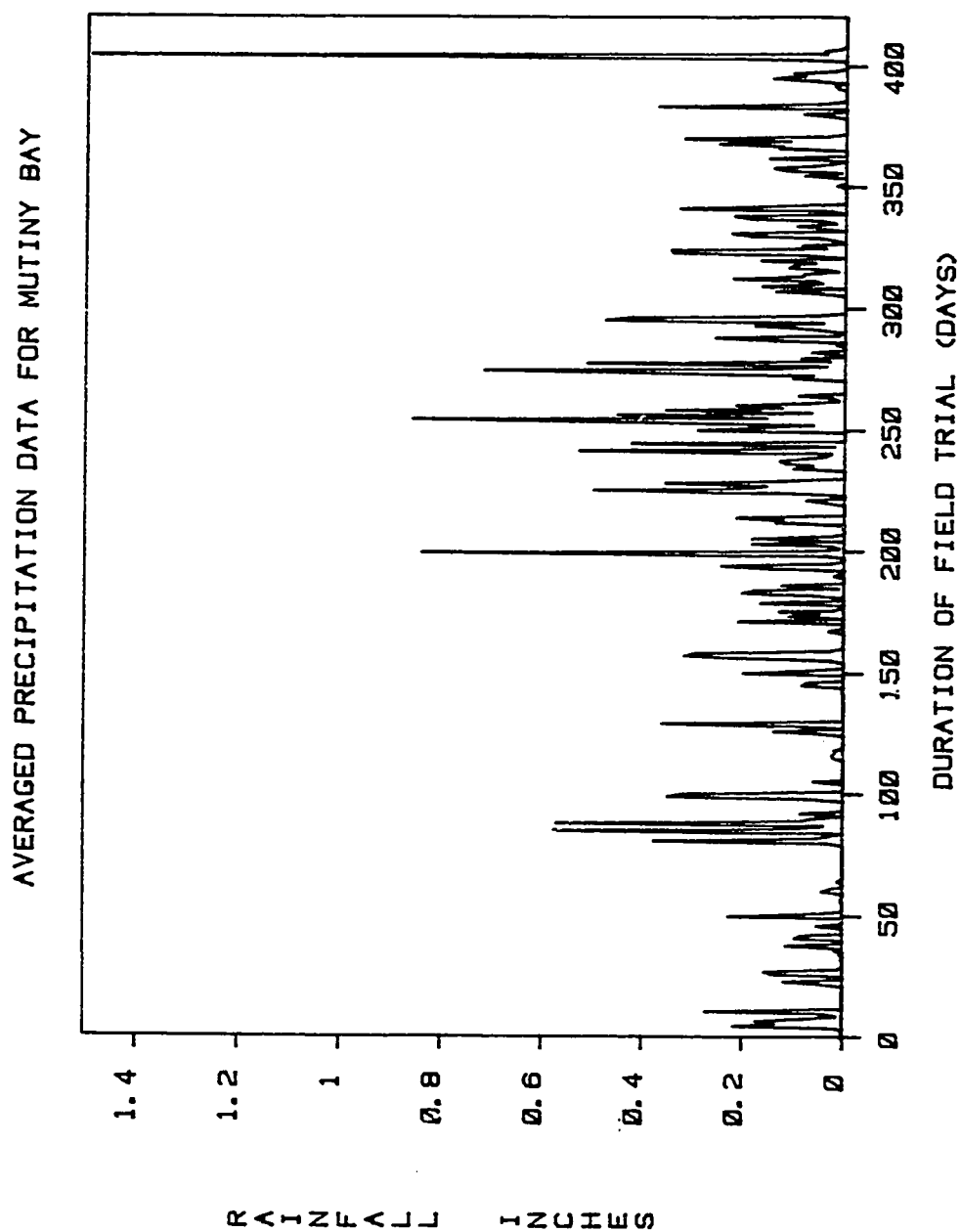


Figure 85. Weighted Precipitation Data for Mutiny Bay During The First 420 Days of the Field Trial.



data given in Fig. 85.

These climactic data were then used to provide the boundary conditions for the solution of the soil-water equation for each day of the model test. It is not immediately apparent how this should best be done. The following method was used after some trial and error work with other possibilities. If the precipitation for a given day had some non-zero value, R_i , then the boundary condition was chosen such that the total flux of water down through the soil for the day, as given by Darcy's law, was equal to R_i . For any given pair of boundary conditions to the soil-water equation, the flux can be simply calculated through the following equation:

$$E_{\text{rain}} = \int_0^{t_{\text{day}}} \frac{k}{\mu} \frac{\partial P}{\partial z}(z=0) dt = \frac{2k}{\mu} \frac{\partial P}{\partial \xi}(\xi=0) \sqrt{t_{\text{day}}} \quad (4-7)$$

This simple result is an artifact of the similarity transformation that was used as an approximate solution to the soil-water equations. The model matched the predicted flux to the day's precipitation through a simple iterative technique. An initial guess to BP1 was made which was known to be too large in absolute value. The program then solved the equation repeatedly, changing BP1 in the correct direction until the calculated flux matched the day's precipitation or until it had tried 20 new BP1's. The full 20 iterations were rarely required to obtain convergence. At the end of this process BP1 became BP0 for the next day, and the value of the saturation which corresponded to this BP1 was stored. This value of

the soil saturation then implied a particular value for the effective diffusivity of the selenite ion as outlined below.

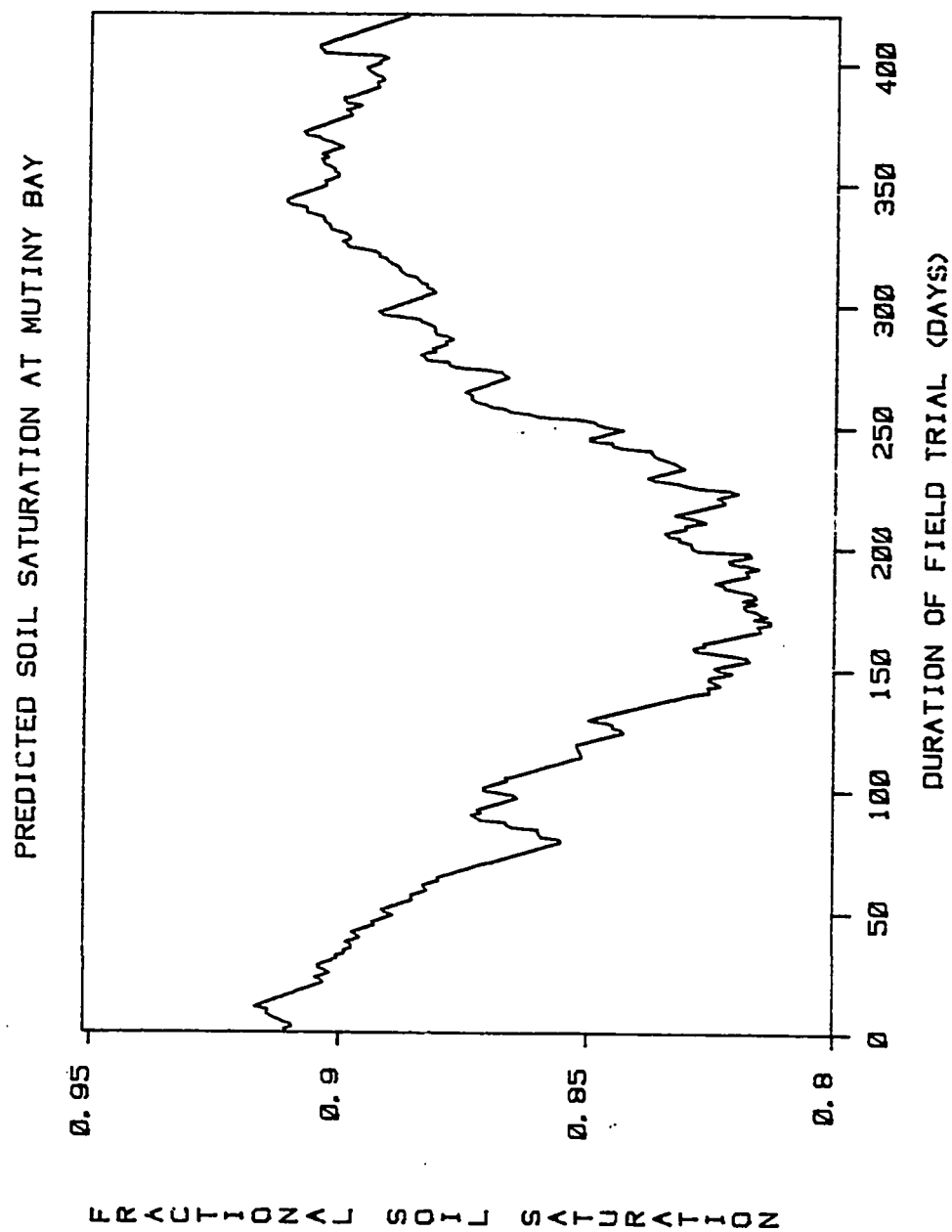
If there was no precipitation for a given day, then it was assumed that the soil dried. Evaporation rate data are rarely available, so it was decided to use the air temperature and current saturation alone in order to set a target value for the flux. In reality, the drying of soils is a highly complex phenomenon, showing no less than three distinct phases (cf. Section 2.2.1). No attempt was made to retain such rigor in this part of the analysis, however, and the following simple expression was used to approximate the day's total evaporation:

