

# A MATHEMATICAL MODEL FOR BIOLOGICAL POLISHING

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## 1.1 Brief Note on Modelling

The object of the dynamical model of biological polishing presented herein is to simulate the biogeochemical processes operating in the removal of heavy metals from mine drainage by means of periphytic algae. The model describes the growth of periphyton, and the interactions between periphyton, effluent, and fertilizer. Eventually it is hoped that it will serve as a management tool in that it will allow the user to determine the number of trees (or other substrate) and the amounts of nutrient to put into an effluent pool to maintain the metal concentrations below some legislatively set value year round.

There are two markedly different approaches to modelling ecosystems in the scientific literature. In the “top down” approach, models are constructed which call for a comprehensive and detailed description of ecosystem components. These models are typically empirical in nature, and based on on-site observations. The “top down” approach is the methodology generally favoured by field biologists probably due to the the great complexity of natural systems they study. In contrast, the “bottom up” approach relies on careful quantification of key inputs, outputs, and internal processes for simulation of system dynamics. This approach is generally favoured by physical scientists and engineers, largely because it has been successful in their respective disciplines for several centuries. The models constructed in this approach are typically mechanistic and mathematical. The model which I will construct is an attempt to bridge the two ways of doing things. I will adopt a mechanistic theoretical perspective and identify the key biogeochemical processes operating in polishing ponds. However, I will use an empirical approach to quantify these complex processes first in the laboratory and then in the field on a site-specific basis. Finally, the mechanistic/empirical model constructed must be calibrated and verified in the field.

## 1.2 Bioaccumulation of Metal Ions by Algae

The active mode of metal accumulation by living cells is normally designated *bioaccumulation*. This process depends on the metabolic activity of living cells, which is itself affected by the presence of metal ions. The ability of an organism to survive in an environment with high concentrations of heavy metals may be due to two not necessarily mutually exclusive reasons: (i) the organism is able to maintain more or less normal metabolic function in the presence of elevated metal concentrations, or (ii) the organism is able to prevent the intracellular buildup of metal concentrations harmful to metabolism. The growth of the organism is expected to be affected in both cases. Organisms have been reported to actually slow their growth in order to prevent the intercellular accumulation of metal ions. In case (ii) metal ions attach to the negatively charged cell walls and surrounding polysaccharides of an organism without entering it.

The total amount of metal sequestered by algae depends on the saturation loading of the algae and surrounding polysaccharides, and the quantity of algae and polysaccharides exposed to the contam-

inated solution. To control the biological polishing process, then, requires an understanding of algal bioaccumulation kinetics and equilibria, and algal growth under various environmental conditions. Therefore, the modelling problem is to write down a set of differential equations which quantify (i) the growth of algae in the environment, (ii) the nutrient flow to and from algae, (iii) the adsorption of dissolved metal ions at low pH, (iv) the sieving of precipitated metal ions at higher pH.

### 1.2.1 Growth of Periphyton

The biomass balance equation for the periphyton is:

$$nA \frac{da}{dt} = nA(G_p - D_p)a - \frac{nAv_p a}{H} \quad (1.1)$$

- $V$  = volume of pond ( $m^3$ )
- $a$  = density of periphyton on carbon substrate (alder, spruce etc.) ( $kg/m^2$ )
- $G_p$  = growth rate of periphyton ( $d^{-1}$ )
- $D_p$  = death rate of periphyton ( $d^{-1}$ )
- $H$  = depth of pond ( $m$ )
- $n$  = number of trees
- $A$  = surface area per tree which supports periphyton growth ( $m^2$ )
- $v_p$  = settling rate of periphyton ( $m/d$ )

Here we assume that no periphyton enters or leaves the pond through inflow or outflow.

The rate of periphyton growth depends on three principal components:

1. Temperature, T
2. Solar radiation, I
3. Nutrients, N
4. Metal concentrations,  $m_a^+$ , on the periphyton

Normally, it is assumed that environmental effects are multiplicative, although there is no *a priori* reason for this. Nevertheless, other algae growth models in the literature based on this assumption have been supported to some extent by data collected. Therefore, we take

$$G_p = \mu_{max,20} G(T)G(I)G(N)G(m_a^+) \quad (1.2)$$

Here  $\mu_{max,20}$  is the maximum growth at optimal conditions (nutrient saturation, no metal sorption).

*The attenuating functions  $G(T)$ ,  $G(I)$ ,  $G(N)$ , and  $G(m_a^+)$  must be either taken from the literature, or determined experimentally.* The disadvantage of the first approach is that literature values vary widely since they are typically average values over many sites. **To reduce model calibration and improve accuracy it is best to determine these functions in the laboratory, and then verify them in the field.** Furthermore, sensitivity analysis of the model will allow us to determine which variables are important, and which are not. This empiric/mechanistic, site-specific approach, I believe, is the best for ecological modelling.

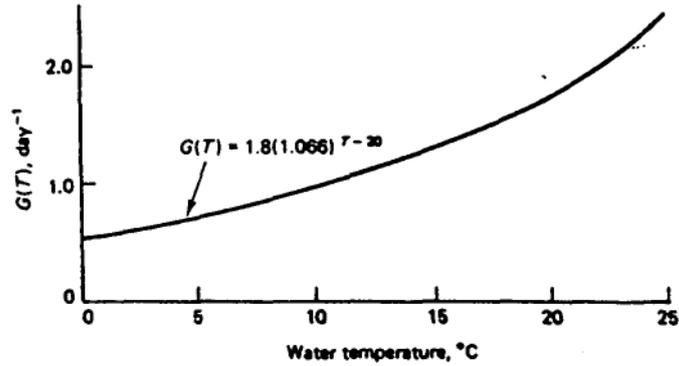


Figure 1.1: Growth vs. temperature

### Temperature Effect

In the case of optimum light, nutrient saturation, and no metal sorption, it has been empirically determined that the growth of algae typically goes as an exponential:

$$G(T) = \Theta_{\mu}^{(T-20)} \quad (1.3)$$

An experiment carried on a sample of periphyton growing in water from the site over a range of temperatures would establish  $\Theta_{\mu}$ . In the environment  $T = T(t)$  over the year, and obviously effects growth. From a meteorologic record the temperature variation with time at a given site can be estimated using nonlinear regression.

### Light Effect

The variation of photosynthesis with light also attenuates growth. There are several models in the literature ranging from Monod-type saturation to exponential growth and decay. For example, the Monod saturation type of factor is:

$$G(I) = \frac{I}{K_I + I} \quad (1.4)$$

Here  $K_I$  is the half-saturation constant. Again, it is preferable to determine the precise form of  $G(I)$  for a specific site in the laboratory rather to rely on literature estimates. Furthermore, light intensity falls off with water depth, and has a diurnal period (photoperiod). The Beer-Lambert Law is used to account for  $I = I(z)$ , and a photoperiod is used to establish an average daily light intensity. Typically, the intensity is averaged over depth and photoperiod to give a pond and daily average value. To account for seasonal variation an additional factor is multiplied:  $I(t) = I_{avg}[1 + \sin(0.008603)]$ . This factor, again, could be established from meteorological records.