$$E_{\text{evap}} = -k_{\text{vap}} D_{\text{vap}} S \quad (4-8)$$

The mass transfer coefficient, k_{vap} , in this equation was chosen by forcing the saturation profile to cycle annually through roughly the same values (see Fig. 86). The program then solved the soil-water equation iteratively as before, changing the boundary condition at the surface, BP1, until the calculated flux matched this target value. Note that for drying the absolute value of BP1 is greater than that of BP0, unlike the wetting case.

For both the wetting and the drying cases, the final value of BP1 chosen was then used to calculate the fractional saturation and hence the effective diffusivity of the selenite ion for that day. Eq. (2-11) was used to calculate this diffusivity.

Figure 86. Saturation at the Soil Surface During the First 420 Days of the Mutiny Bay Field Trial ($k_{\text{vap}} = 2.11 \text{ cm/s}$).



This gave an effective mobility for the selenite ion based on the soil moisture content and temperature alone. The effect of vertical water movement was then accounted for in the following manner. As noted earlier, a tested correlation of effective diffusivity as a function of Peclet number is available. The parameters required to define a Peclet number for this system include a velocity, a characteristic length, and the inherent molecular diffusivity.

The correlation specifically requires an interstitial velocity. The soil-water model used in this study incorporated a similarity transformation in which the interstitial velocity is a function of both time and position. This complication was obviated through a rather gross approximation, in which the vertical velocity for the day was simply set to be the absolute value of the total precipitation (or evaporation as calculated above) divided by the length of the day and the product of the porosity and the saturation (to convert to an interstitial velocity):

$$v_z = \frac{|E_{\text{evap or rain}}|}{S_{\text{po}} t_{\text{day}}} \quad (4-9)$$

The characteristic length required is the mean particle diameter. As discussed earlier, the mean particle size found for this Mutiny Bay soil was 0.15 cm. Since the soil is a polydisperse medium, a correlation based on monodisperse packed beds will not be strictly valid. In addition, this correlation was developed for saturated systems. Unfortunately, no such correlations have been developed for

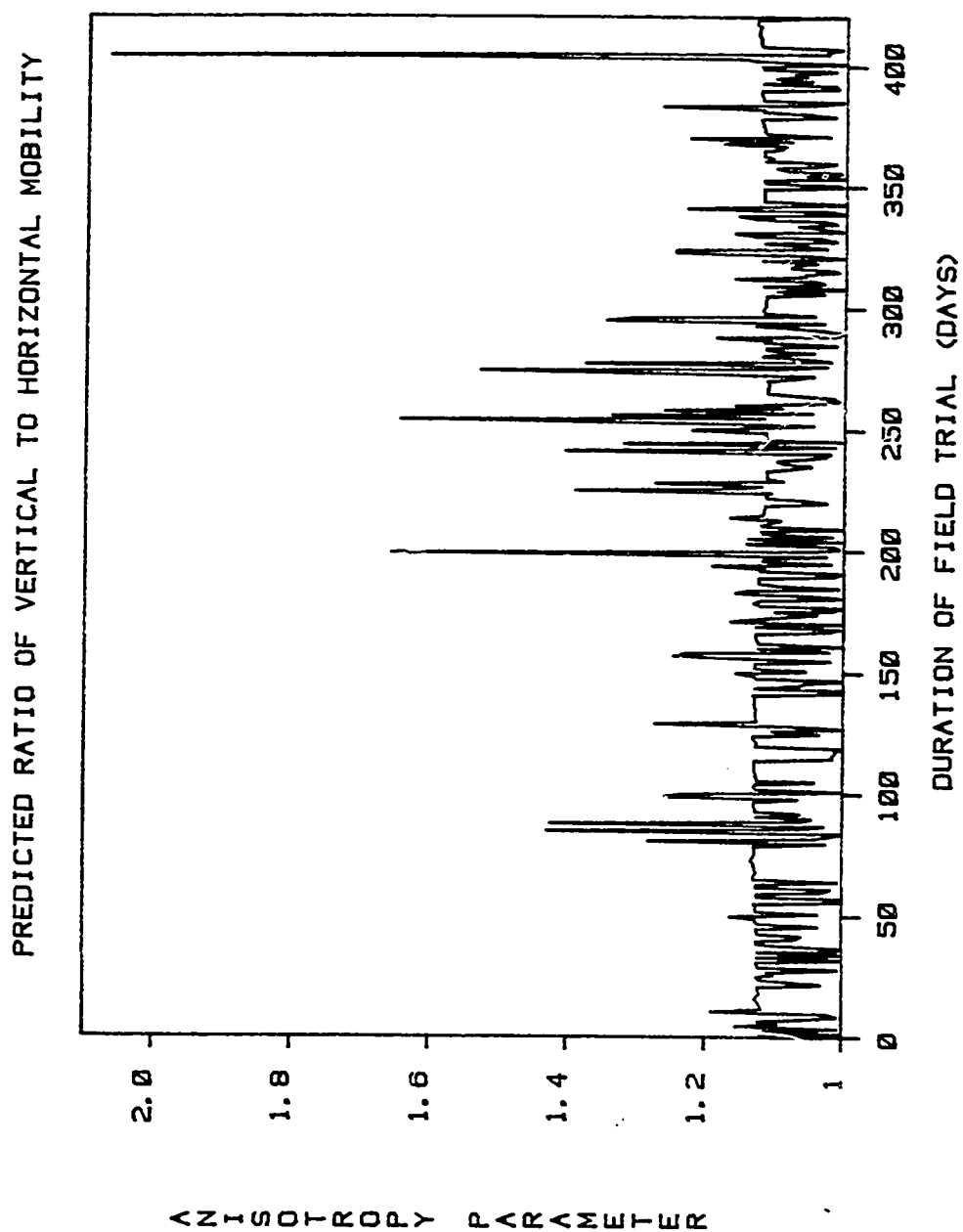
either unsaturated or polydisperse systems, thus this is best relationship available. Since the velocities involved in the soil-water model are so low, the effect on the diffusivity is rather small, and significant differences with more precise correlations would not be expected.