### Nutrient Effect

This factor couples the growth model to the nutrient model. There is good evidence that algal growth is modulated by saturation kinetics of the Monod-type:

$$G(N) = \frac{N}{K_{mN} + N} \quad (1.5)$$

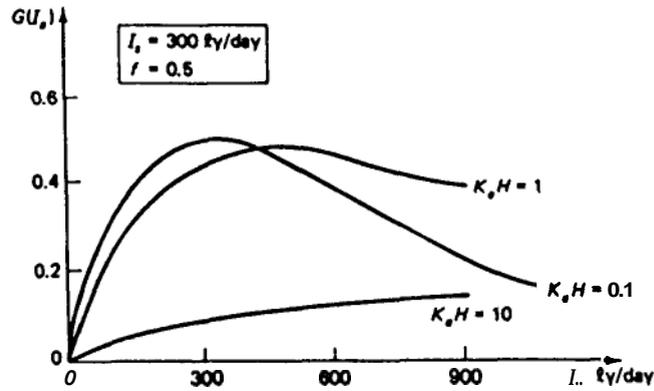


Figure 1.2: Growth .vs. light intensity

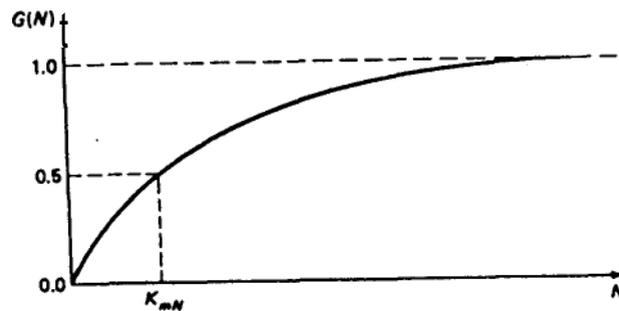


Figure 1.3: Growth .vs. limiting nutrient

Here  $N$  represents the nutrient concentration (for example, phosphorus or nitrogen). When there are several nutrients necessary for plant growth, the one which is in shortest supply (not concentration) for the plant limits growth (“Liebig’s Law of the Minimum”):

$$G(N) = \min \left\{ \frac{N_1}{K_{mN_1} + N_1}, \frac{N_2}{K_{mN_2} + N_2}, \dots \right\} \quad (1.6)$$

### Effect’of $m_a^+$

The quantification of the effect of metal concentrations is probably the most difficult. The Boojum data base provides some of the needed information but further laboratory experimentation is needed. For example, if metal concentrations in the plant are maintained at different levels, how does the plant grow relative to a control? To do these experiments, one should first establish, through experiment, the kinetics of bioaccumulation on periphyton.

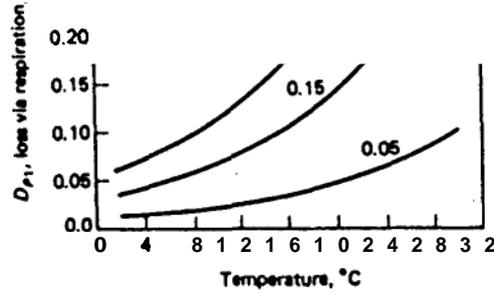


Figure 1.4: Respiration .vs. temperature

### 1.2.2 Death Rate $D_p$

Periphyton will not grow indefinitely. Due to changing environmental factors the balance between growth and death  $G - D_p$  can shift from positive (i.e. net increase in biomass) to negative (i.e. net decrease of biomass). There are several causes for a decreasing periphyton population, time of year being the most obvious (reduced temperature and sunlight). In addition periphyton have grazers, except at low pH. **Also**, herbivorous zooplankton and higher lever grazing can be a source of periphyton loss. To begin with, I shall not include these relations in the model (although later on they will be incorporated). I assume the main source of periphyton loss is due to endogenous respiration in which organic carbon making up the algae is oxidized and excreted to the environment as  $CO_2$  and other by products:

$$D_p = R \quad (1.7)$$

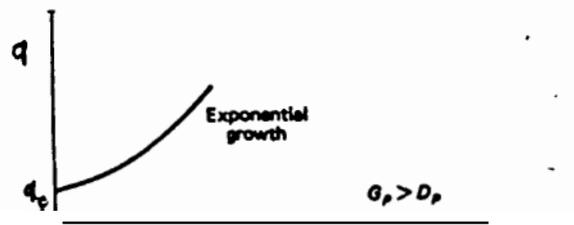
There is evidence in some studies of algal growth that respiration depends on light intensity, but the results are not conclusive. Temperature dependence, on the other hand, is well established. It has been empirically determined for a number of species of algae that respiration varies according to the exponential relation:

$$R(T) = R_{20}\Theta_R^{(T-20)} \quad (1.8)$$

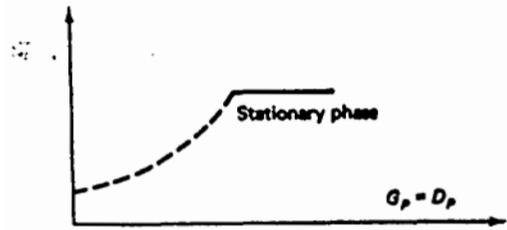
The values of the kinetic constant  $R_{20}$  and  $\Theta_R$  can be found either in the literature, or, preferably, by laboratory experimentation on site-specific periphyton.

### 1.2.3 Nutrient Relationships

The growth of the periphyton depends on the availability of nutrients through the attenuating factor  $G(N)$ . The nutrients, however, also are governed by a mass balance relation which couples nutrient flow in and out of the pond to uptake by periphyton. Nutrients are typically phosphorus, nitrogen, and carbon. The nutrient/food chain relationships are very complex and I shall give only a very simplified version to begin with. Below is a model nutrient cycle for the uptake and release of dissolved available phosphorus by the algae, the conversion of unavailable phosphorus to available



(a)



(b)



$$V \frac{dp_1}{dt} = W_1 - Qp_1 - K_{11}Vp_1 + D_p n A c_p a \quad (1.9)$$

$$V \frac{dp_2}{dt} = W_2 - Qp_2 + K_{12}Vp_1 - G_p n A c_p a \quad (1.10)$$

Here

$p_1$  = unavailable phosphorus ( $mg/l$ )

$p_2$  = available phosphorus ( $mg/l$ )

$W_1$  = input of less available phosphorus ( $mg/l$ )

$W_2$  = input of available phosphorus ( $mg/l$ )

$Q$  = outflow rate ( $l/s$ )

$c_p$  = phosphorus to chlorophyll ratio for periphyton ( $mgp/mg chl$ )

$K_{11}$  = rate of conversion of available phosphorus to unavailable and settling loss ( $d^{-1}$ )

$K_{12}$  = rate of conversion of unavailable to available phosphorus ( $d^{-1}$ )

Similar nutrient cycles for nitrogen and carbon can be written down; in fact, for polishing ponds under study, carbon is typically the limiting nutrient, and the other nutrients can be assumed saturated.