Use of this correlation yields an anisotropy factor, defined as D_{ez}/D_{er} , greater than one for each of the days of the study. The actual values found for the first 420 days of the Mutiny Bay field test study are summarized in Fig. 87. It should be noted that the range of values predicted is not very large, and the amount of vertical "stretching" of the diffusion profiles is therefore not very great.

Another term required in order to test the model was the effective root density in the vicinity of the pellet. The seedlings planted in this particular study were Styro-8's, in which the root ball is a packed cylinder of material. The tablets were placed immediately adjacent to the roots with the axial faces oriented parallel to the ground. Farnum's results indicated that the roots from such seedlings penetrate quickly into the surrounding medium,⁽⁵⁰⁾ with an effective root density of about 0.27 g/cm^3 near the root axis. This was the value used to convert the intrinsic maximum rate of absorption from a mass of root basis to a volumetric basis, as required.

The maximum rate of deactivation of the selenium was similarly converted from a mass of soil basis to a volumetric basis. In this

Figure 87. Predicted Variability of the Anisotropy Factor
For the First 420 Days of the Mutiny Bay Field Trial.



case, however, the conversion could be carried out on firmer ground because of the more reliable value for the soil's bulk density.

The Thiele moduli in both the axial and radial directions could now be calculated directly:

$$h_{Tr}^2 = \frac{r_o^2 \rho_{root} v_{max}^a}{D_e K_m^a} \quad (4-10)$$

$$h_{Tz}^2 = \frac{4z_o^2 \rho_{root} v_{max}^a}{D_{ez} K_m^a} \quad (4-11)$$

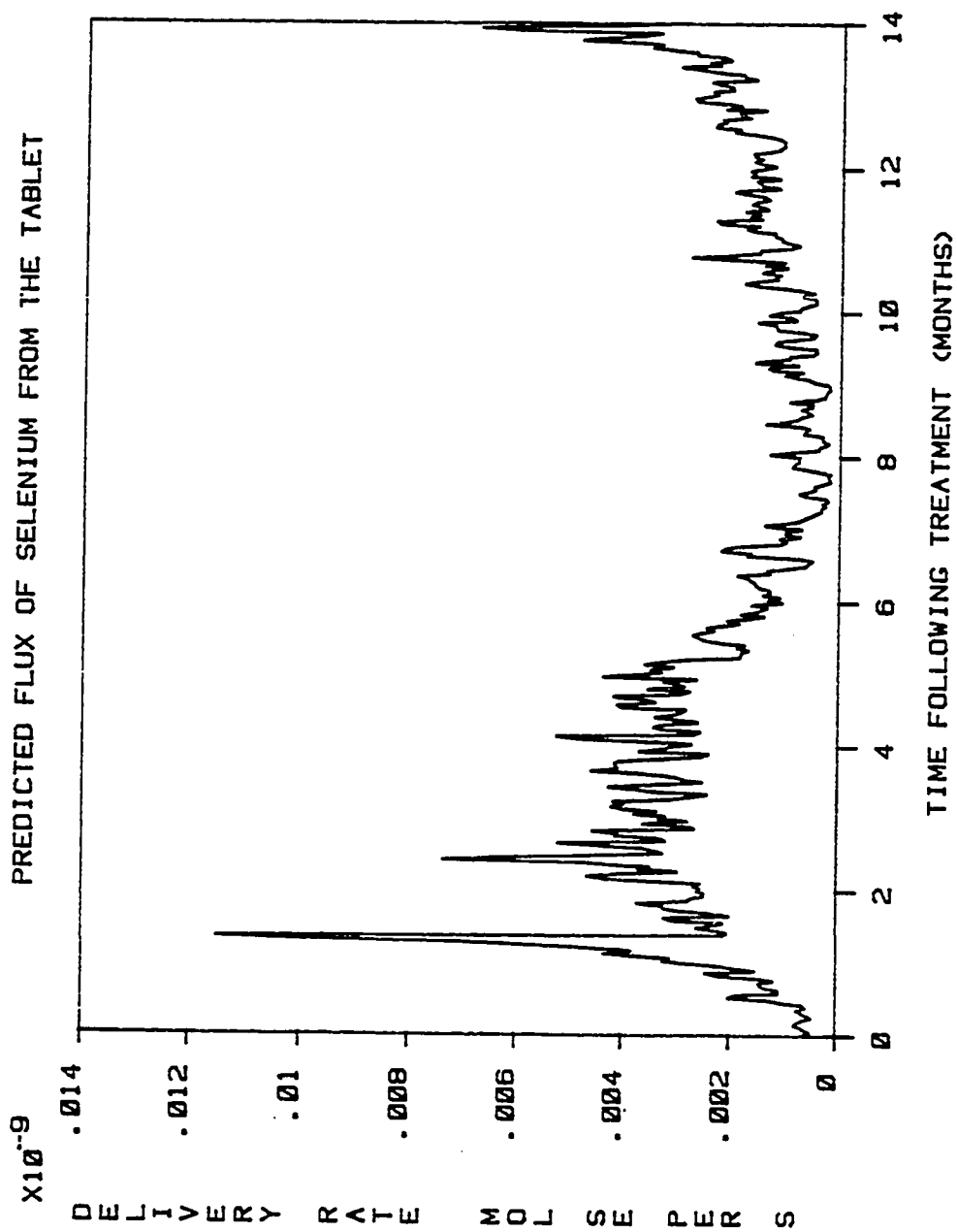
With the two Thiele moduli available it was now possible to apply the results of the solution to the 2-D reaction/diffusion equation. Solutions to this 2-D equation had been mapped (see Fig's. 33 and 34) as a function of the h_T 's and it was simply a matter of interpolating the flux from each face for each of the days of the test. The "density" of the number of convergent solutions in the important range of the Thiele moduli and other parameters was increased in order to better characterize the flux from the tablet. Since the model had been solved only for the steady state, a major assumption inherent to this technique was that the concentration profiles instantaneously adjusted to the new values of the mobility at the beginning of each day. The validity of such an analysis may be investigated through consideration of the characteristic times for the transport phenomena involved.

The times to be compared are diffusion times through the soil and times over which the boundary conditions changed significantly. The

variation in the boundary conditions that gave fluxes in agreement with the meteorological data was quite small, such that large changes in the saturation never took place. Thus the changes in the effective diffusivity were never so great over short periods of time that the profiles would have had to change drastically.

The Se delivery rate predicted by the model for each of the first 420 days is shown in Fig. 88. In order to dimensionalize the flux given by the PTSOR program, it was necessary to specify the concentration of selenite ion at the tablet surface for each day. The accelerated dissolution studies yield a means of carrying out such a calculation. The most convenient means of handling the data is to plot the "delivery concentration," or selenite ion concentration at the surface of the tablet as a function of M , the cumulative amount of selenium which has already left the tablet. The dissolution studies showed that, after a lag period, this concentration fell in a roughly exponential decay as the delivery proceeded. They also showed that the concentration was a rather mild function of the amount of exchangeable anions in solution. The ions present in water at equilibrium with samples of the Mutiny Bay soil had been below the level at which the conductivity meter could determine them, and the ionic strength was therefore assumed to be at the measurement threshold of the device. This required an assumption of the molar conductivity, and the conservative value of $100 \text{ ohms cm}^2/\text{mol}$ was employed to give an ionic strength of $1.44 \times 10^{-3} \text{ M}$. This allowed calculation of M_0 and k_0 for the model test run, assuming that anion

Figure 88. Predicted Devlivery Rate of Selenium from the Tablet
During the First 420 Days at the Mutiny Bay Field Trial.



chemical identity was of secondary importance to the overall ionic strength. Without a series of experiments to determine particular interactions of selenite ion and other anions with the melamine-formaldehyde anionic exchange resin, it is not possible to be any more specific concerning this.