In summary the growth of the periphyton and relation to temperature, sunlight, and nutrients over the year is expected to be something like that shown in the diagram below:

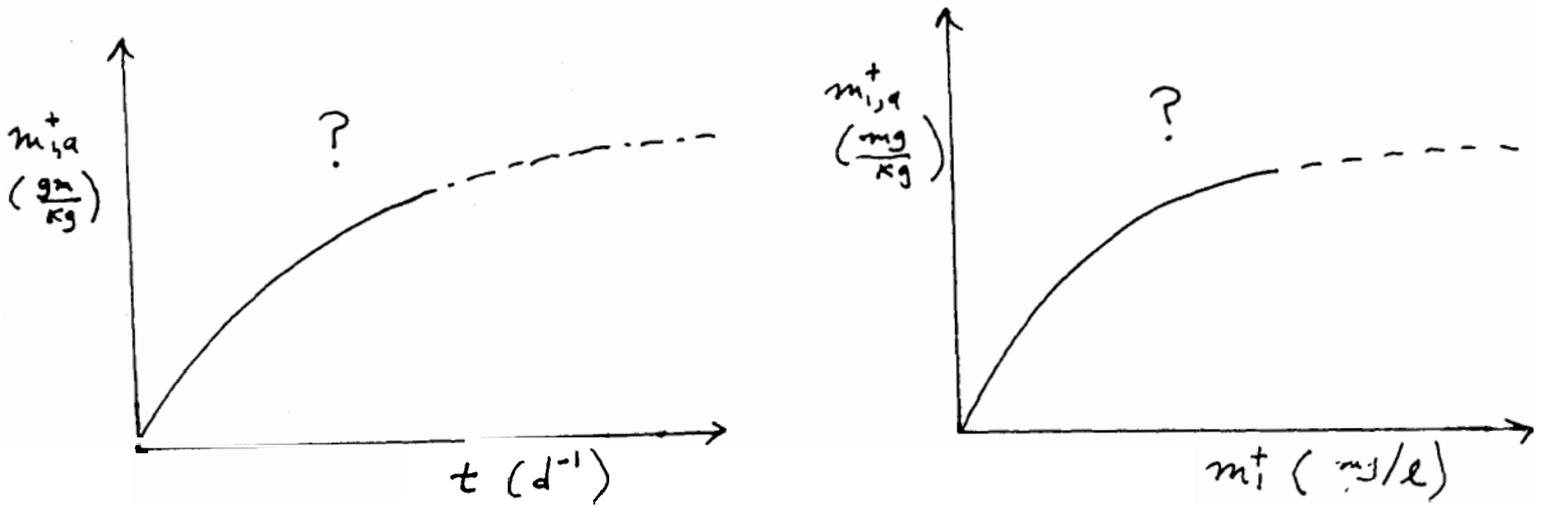


Figure 1.7: Kinetics and equilibrium adsorption

Here

- $m_1^+$  = concentration of soluble metal ( $mg/l$ )
- $Q$  = inflow rate (=outflow rate) ( $mg/l$ )
- $m_{in}^+$  = inflow concentration of soluble metal ( $mg/l$ )
- $k_{1,ad}$  = reaction rate of adsorption of metal onto periphyton ( $d^{-1}$ )
- $m_{1,a}^+$  = concentration of adsorbed metal ions on periphyton surface  
= ( $mg\ metal\ adsorbed/kg\ of\ periphyton$ )

If the adsorption takes place on a time scale  $\tau_{adsorb} \ll \tau_{contact}$ , then a quasi-equilibrium assumption is a good one. The kinetics of adsorption and the loading curve of metal on periphyton should be determined in the laboratory using field samples: If a quasi-equilibrium assumption is justified the term  $k_{1,ad}f(m_{1,a}^+)$  can be dropped from Eq. 1.11 and Eq. 1.12 can be replaced by an equilibrium relation between  $m_1^+$  and  $m_{1,a}^+$ . One might model the equilibrium loading of metal on the periphyton by a Langmuir isotherm:

$$m_{1,a}^+ = \frac{bm_1^+}{K_{m_1^+} + m_1^+} \quad (1.13)$$

### 1.3 Sieving of Precipitated Metal in Solution

For higher pH, metals cations begin to precipitate out of solution. The precise value at which a given dissolved species precipitates depends on the specific geochemistry of the system under study. Nevertheless, as a first step we divide the metal removal mechanisms into two types: electrostatic adsorption and physically driven sieving. While adsorption is a chemical process which removes dissolved species, sieving is a physico-chemical process which removes precipitated species suspended in solution. **As** the solution laden with precipitate flows past a plant, the particulate is forced up against the plant where it attaches to either polysaccharides surrounding the plant, or directly onto the cell wall. This is the “sticky-sieve” model. **A** number of questions arise. Is the process in quasi-equilibrium, with some fixed metal concentration on the plant **as** in the case of equilibrium adsorption? Or is it a cumulative one, inherently kinetic? Again, these questions depend on whether

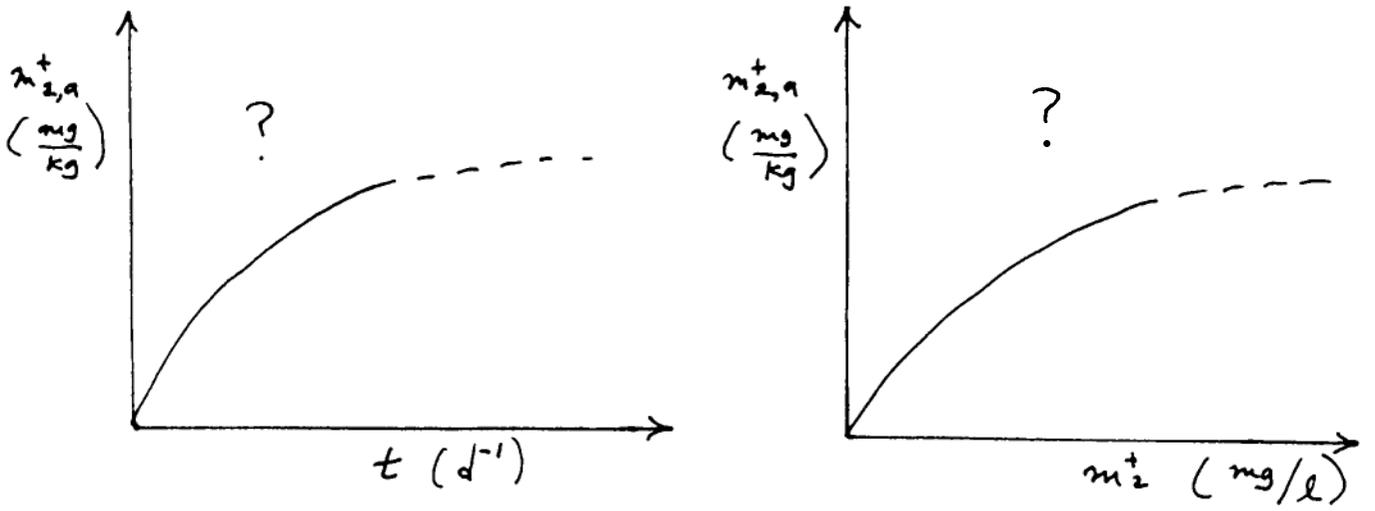


Figure 1.8: Kinetics and loading for sieving

$\tau_{sieving} \ll \tau_{residence}$  or if  $\tau_{sieving} \gg \tau_{residence}$ , and should be properly determined in the laboratory. Here I present a tentative mathematical model for sieving. In the case  $\tau_{sieving} \gg \tau_{residence}$ , sieving is a steady build-up of precipitate on the algae. The total amount of metal sieved by periphyton is proportional to the precipitate laden flow across the algae; it is also proportional to the total area of the algae exposed to the flow (which is itself proportional to the growth rate of the algae); certainly, it is proportional to  $m_2^+$ ; and presumably to the saturation loading of the periphyton. We take as a model then:

$$\left\{ \frac{dm_2^+}{dt} \right\}_{sieving} = -k_{sieve} v_{flow} m_2^+ A_{eff} = -\frac{dm_{2,a}^+}{dt} \quad (1.14)$$