A bootstrap technique could then be used to calculate the effective delivery concentration for each day. At the outset of the test, the model predicted a mass transfer coefficient from the tablet of 1.0×10^{-8} . The dissolution studies suggested that an initial delivery concentration of 0.01 M could be expected for a solution at the low ionic strength of the Mutiny Bay soil-water. The amount of selenium predicted to leave the tablet during this first day was thus 1.0×10^{-12} mol Se, and this gave the new cumulative selenium loss with which to calculate the new delivery concentration for the second day of the test.

In such a way it was then possible to step through each day of the test and calculate the total flux for each 24 hour period. This could be translated into an absorption rate through simple multiplication by the efficiency of pickup predicted by the relative values of the absorption and deactivation kinetic parameters. The intrinsic values for the kinetics of these two processes, coupled with the effective root and soil densities, suggested an efficiency of selenium pickup by the Douglas-fir seedlings of 4.54×10^{-4} . For each day of the study the absorption rate was thus given by:

$$R_a = 4.54 \times 10^{-4} \int_0^{z_o} D \frac{\partial C}{\partial r}(r=r_o) 2\pi r dz + \int_0^r D \frac{\partial C}{\partial z}(z=z_o) \pi r^2 dr \quad (4-12)$$

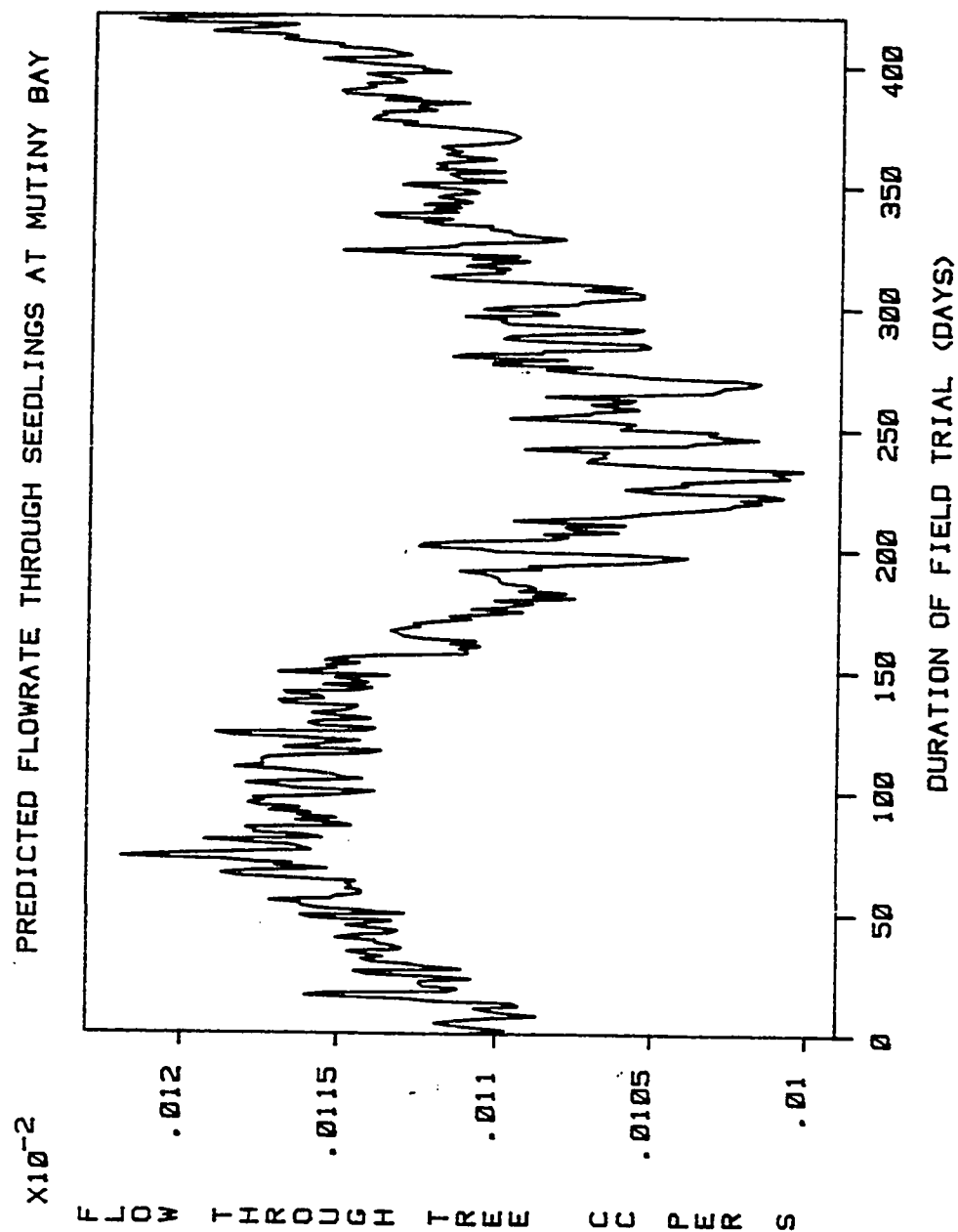
This gave the input rate to the root compartment for each day of the study. In order to apply the equations derived for the concentration of selenium in each of the compartments it was necessary to substitute a value for Q, the volumetric flowrate through the tree. As noted earlier, a simplified version of Farnum's analysis was used to derive the dependence of Q on environmental conditions. This simplified model gave Q for the first 420 days of the Mutiny Bay test as shown in Fig. 89. Generation of these results necessitated an expression for the pressure at the needle stomata, which was given by the following:

$$P_{\text{stomata}} = -k_{\text{vap}} D_{\text{vap}} \quad (4-13)$$

This equation conforms to the intuitive expectation that the evaporation rate will increase with temperature, and the agreement with Farnum's data is within 20%.

Use of these values for Q then allowed the calculation of the concentration of selenium in both the root and foliage compartments as a function of time. The volatilization rate constant had been determined to be approximately $6.4 \times 10^{-7} \text{ s}^{-1}$. During each day the rate of absorption, R_a , and the volumetric flowrate, Q, were assumed to be constant. The volume of the root compartment was simply set to 8 cm^3 , as specified by the Styro-8 containers in which the seedlings came.

Figure 89. Predicted Internal Flowrate through the Seedlings at Mutiny Bay During the First 420 Days of the Field Trial.



The volume of the foliage compartment was estimated through the following equation:

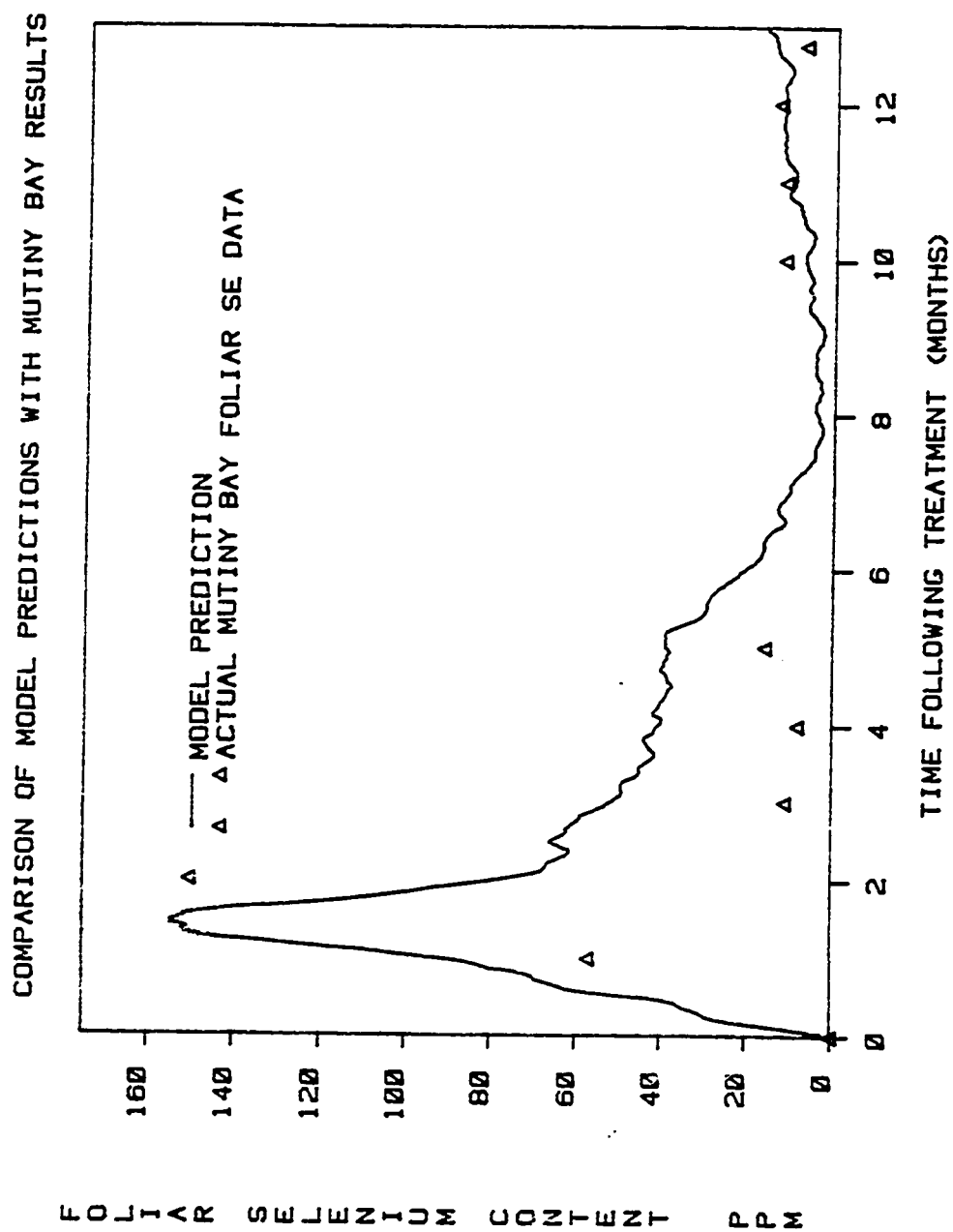
$$V_f = V_{\text{final}} - (e^{-k_{\text{grow}} t} ((V_{\text{final}} - V_{\text{initial}}) + ((V_{\text{final}} - V_{\text{initial}}) k_{\text{grow}} t))) \quad (4-14)$$

This equation merely utilizes the height gain results from the field data in order to estimate the rate of volume change of the foliage.

A slight lag in the level of selenium in the foliar compartment was ignored in the model. This lag occurs because the concentration wave from the root compartment takes a finite time to reach the foliage. As noted by Farnum, however, this time is on the order of minutes, and is therefore of little relevance to the time regime of interest. The coupled differential equations which govern the compartments each require an initial condition for the Se concentration. For the first day of the study this concentration was set to zero. It was thereafter set to the value predicted at the end of the preceeding day.

The predicted behavior of the foliar selenium content as a function of time following treatment with the tablet is shown in Fig. 90. It can be seen that a peak is predicted at a time of 2 months, as was observed in the field data (the triangles in Fig. 90). Quantitative agreement was acceptable, given the uncertainties both in the foliar analyses and the model assumptions.

Figure 90. Comparison of Model Predictions with Foliar Levels Observed at the Mutiny Bay Field Trial.



Chapter V: Conclusions

The research project met its primary practical goal, which was the development of a slow release systemic repellent for the protection of tree seedlings from deer. The tablet proved to be a stable source of selenite ion for quite long periods of time in the soil: nearly two years in the field trials which were begun in this study. The browse reduction results were encouraging, and have spurred on others in an attempt to develop a commercial product based on the tablet.

Of more academic interest was the modeling work, although the success achieved indicates that such modeling approaches could provide much useful information to those designing sustained delivery systems for application to the soil. The foliar concentrations of selenium observed in the studies were highly variable and erratic at all of the sites except for Mutiny Bay. This prevented the model from being tested adequately except against the Mutiny Bay foliar results. The relatively good agreement observed between the predicted and observed foliar concentrations was evidence that the effects ignored in the theoretical development were of second order importance, as had been hoped at the outset.

Among the recommendations for future work in this area are the following:

1. The use of powdered selenite salts as the basis of the product is somewhat undesirable, because of some severe toxicity associated with acute reactions to optical intrusion

of the salt. Thus the alternate devices constructed in this study, such as the impregnated fibrous materials might be more attractive, because they involve the handling of liquid solutions rather than powders. The major obstacle to overcome, however, is the rather low level of loading that has so far been achieved with such systems.

2. Further modeling work on the diffusion of active agents thorough soil should include the effect of voids and convection. These effects must be accounted for when answering questions about ground water contamination. Statistical methods would probably be required in order to gain meaningful results.

3. The dissolution apparatus constructed in the study gave quite good results and would appear to be a useful technique for the evaluation of other sustained delivery systems.

4. The ion exchange resin constructed in the tablet is of a novel type and may prove interesting in other applications. The use of other melamine salts as the starting material might give a product that is capable of participating in novel chemical synthetic routes.

5. The general philosophy of the application of chemical engineering principles in previously "uncharted waters" is one

which was central to the author's (and advisor's) thinking during this project. It is believed that this approach lends itself to interesting discoveries, both through serendipity and through hard work.

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Appendix A: Computer Programs

The project of course involved the use of many computer programs, but only the two most important ones are listed here. The first, PTSOR, is the successive overrelaxation technique used to solve the two dimensional diffusion equation for a cylindrical geometry. The second, MOBILITY, solves the soil water problem by the use of a similarity transformation. The boundary conditions are changed each day as they are influenced by meteorological data (see Section 4.14).