Here

- $m_2^+$  = concentration of precipitated metal in solution (mg/l)
- $m_{2,a}^+$  = mass specific concentration of sieved metal on plant (mg/kg)
- $k_{sieve}$  = saturation constant i.e. sieving limited by the concentration  $m_{2,a}^+$  (dimensionless)
- $v_{flow}$  = average flow velocity around plant in pond  
=  $L_{pond} / \tau_{residence}$
- $A_{eff}$  =  $c_{surf} \cdot n A a(t)$   
= total plant surface area
- $c_{surf}$  = plant surface area per unit of plant biomass ( $m^2/kg$ )

The mass balance for precipitated metal in solution is therefore:

$$V \frac{dm_2^+}{dt} = Q m_{2,in}^+ - Q m_2^+ - k_{settle} m_2^+ - k_{sieve} v_{flow} m_2^+ A_{eff} \quad (1.15)$$

If  $\tau_{sieving} \ll \tau_{residence}$ , then the time to reach saturation is comparatively fast. In this case quasi-equilibrium holds between precipitate in solution and on algae, and the last term in the above equation would be replaced by a Monod-type saturation expression. Whether or not this is the case must be determined in the laboratory under controlled conditions.

## 1.4 Mathematical Model as a Control System

The application of mathematical models to problems of environmental remediation is best done in the context of an on going interaction between modelling and experimentation. Moreover, in this case models are valuable aids for designing field sampling programmes and for identifying the key processes operating in a given system. If a sampling programme is done outside the context of a quantitative model, then the modeller is faced with a difficult (maybe impossible) task of retrofitting models to data sets which may not contain the key measurements needed to calibrate the model. The integrated approach—the “up/down approach”—is the one which has the best chance of producing quantitative models which accurately predict system behaviour in response to external forcing and to controls.

The set of differential equations presented above are a comparatively simple mechanistic model of bioaccumulation. For the present time, we divide biopolishing into two types: electrostatic adsorption and mechanical sieving. For lower pH electrostatic adsorption is dominant, whereas for higher pH mechanical sieving is dominant. In the case of electrostatic adsorption, there are five dependent variables:

$$a, p_1, p_2, m_1^+, m_{1,a}^+ \quad (1.16)$$

If electrostatic adsorption is kinetic on physical time scales, the five equations governing these variables are Eq. 1.1, Eq. 1.9, Eq. 1.10, Eq. 1.11, and Eq. 1.12. If quasi-equilibrium holds between  $m_1^+$  and  $m_{1,a}^+$ , then Eq. 1.10 is replaced with Eq. 1.13. Similarly, in the case of mechanical sieving, there are five dependent variables:

$$a, p_1, p_2, m_2^+, m_{2,a}^+ \quad (1.17)$$

If sieving kinetics take place on a time scale comparable to the physical flow past a periphyton plant, the governing equations are Eq. 1.1, Eq. 1.9, Eq. 1.10, Eq. 1.14, and Eq. 1.15. In the case a quasi-equilibrium holds between  $m_2^+$  and  $m_{2,a}^+$ , Eq. 1.14 would be replaced by another expressing equilibrium between precipitates in solution and on periphyton.

There are several kinetic and equilibrium constants which must be determined either through literature estimates or direct experimentation on a site-specific basis:

$$\mu_{max,20}, K_I, \Theta_\mu, \Theta_R, R_{20}, Q, k_{settle}, K_{11}, K_{12}, k_{sieve} \quad (1.18)$$

In addition there are the rate constants associated to Eq. 1.10 or Eq. 1.13, and Eq. 1.14 or a corresponding equilibrium expression. Finally, there are site-specific constants  $v_p$ ,  $c_p$ ,  $v_{flow}$ , and  $c_{surf}$ .

It should be emphasized the model presented is not just of academic interest, but can also serve as a management tool. This becomes clear when one recognizes that some of the functions and parameters are in fact control functions and parameters. Importantly, the output of the model, that is  $m^+(t)$ , changes depending on the value of these externally adjustable functions and parameters. For example, changing  $k_{exchange} = Q/V$  is physically equivalent to changing the flow rate into the pond, the volume of the pond, or a combination of both. Changing  $nA$  amount to changing the number of trees in the pond, the surface area of the tree, or a combination of both. The nutrient loading functions  $W_1(t)$  and  $W_2(t)$  represent the times at which a given amount of fertilizer is applied. By changing them the growth of the periphyton is altered, and consequently the uptake of  $m^+$ . The ultimate aim of biological polishing models, once they are calibrated and verified, is to adjust the control functions and parameters so the  $m^+(t)$  remains below some legislatively set value, and to optimize the entire process on the basis of management criteria.

## 1.5 Computing Facilities Needed

To solve the coupled set of differential equations representing the system dynamics requires access to a sufficiently powerful computer. At the U. of T. an account on a local area minicomputer (UNIX operating system) interfaced with a desk top PC would be ideal. The cost of this, I estimate, will be no more than \$ 50/month (the actual amount depends on how much CPU I use in a month, and can be monitored). Alternatively, Boojum Research could purchase dynamical systems software supportable by a 486 PC, which I could then run on my own PC. The cost of an entire package of this sort would be up to \$2000 (I have some sales literature on the software if you would like to see it).

To solve the system of differential equations given above, I must learn how to use the various computer mathematics libraries available at the U. of T. This will take a few weeks. Once I have done this I will be ready to compute the simple model presented and generate some simulated time curves of metal concentrations in polishing ponds over the year.

# Research Interests

## 1.1 Introduction

Below I describe in a general manner the basic physics which underlies ecological modelling. First, I briefly summarize the theory of self-organization developed by the Belgian physical chemist and Nobel laureate Professor Ilya Prigogine and his group in Brussels (incidentally, Prigogine was one of my Ph.D. examiners). I then outline the role of nonlinear mathematics within this theory. Finally, I describe in more detail the ecological research I have undertaken at Boojum Research and Technologies.