PTSOR

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DIMENSION C(0:50,0:50), RESID(50,50), RZ(0:50,0:50)
DIMENSION X(0:50), Y(0:50), ZZ(0:50), Z(0:50)
DIMENSION R(0:50), RR(0:50)
REAL KA, KD
OPEN (UNIT=1, TYPE='OLD', NAME='PAR.DAT')
OPEN (UNIT=3, TYPE='NEW', NAME='CONC.DAT')
READ(1,1) N, NB, HTRSQD, HTZSQD, F
1 FORMAT(2I3,3E14.7)
READ(1,2) ERROR, KA, KD, BETA
2 FORMAT(4E14.7)
READ(1,292) X0, XTOT
292 FORMAT(2E14.7)
XX=FLOAT(N)
XX=XTOT/XX
X(0)=X0
Y(0)=X0
DO 3 I=1,N
  X(I)=X(I-1)+XX
  Y(I)=Y(I-1)+XX
3 CONTINUE
DO 4 I=0,N
  AA=((X(I)**2)/((HTRSQD)*(XX**2)))
  BB=((X(I)-(X(I)/(HTRSQD*ALOG(1.0/X(I)))))/(2.0*XX))
  R(I)=AA+BB
  RR(I)=AA-BB
  AA=((Y(I)**2)/((HTZSQD)*(XX**2)))
  BB=(Y(I)/(2.0*HTZSQD*XX))
  Z(I)=AA+BB
  ZZ(I)=AA-BB
4 CONTINUE
```

```

DO 6 I=1,N-1
  DO 5 J=1,NB
    AA=(2.0*(X(I)**2))/(HTRSQD*(XX**2))
    BB=(2.0*(Y(J)**2))/(HTZSQD*(XX**2))
    RZ(I,J)=AA+BB
5  CONTINUE
6  CONTINUE
  DO 8 I=1,NB
    DO 7 J=NB+1,N
      AA=(2.0*(X(I)**2))/(HTRSQD*(XX**2))
      BB=(2.0*(Y(J)**2))/(HTZSQD*(XX**2))
      RZ(I,J)=AA+BB
7  CONTINUE
8  CONTINUE
  CALL FILL(C,N,NB,Y)
  DO 9 I=NB,N
    C(I,NB)=1.0
    C(NB,I)=1.0
9  CONTINUE
  DO 10 I=0,N
    C(0,I)=0.0
    C(I,0)=0.0
10 CONTINUE
  NITER=0
  INT=1
100 CONTINUE
  NITER=NITER+INT
  DO 222 II=1,INT
    DO 14 J=1,NB-1
      DO 13 I=1,N-1
        CB=C(I,J)
        W=(R(I)*C(I+1,J))+(RR(I)*C(I-1,J))
        W=W+(Z(J)*C(I,J+1))+(ZZ(J)*C(I,J-1))
        DF=-(RZ(I,J)+F+1.0)
        COLD=2.0
        DO 11 K=1,5
          IF(ABS(COLD-C(I,J)).LT.ERROR) GOTO 12
          AB=C(I,J)/(1.0+(KA*C(I,J)))
          DE=F*C(I,J)/(1.0+(KD*C(I,J)))
          COLD=C(I,J)
          C(I,J)=COLD-((W-(AB+DE+(RZ(I,J)*COLD)))/DF)
11      CONTINUE
12      C(I,J)=CB+(BETA*(C(I,J)-CB))
13      CONTINUE
        C(N,J)=(1.0/3.0)*((4.0*C(N-1,J))-C(N-2,J))
14 CONTINUE
    DO 18 I=1,NB-1
      DO 17 J=1,N-1
        CB=C(I,J)
        W=(R(I)*C(I+1,J))+(RR(I)*C(I-1,J))
        W=W+(Z(J)*C(I,J+1))+(ZZ(J)*C(I,J-1))
        DF=-(RZ(I,J)+F+1.0)
        COLD=2.0

```

```

DO 15 K=1,5
  IF (ABS(COLD-C(I,J)).LT.ERROR) GOTO 16
  AB=C(I,J)/(1.0+(KA*C(I,J)))
  DE=F*C(I,J)/(1.0+(KD*C(I,J)))
  COLD=C(I,J)
  C(I,J)=COLD-((W-(AB+DE+(RZ(I,J)*COLD)))/DF)
15 CONTINUE
16 C(I,J)=CB+(BETA*(C(I,J)-CB))
17 CONTINUE
  C(I,N)=(1.0/3.0)*((4.0*C(I,N-1))-C(I,N-2))
18 CONTINUE
  TOTRES=0.0
  DO 20 I=1,N-1
    DO 19 J=1,NB-1
      W=(R(I)*C(I+1,J))+(RR(I)*C(I-1,J))
      W=W+(Z(J)*C(I,J+1))+(ZZ(J)*C(I,J-1))
      AB=C(I,J)/(1.0+(KA*C(I,J)))
      DE=F*C(I,J)/(1.0+(KD*C(I,J)))
      RESID(I,J)=W-(AB+DE+(RZ(I,J)*C(I,J)))
      TOTRES=TOTRES+ABS(RESID(I,J))
19 CONTINUE
20 CONTINUE
  DO 22 I=1,NB-1
    DO 21 J=NB,N-1
      W=(R(I)*C(I+1,J))+(RR(I)*C(I-1,J))
      W=W+(Z(J)*C(I,J+1))+(ZZ(J)*C(I,J-1))
      AB=C(I,J)/(1.0+(KA*C(I,J)))
      DE=F*C(I,J)/(1.0+(KD*C(I,J)))
      RESID(I,J)=W-(AB+DE+(RZ(I,J)*C(I,J)))
      TOTRES=TOTRES+ABS(RESID(I,J))
21 CONTINUE
22 CONTINUE
  IF (TOTRES.LT.1.0) GOTO 220
222 CONTINUE
  GOTO 227
220 CONTINUE
  WRITE(5,223) HTRSQD, HTZSQD, NITER
223 FORMAT(1X,'RADIAL HTSQD IS',E14.7,' AXIAL HTSQD IS',E14.7,' IT',
    & 'ERATION NO.',I5)
  WRITE(5,147)
147 FORMAT(1X,'USE FLX PROGRAM FOR RESULTS')
  GOTO 225
227 CONTINUE
  WRITE(5,201) BETA, NITER, TOTRES
201 FORMAT(1X,'BETA=',E14.7,', AFTER ',I4,' ITER, RES=',E14.7)
  WRITE(5,202)
202 FORMAT(1X,'HOW MANY MORE ITERATIONS ?')
  READ(5,203) INT
203 FORMAT(I4)
  IF (INT.NE.0) GOTO 100
225 CONTINUE

```

```

DO 26 I=0,N
  DO 25 J=0,NB
    RRR=ALOG(1.0/X(I))
    ZZZ=ALOG(1.0/Y(J))
    WRITE(3,244) C(I,J)
244    FORMAT(1X,E14.7)
  25 CONTINUE
26 CONTINUE
  DO 30 I=0,NB
    DO 29 J=NB+1,N
      WRITE(3,228) C(I,J)
228    FORMAT(1X,E14.7)
  29 CONTINUE
30 CONTINUE
  STOP
  END
  SUBROUTINE FILL(CCC,NSIZE,NBORD,YYY)
  DIMENSION CCC(0:50,0:50), YYY(0:50)
  DO 32 I=NBORD,NSIZE-1
    DO 31 J=1,NBORD-1
      CCC(I,J)=YYY(J)*2.7182818
      CCC(J,I)=CCC(I,J)
31    CONTINUE
32 CONTINUE
    DO 34 I=1,NBORD-1
      DO 33 J=1,I
        CCC(I,J)=YYY(J)*2.7182818
        CCC(J,I)=CCC(I,J)
33    CONTINUE
34 CONTINUE
  RETURN
  END

```

MOBILITY