## 1.2 Self-Organization of Ecosystems

Perhaps the most conspicuous aspect of nature is that it is in constant change, and that this change is not ordinarily reversible. One of the most profound discoveries of recent times is that irreversible processes operating far from thermodynamic equilibrium can be the source of order. If a physical system (i) exchanges both energy and matter with the external environment, (ii) has catalytic, cross-catalytic, or autocatalytic chemical kinetics, and (iii) is constrained by the surroundings, then self-organization is possible. Under appropriate conditions, stable states characterized by spatial and temporal order may spontaneously appear from unstable, nonequilibrium states—these are referred to as dissipative structures by Prigogine and his co-workers. Most interestingly, ecosystems satisfy all these criteria: they exchange matter and energy with the surroundings; the hydrobiogeochemical reactions occurring within them are in general complex and nonlinear; and they are constrained by their external environment. Therefore, the structure and function of ecosystems can, in a very basic way, be understood as a problem of self-organization of nonequilibrium matter.

## 1.3 Mathematical Analysis of Complex Systems

The mathematical language used to describe complex physical systems is dynamical systems analysis, a branch of mathematics originated by Poincaré. The basic idea is to represent the instantaneous state of a physical system as a point in mathematical phase space. The dynamical evolution of the system, which is given in terms of a set of evolution equations, is then a trajectory in this space. In thermodynamics, the phase space is a Hilbert-Sobolev space of local thermodynamic state variables, and the evolution equations are various nonlinear conservation equations. Similarly, in chemical and biochemical systems, the phase space is usually a Hilbert-Sobolev space of local quantities, and the evolution equations are a coupled set of nonlinear partial differential equations. On the basis of nonlinear mathematics, it is possible to explain the ordered and structured patterns observed in many far from equilibrium systems. Nonlinear mathematics is central to the theory of self-organization: stability analysis, bifurcation analysis, perturbation methods, and computer modelling are all part of the theories' machinery.

## 1.4 Hydro-biogeochemical Ecological Models

Currently, I am an NSERC fellow at Boojum Research and Technology, an environmental engineering firm based in Toronto. Boojum uses microbiological methods to control acid mine drainage, and is a pioneer in this field. From the standpoint of physics, the ecological systems that Boojum studies and manages are thermodynamically open, hydro-biogeochemical systems. It is possible to model these systems mathematically. To begin with, putative models would be dynamic because flow velocities, chemical concentrations, sediment, microbial count, and biota vary with time. Furthermore, the models ought to be internally descriptive, causal models, because only by examining the operation and interrelations of basic physical, chemical, and biological processes is a deeper understanding of hydro-biogeochemical systems possible (a “black box” approach, which is sometimes adopted in ecological modelling, is not nearly as powerful for it only relates observations, but does not explain them at a more fundamental level). Casual models are quantified by means of differential equations which represent the actual physical, chemical, and biological processes taking place in the system. *Finally, it should be emphasized that mathematical models of tailing ponds, polishing ponds, and open pits are intended not only as research tools but also as environmental management tools, useful for testing engineering measures before they are actually implemented on site. Also, simulation packages can be useful in promoting sales for they enable a potential client to see the effects of various engineering measures in simulated time, and thereby to gain confidence in the technology.*

In the following, I first summarize the basic physics of open thermodynamic systems, and discuss how it applies to ecological systems. Next, I outline a simplified modelling approach which is useful for ecological systems, and give a few examples to illustrate the method. I also briefly discuss the exciting possibility of nonlinear dynamics in ecological systems. Finally, I cite a wetland model which resembles a Boojum polishing pond, and comment on the work to be done.

### 1.4.1 Irreversible Thermodynamics

Consider an open macroscopic system in a volume  $V$  bounded by a closed surface  $\Sigma$  (see Fig. 1.1). An extensive quantity  $F(t)$  for  $V$  is given as:

$$F(t) = \int \rho(\mathbf{r}, t) f(\mathbf{r}, t) dV \quad (1.1)$$

Here  $f(\mathbf{r}, t)$  represents the density of  $F(t)$  per unit mass (specific variable), and  $\rho(\mathbf{r}, t)$  represents the mass per unit volume as a function of position and time. For example, if  $f(\mathbf{r}, t) = 1$ , then  $F(t) = M(t)$  is the mass as a function of time within  $V$ . Under the most general nonequilibrium conditions, an arbitrary extensive quantity  $F(t)$  is not expected to be conserved (for example, matter is produced and consumed within  $V$ , and exchanged with the environment):

$$\frac{dF(t)}{dt} = P[F] + \phi[F] \quad (1.2)$$

Here  $P[F]$  is a source production term and  $\phi[F]$  is a flow term describing the exchange of  $F$  with the surroundings.

With various choices of  $f(\mathbf{r}, t)$ , Eq. 1.2 leads to the following set of balance equations [1]:

$$\frac{\partial \rho_\gamma}{\partial t} = -\nabla \cdot (\mathbf{J}_\gamma + \rho_\gamma \mathbf{v}) + \sum_r \nu_{\gamma r} v_r \quad (1.3)$$

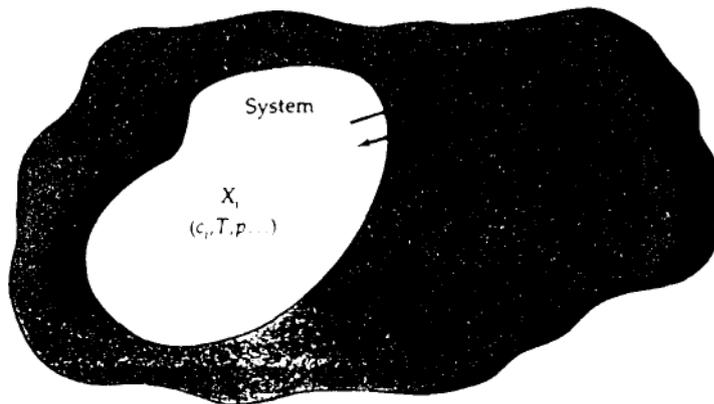


Figure 1.1: Open thermodynamic system.

$$\frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{J}_e \quad (1.4)$$

$$\frac{\partial s}{\partial t} = -\nabla \cdot \mathbf{J}_s + \sigma \quad (1.5)$$

$$\frac{\partial(\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{v} \mathbf{v}) \quad (1.6)$$

Here  $\rho_y$  is mass per unit volume of component  $y$ ;  $\mathbf{J}_y$  is diffusion flux;  $\mathbf{v}$  is the center of mass velocity;  $\nu_{y,r}$  are the stoichiometric coefficients;  $v_r$  are reaction rates;  $u$  is energy density;  $\mathbf{J}_e$  is energy flux;  $s$  is entropy density;  $\mathbf{J}_s$  is entropy flux;  $\sigma = \sum_i J_i X_i$  is the entropy production;  $\mathbf{P}$  is the pressure tensor. To close these equations a phenomenological relation between thermodynamic fluxes  $J$ , and forces  $X_i$ , and a local equation of state is needed. For a chemical/biochemical system, the reaction terms are specified separately, usually on the basis of chemical/biochemical kinetic theory. *In summary, these equations in principle describe the physical, chemical, and biochemical interactions in a multi-component nonequilibrium system.*

We can recast Eq. 1.3-Eq. 1.6 (a set of coupled partial differential equations) in a more compressed notation:

$$\frac{\partial \chi^i(\mathbf{r}, t)}{\partial t} = \mathcal{F}^i(\chi_1, \dots, \chi_n) \quad i = 1, \dots, n \quad (1.7)$$

Here  $\{\chi^i(\mathbf{r}, t), i = 1, \dots, n\}$  are the state variables  $\rho, \mathbf{v}, u, s,$  and  $v_r$ , and  $\mathcal{F}^i$  are complicated functions of the  $\chi^i$ 's and their derivatives. The main point of a dynamical formalism is the ability to follow the evolution of a system in time. This we can visualize geometrically as follows: the instantaneous state of the system is given by a point in the Hilbert-Sobolev space  $\{\chi_1, \dots, \chi_n\}$ , and the time evolution of this state, given by the evolution equations Eq. 1.7, is a trajectory in this space (see Fig. 1.2). Physically, the point in phase space is the system with particular chemical concentrations, flows, energy density, etc., and the trajectory corresponds to these values changing in time.

## 1.4.2 Multiple-unit Models

In principle, the coupled set of nonlinear partial differential equations given in Eq. 1.3 describe any physical system, including ecological ones. However, in applying them to natural settings one

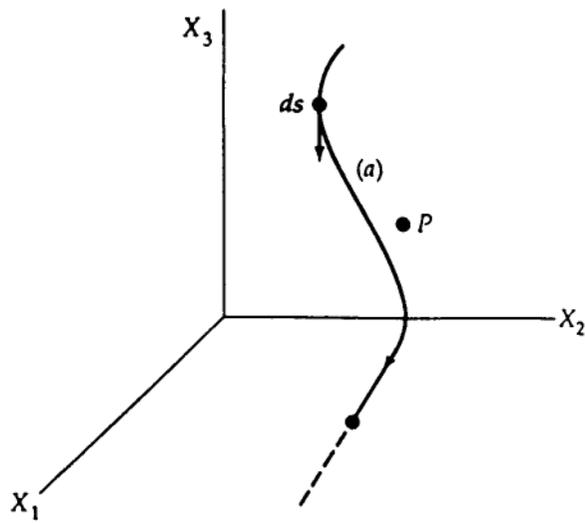


Figure 1.2: Evolution in state space.

is immediately overcome by the complexity of even the simplest ecological systems. The chief obstacle is not the mathematical solution of this coupled set of nonlinear p.d.e's (although this is a nontrivial problem in itself and can only be done computationally) but the limited knowledge of the basic hydrological and biogeochemical processes taking place in ecosystems. **Therefore, the first problem in ecological modelling is selecting the appropriate complexity and structure for a given ecosystem.** This crucially important step is done at the conceptual stage before the machinery of the mathematics is brought to bear. Therefore, while the set of partial differential equations in Eq. 1.7 in principle includes all details of any possible system, the uncertainty of the precise physical, chemical, and biological processes, make it counterproductive to invest too much effort in constructing extremely detailed, complex models—models which ultimately do not give reliable knowledge of actual ecosystems. To use Eq. 1.7 it is necessary to reduce it to a more manageable set by identifying only those processes which are important to a particular ecosystem under study, and to simplify the processes **as much as possible** without ejecting the key dynamics (note, however, the basic physics principles expressed in Eq. 1.7 are still present and act **as** a constraint on any simplifications).

One fruitful approach along these lines is the “lumped parameter model” [2]. In this method the spatial variation of state variables and parameters is simplified by dividing the system into compartments corresponding to spatial regions, and assigning time-dependent state variables to these compartments. Under these assumptions, the original coupled set of partial differential equations Eq. 1.7 reduces to a coupled set of ordinary differential equations. **As** an example of this approach, consider a single chemical compound introduced into a well-mixed lake. This system is easily described by a single-unit or “one-box” model (see Fig. 1.3): the concentration is the state variable  $C$ , and the time evolution of the concentration is quantified by the following ordinary differential equation:

$$\frac{dC}{dt} = k_w C_{in} - k_w C - k_r C \quad (1.8)$$

Here  $C_{in}$  is the externally imposed inflow concentration, and  $k_w$  and  $k_r$  are the water exchange rate and reaction rate in the lake respectively.

To introduce spatial variation in the concentration  $C$ , a first step might be a double-unit or “two-box” model quantified by a coupled system of two ordinary differential equations (see

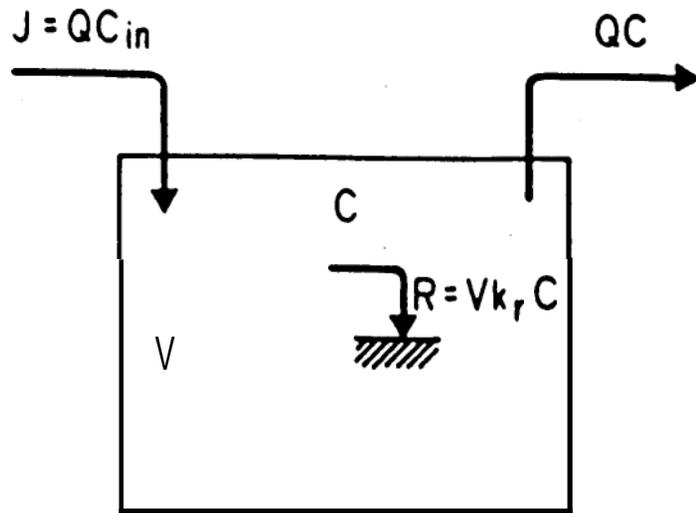
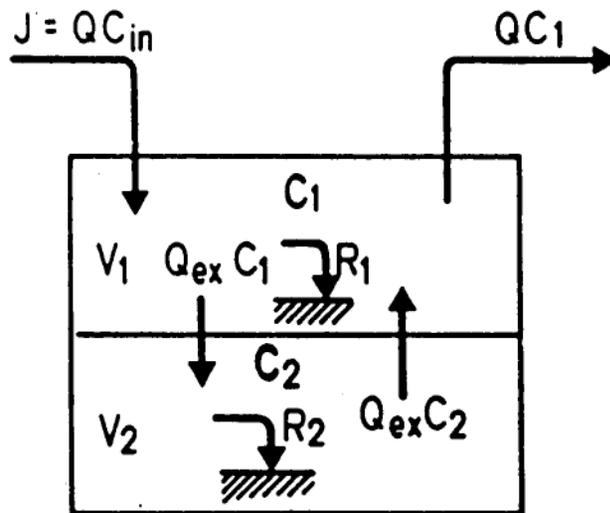


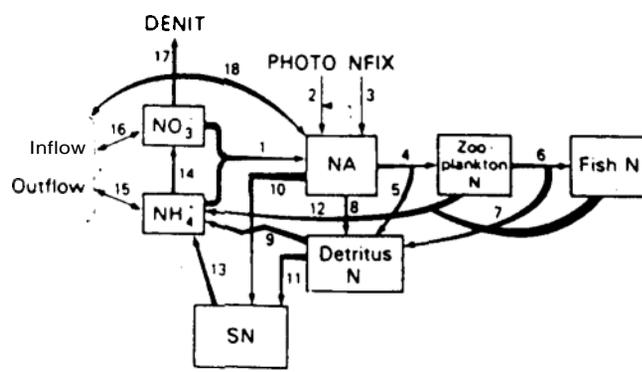
Figure 1.3: One-box model



$$R_1 = V_1 k_{r,1} C_1$$

$$R_2 = V_2 k_{r,2} C_2$$

Figure 1.4: Two-box model



The nitrogen cycle in an aquatic ecosystem. The processes are: (1) Uptake of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  by algae, (2) Photosynthesis, (3) Nitrogen fixation, (4) Grazing with loss of undigested matter, (5), (6) and (7) are predation and loss of undigested matter by predation, (8) Mortality, (9) Mineralization, (10) Settling, (11) Settling of detritus, (12) Settling, (13) Release from sediment, (14) Nitrification, (15), (16) and (18) Input/output, (17) Denitrification.