```

DIMENSION PR(4,100), THI(4,100), TLO(4,100), D(4), W(4)
DIMENSION XST(4), YST(4), SATRTN(100), TIME(100)
DIMENSION RAIN(100), HITEMP(100), TEMPLO(100), SAT(0:100)
DIMENSION P(0:100), RESID(100), Y(0:100), RKR(0:100), DS(0:100)
DIMENSION FLUXT(-1:1), AM(5,10), POLD(0:100)
OPEN(UNIT=1, TYPE='OLD', NAME='CLIMATE.DAT')
OPEN(UNIT=2, TYPE='OLD', NAME='REFDATA.DAT')
OPEN(UNIT=3, TYPE='NEW', NAME='TIME.DAT')
OPEN(UNIT=4, TYPE='NEW', NAME='PHENOMENA.DAT')
OPEN(UNIT=7, TYPE='NEW', NAME='T.EAS')
OPEN(UNIT=8, TYPE='NEW', NAME='DIFF.EAS')
OPEN(UNIT=9, TYPE='NEW', NAME='Q.EAS')
OPEN(UNIT=10, TYPE='NEW', NAME='VZ.EAS')
OPEN(UNIT=12, TYPE='OLD', NAME='SLOCATION.DAT')
OPEN(UNIT=13, TYPE='NEW', NAME='SATO.EAS')
OPEN(UNIT=14, TYPE='NEW', NAME='LOCALCLMT.DAT')

```

```

OPEN(UNIT=15, TYPE='NEW', NAME='ZDAY.EAS')
OPEN(UNIT=16, TYPE='NEW', NAME='SAT1.EAS')
OPEN(UNIT=17, TYPE='NEW', NAME='SAT2.EAS')
OPEN(UNIT=18, TYPE='NEW', NAME='SAT3.EAS')
OPEN(UNIT=19, TYPE='NEW', NAME='SAT4.EAS')
OPEN(UNIT=20, TYPE='NEW', NAME='SAT5.EAS')
OPEN(UNIT=21, TYPE='NEW', NAME='SAT6.EAS')
OPEN(UNIT=22, TYPE='OLD', NAME='OLDSAT.DAT')
NSTN=0
NPLOTS=15
1 CONTINUE
NSTN=NSTN+1
READ(1,2) XST(NSTN), YST(NSTN), NDATA, A, B
2 FORMAT(4X,F5.1,1X,F5.1,1X,I3,1X,2E11.4)
DO 4 I=1,NDATA
    READ(1,3) M, ND, NY, PR(NSTN,I), THI(NSTN,I), TLO(NSTN,I)
3    FORMAT(I2,1X,I2,1X,I4,2X,F5.2,1X,F5.1,1X,F5.1)
4 CONTINUE
    WRITE(5,5) NSTN
5    FORMAT(1X,'HAVE READ IN ',I1,' STATIONS, TYPE 1 FOR MORE')
    READ(5,6) MODE
6    FORMAT(I1)
    IF (MODE.EQ.1) GOTO 1
    READ(12,7) XSITE, YSITE
7    FORMAT(F5.1,1X,F5.1)
    TD=0.0
    DO 8 I=1,NSTN
        D(I)=SQRT(((XST(I)-XSITE)**2)+((YST(I)-YSITE)**2))
        WRITE(5,*) D(I)
        TD=TD+D(I)
8 CONTINUE
    DO 9 I=1,NSTN
        W(I)=0.5*(1-(D(I)/TD))
        WRITE(5,*) W(I)
9 CONTINUE
    DO 11 I=1,NDATA
        RAIN(I)=0.0
        HITEMP(I)=0.0
        TEMPLO(I)=0.0
        DO 10 J=1,NSTN
            RAIN(I)=RAIN(I)+(W(J)*PR(J,I))
            HITEMP(I)=HITEMP(I)+(W(J)*THI(J,I))
            TEMPLO(I)=TEMPLO(I)+(W(J)*TLO(J,I))
10    CONTINUE
        WRITE(14,*) RAIN(I), HITEMP(I), TEMPLO(I)
11 CONTINUE
    READ(2,12) N, NTIME, PBO, TROSTY, DIFFSE, DIFFO, SOR
12 FORMAT(2I3,4E14.7,F7.4)
    READ(2,13) RHO, G, RLNGTH, PERMO, POROUS, VISCOS
    READ(2,13) SR, A, B, ETA, RLAMDA, X
    READ(2,132) RESIST, EVAPRT

```

```

132 FORMAT(2E14.7)
13  FORMAT(6E11.4)
    TC=POROUS*RLNGTH*VISCOS/(PERMO*RHO*G)
    PC=RHO*G*RLNGTH
    TDAY=86400.0/TC
    YY=FLOAT(N)
    YY=0.9999998/YY
    Y(0)=0.0000001
    DO 14 I=1,N
        Y(I)=Y(I-1)+YY
        Z=(ALOG(1.0/Y(I)))*RLNGTH*SQRT(TDAY)
        WRITE(15,144) Z
144  FORMAT(1X,E14.7)
14  CONTINUE
    RN=FLOAT(N)
    AAA=(SR-1.0)*ETA*RLNGTH/A
    DO 41 II=1,NDATA
        TEMPAV=0.5*(HITEMP(II)-TEMPLO(II))
        TK=((TEMPAV-32.0)*0.5555555)+273.16
        WVAPRS=EXP(18.3036-(3816.44/(TK-46.13)))
        WDIFF=0.00000043409*(TK**2.334)
        PLEAF=-WDIFF*EVAPRT
        FLUX=RAIN(II)*2.54
        IF (FLUX.GT.0.0) GOTO 15
        FLUX=-WDIFF*SAT(N-1)
        GOTO 16
15  IF (PBO.EQ.0.0) GOTO 33
16  CONTINUE
    VZ=ABS(FLUX)/(86400.0*SAT(N-1)*POROUS)
    PB1=-4.0
    PBINC=2.0
    NINC=1
17  CONTINUE
    DO 18 J=0,N
        PPP=FLOAT(J)
        P(J)=PBO+(PPP*(PB1-PBO)/RN)
        POLD(J)=P(J)
        RKR(J)=1.0/(1.0+(((P(J))*RLNGTH/B)**RLAMDA))
        BB=((RLNGTH*(-P(J))/A)**(ETA-1))
        CC=((1.0+(((P(J))*RLNGTH/A)**ETA))**2)
        DS(J)=AAA*BB/CC
18  CONTINUE
    DIFFZO=DIFFO*RKR(N)/TROSTY
    NITER=0
    INT=1

```