Figure 1.5: Nitrogen cycle in an aquatic ecosystem.

Fig. 1.4):

$$\begin{aligned} \frac{dC_1}{dt} &= k_w C_{in} - k_w C_1 - k_{r,1} C_1 - k_{ex,1} (C_1 - C_2) \\ \frac{dC_2}{dt} &= -k_{r,2} C_2 - k_{ex,2} (C_2 - C_1) \end{aligned} \quad (1.9)$$

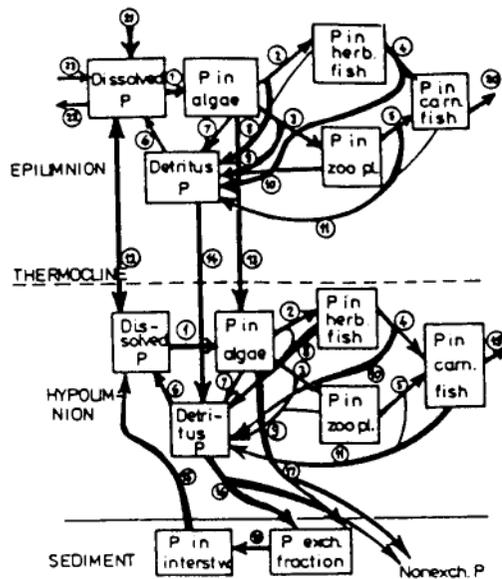
Here  $C_1$  and  $C_2$  are the concentrations of the compound in the two spatial compartments,  $k_{ex,i}$ ,  $i = 1, 2$  are the exchange flows between the compartments, and  $k_{r,i}$ ,  $i = 1, 2$  are the reaction constants in the two compartments. Note that in both cases the inflow rate  $C_{in}$  is an externally fixed variable, sometimes called a “forcing function”. Typically, in real systems it is external variables which when altered produce changes in the state of the system; therefore, these variables are crucial to ecological engineering, since here the basic question often is, “if an inflow rate is varied, how does the system react?”.

More complex box models are shown in conceptual diagrams in Fig. 1.5 (nitrogen cycle in an aquatic ecosystem) and Fig. 1.6 (phosphorus cycle in an eutrophication model). The conceptual diagrams illustrate the state variables, the external variables and how these are interrelated by processes. In the mathematical models corresponding to these conceptual diagrams, each box  $l$  is represented by a single state variable  $\chi(t)_l$ , and the arrows linking the boxes are represented by mathematical expressions coupling  $\chi_l$  and  $\chi_k$ ,  $k \neq l$ . The evolution of each state variable is described by a kinetic equation, similar to those given for the one and two box lake models.

It is straightforward to generalize to an  $m$ -unit system ( $m$ =number of boxes) in which each unit (box) might be described by several state variables, and each variable in a box linked to other variables by specific functions (see Fig. 1.7). The evolution equation for a multiple-unit model is a set of coupled ordinary differential equations [3]:

$$\begin{aligned} \frac{d\chi_l^i(t)}{dt} &= \mathcal{F}_l^i(\chi_l^1, \dots, \chi_l^m) + g_l^i(\chi_{l-k}^i, \dots, \chi_{l+k}^i) \quad i = 1, \dots, n \\ & \quad l = 1, \dots, m \end{aligned} \quad (1.10)$$

Here  $g_l^i$  is the contact function which links a state variable  $\chi_l^i$  to  $2k$  other state variables,  $2k$  being the connection number of the  $i$ th – site. Frequently ecological systems exhibit a structural hierarchy; this is represented by larger boxes enclosing groups of smaller boxes in Fig. 1.7. The



Eutrophication model illustrated by use of P-cycling. Arrows indicate processes. A thermocline is considered. Explanation of numbers are as follow: 1) uptake of phosphorus by algae 2) grazing by herbivorous fish 3) grazing by zooplankton 4, 5) predation on fish and zooplankton respectively by carnivorous fish. 6) mineralization 7) mortality of algae 8, 9), 10), 11) grazing and predation loss 12) exchange of P between epilimnion - hypolimnion 13) settling of algae (epilimnion - hypolimnion) 14) settling of detritus (epilimnion - hypolimnion) 15) diffusion of P from interstitial - to lake water 16) settling of detritus (hypolimnion - sediment) (a part goes to the non-exchangeable fraction) 17) settling of algae (hypolimnion - sediment) (a part goes to the non-exchangeable fraction) 18) mineralization of P in exchangeable fraction 19), 20) fishery 21) precipitation 22) outflows 23) inflows (tributaries).

Figure 1.6: Phosphorus cycle in an eutrophication model.

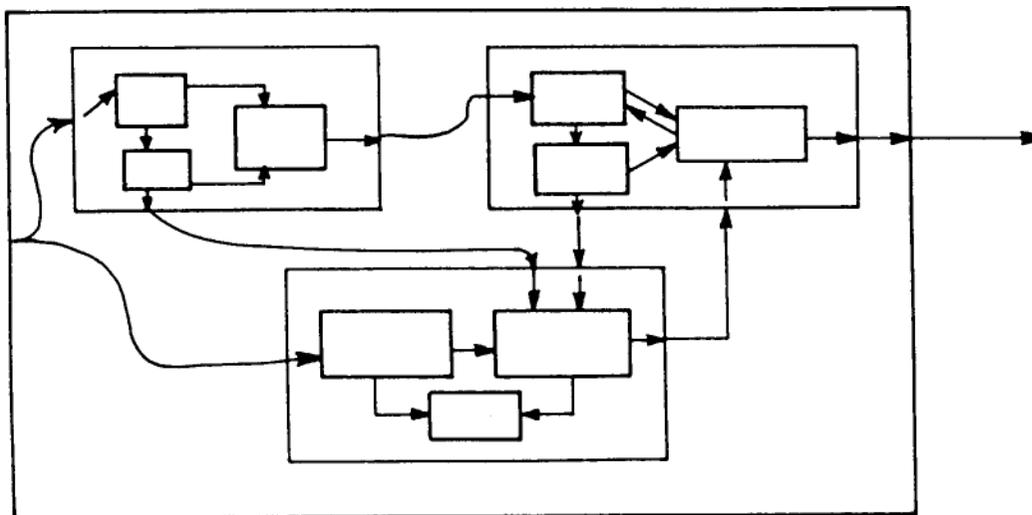
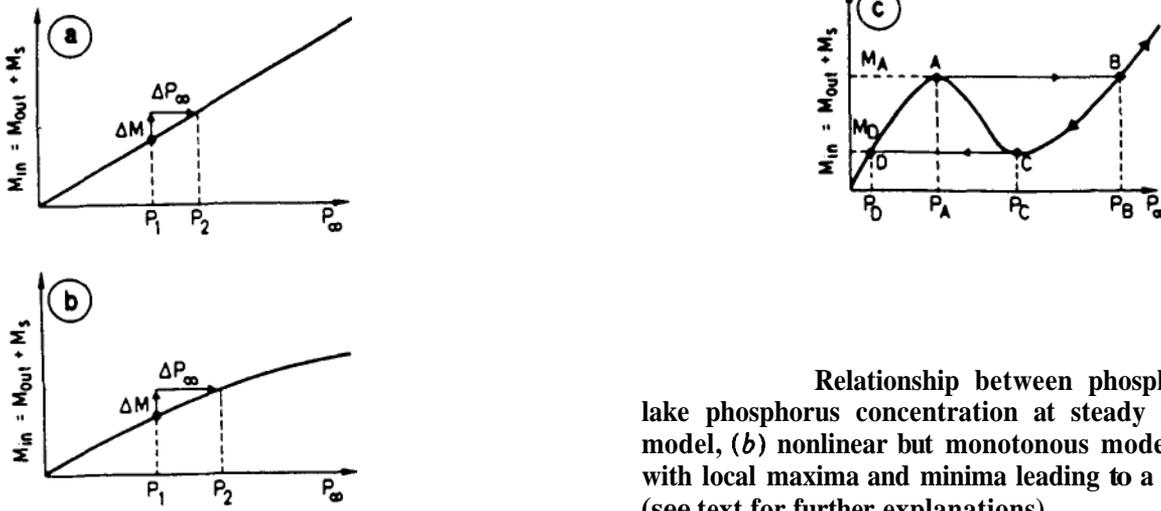