```

19 CONTINUE
  NITER=NITER+INT
  DO 21 III=1,INT
    TOTRES=0.0
  DO 20 I=1,N-1
    AA=Y(I)*(ALOG(1.0/Y(I))*DS(I))/2.0
    BB=(Y(I)**2)*((RKR(I+1)-RKR(I-1))/(2.0*YY))
    CC=Y(I)*RKR(I)
    DD=((P(I+1)-P(I-1))/(2.0*YY))*(AA+BB+CC)
    EE=((Y(I)**2)*RKR(I)*(P(I+1)+P(I-1)))/(YY**2)
    P(I)=(DD+EE)*(YY**2)/(2.0*(Y(I)**2)*RKR(I))
    P(I)=POLD(I)+(SOR*(P(I)-POLD(I)))
    POLD(I)=P(I)
    RKR(I)=1.0/(1.0+(((P(I))*RLNGTH/B)**RLAMDA))
    BB=((RLNGTH*(-P(I))/A)**(ETA-1.0))
    CC=((1.0+(((P(I))*RLNGTH/A)**ETA))**2)
    DS(I)=AAA*BB/CC
    AA=Y(I)*(ALOG(1.0/Y(I))*DS(I))/2.0
    BB=(Y(I)**2)*((RKR(I+1)-RKR(I-1))/(2.0*YY))
    CC=Y(I)*RKR(I)
    DD=((P(I+1)-P(I-1))/(2.0*YY))*(AA+BB+CC)
    EE=((Y(I)**2)*RKR(I)*(P(I+1)+P(I-1)))/(YY**2)
    RESID(I)=P(I)-((DD+EE)*(YY**2)/(2.0*(Y(I)**2)*RKR(I)))
    TOTRES=TOTRES+ABS(RESID(I))
    SAT(I)=SR+((1.0-SR)/(1.0+(((P(I))*RLNGTH/A)**ETA)))
20 CONTINUE
21 CONTINUE
  SLOPE=(P(N-2)-(4.0*P(N-1))+(3.0*P(N)))/(2.0*YY)
  SLOPE=-SLOPE*0.9999999
  SURFAC=-PC*SLOPE*2.0*SQRT(TDAY)*RKR(N)*PERMO*TC/(RLNGTH*VISCOS)
  WRITE(5,22) SURFAC, FLUX, PBO, PB1
22 FORMAT(1X,'FLUX IS',E11.4,' RAIN WAS',E11.4,' PBO IS',E11.4,
& ' AND PB1 IS',E11.4)
  IF (NINC.GT.20) GOTO 27
  IF ((ABS(SURFAC-FLUX)).LT.0.001) GOTO 27
  IF (SURFAC.GT.FLUX) GOTO 23
  PB1=PB1+PBINC
  GOTO 24
23 CONTINUE
  PB1=PB1-PBINC
24 CONTINUE
  PBINC=PBINC/2.0
  NINC=NINC+1
  GOTO 17
27 CONTINUE

```



```

      WRITE(5,28) II
28  FORMAT(1X,'THIS IS THE ',I3,'TH DAY OF THE CURRENT RUN')
      M=NDATA-II
      WRITE(5,29) M
29  FORMAT(1X,'THERE ARE ',I3,' DAYS LEFT IN THIS SET')
      WRITE(5,30) NITER, TOTRES
30  FORMAT(1X,'AFTER ',I3,' ITERATIONS, TOTRES=',E14.7)
      NINC=0
      PBINC=PBINC*128.0
33  CONTINUE
      S=SR+((1.0-SR)/(1.0+(((PB1)*RLNGTH/A)**ETA)))
      WRITE(13,34) S
      DIFEFF=DIFFSE*RKR(N)/TROSTY
      QFLOW=(PB1-PLAFA)/RESIST
      WRITE(10,34) VZ
      WRITE(9,34) QFLOW
      WRITE(8,34) DIFEFF
      WRITE(7,35) II
34  FORMAT(1X,E14.7)
35  FORMAT(1X,I3)
      PBO=PB1
      IF ((MOD(II,15)).NE.0) GOTO 41
      NPLOTS=NPLOTS+1
      DO 40 I=0,N
          S=SAT(I)
          WRITE(NPLOTS,39) S
39  FORMAT(1X,E14.7)
40  CONTINUE
41  CONTINUE
42  CONTINUE
      STOP
      END

```

Appendix B: Derivation of Release Equation

Mass transfer from a tablet in the dissolution accelerator is modeled as a two step process in this analysis. First there is diffusion through lengthening pores within the tablet. Then the material must diffuse through the thin external boundary layer (see Levich⁽⁹⁶⁾). A schematic picture of this process was already presented (see Fig. 14, p. 87). This discussion is limited to the mathematical technicalities involved in the derivation of eq.'s. (2-28) and (2-29).

The flux through the external boundary layer is given by:

$$J_{\text{ext}} = k_{\text{ext}}(C_t - C_o) \quad (\text{B-1})$$

The terms have been defined previously. Two equations for flux through one of the pores have already been presented. These are now presented again:

$$J_{\text{pore}} = \frac{D(C_s - C_t)}{L} \quad (\text{B-2})$$

$$J_{\text{pore}} = \frac{\rho}{MW} \frac{dL}{dt} \quad (\text{B-3})$$

The first step is to eliminate C_t from the equations. This is done by noting that the flux given in eq. (B-2) is $1/p$ greater than the flux given in eq. (B-1), where p is the fraction of the nominal axial face of the tablet taken up by pores. This assumes that all of

the pores in the tablet have the same length, or at worst that their cumulative sum is equal to this simple averaged flux. Thus, multiplying eq. (B-2) by p , equating with eq. (B-1), and isolating C_t , the following result is obtained:

$$C_t = \frac{kC_o + (\rho DC_s/L)}{k + (\rho D/L)} \quad (B-4)$$

The concentration of selenium in the bulk solution may be found by integrating eq. (B-3) directly:

$$C_o = \frac{A \int_0^t J dt}{V} = \frac{A \int_0^t \frac{p\rho}{MW} \frac{dL}{dt} dt}{V} = \frac{\rho ApL}{MW V} \quad (B-5)$$

The axial area of the tablet has been assumed constant and set equal to A . The solution volume is also assumed constant, and is given by V . This relationship simply states that everything which dissolves out of the pores goes into solution.

Substituting these expressions for C_t and C_o into eq. (B-1) and equating with eq. (B-3) then gives a differential equation for the pore length as a function of time (eq. (2-28) in the text):

$$C_s - \frac{\rho ApL}{MW V} = \left(\frac{L}{pDC_s} + \frac{1}{k} \right) \frac{p\rho}{MW} \frac{dL}{dt} \quad (B-6)$$

This equation is nondimensionalized with the following characteristic parameters:

$$C^* = \rho / MW \quad (B-7)$$

$$L^* = V/A \quad (B-8)$$

$$t^* = \frac{V^2}{D A^2} \quad (B-9)$$

Dividing each dimensional variable in (B-6) by its corresponding characteristic parameter, and identifying the dimensionless variables with primes, the following equation is obtained:

$$C'_S - pL' = \left(\frac{L'}{p} + \frac{L^*}{k t^*} \right) \frac{dL'}{dt'} \quad (B-10)$$

$$L'(0) = 0$$

This separable equation is easily integrated using tables presented in the Chemical Rubber Company Handbook:⁽³⁾

$$t' + K_{int} = - \frac{1}{p} \left(\frac{L'}{p} + \left(\frac{C'_S}{p^2} + \frac{L^*}{k t^*} \right) \ln(C'_S - pL') \right) \quad (B-11)$$

The result is rearranged to give the following:

$$t' = \frac{1}{p} \left(\left(\frac{C'_S}{p^2} + \frac{L^*}{k t^*} \right) \ln \left(\frac{C'_S}{C'_S - pL'} \right) - \frac{L'}{p} \right) \quad (B-12)$$

Going back to dimensional variables, the result presented in the text as eq. (2-29) is then obtained.

VITA

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"Controlled Release Animal Repellents in Forestry," in Bioactive Polymeric Systems, eds., C.G. Gebelein and C.E. Carraher, Plenum, in press.

"Controlled Release Technology: Developing a Slow Release Systemic Repellent for the Protection of Tree Seedlings from Deer," in Controlled Release of Bioactive Materials, 10th International Symposium, San Francisco, CA, July 24-27, 1983, Chrmn., J. Heller and H. Jaffe, Controlled Release Society, pp 180-187.

"The Reduction of Deer Browsing of Douglas-fir (Pseudotsuga menziesii) Seedlings by Quadrivalent Selenium," Forest Ecol. Manage., in press.

Papers presented at:

American Chemical Society Meeting, Seattle, WA, March 22, 1983.

National Society of Foresters Meeting, Corvallis, OR, May 6, 1983.

Controlled Release Society Meeting, San Francisco, CA, July 25, 1983.

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