Figure 1.7: Multiple-unit model



Relationship between phosphorus input and lake phosphorus concentration at steady state: (a) linear model, (b) nonlinear but monotonous model, and (c) model with local maxima and minima leading to a hysteresis effect (see text for further explanations).

Figure 1.8: Phosphorus inflow .vs. steady state concentration

larger boxes are referred to as submodels, and are often useful if certain processes are loosely coupled together. As before, the state of an ecosystem is represented as a point in the Hilbert space  $\{x^i\}$ , and its dynamical evolution trajectory in this state space. A steady state is one for which  $\frac{dx^i}{dt} = 0$  for all  $i$  and  $k$ . The importance of steady states is clear: they represent the ecosystem in dynamic balance, concentrations at a constant value, processes in equilibrium or steady nonequilibrium. In general, both the steady state and time dependent solutions of Eq. 1.6 must be evaluated by numerical methods. The stability of the steady state is then determined by the usual methods of linear stability analysis (stability of the steady state is certainly important for environmental management). Finally, and most importantly, the verification, sensitivity analysis, and calibration of the model is done using the available data base for the system.

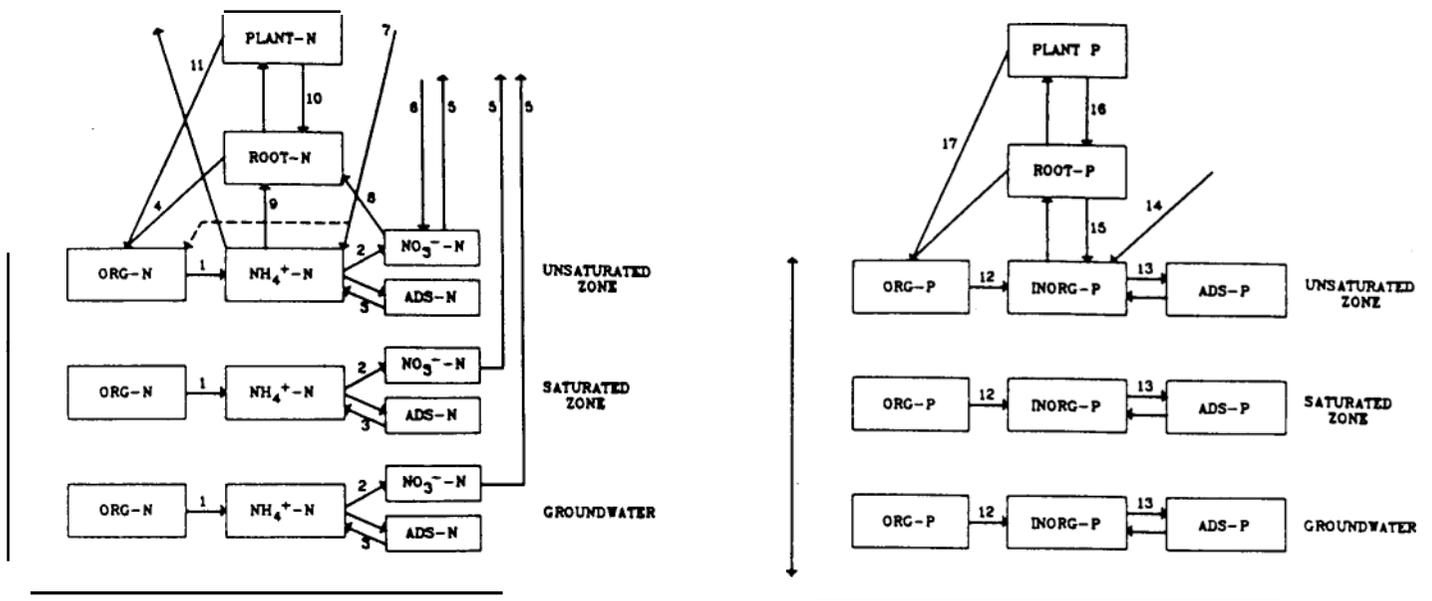
One expects a rich variety of behaviour for an ecological system modelled on this basis, especially if the Eq. 1.10 is nonlinear. To illustrate the potential importance of nonlinearities, consider a simple eutrophication lake model [4]:

$$\frac{dP}{dt} = P_i + \sigma P \quad (1.11)$$

Here  $P_{in}$  is the inflow phosphorus concentration, and  $P$  the phosphorus concentration in the lake. If the parameters  $\rho$ ,  $\beta$ , and  $\sigma$  are independent of  $P$ , then Eq. 1.11 is a linear model with one single steady state solution.

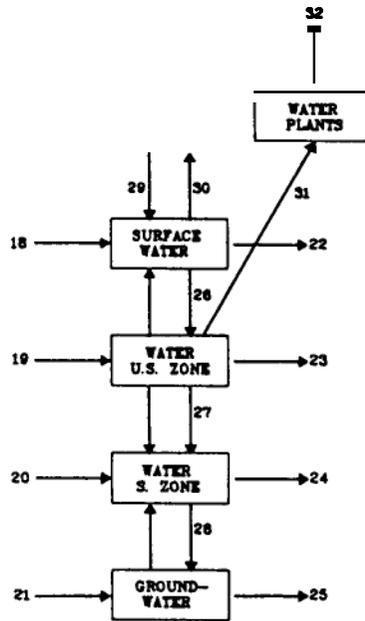
$$P_{\infty} = P_{in} \frac{\rho}{\beta\rho + \sigma} \quad (1.12)$$

We see that phosphorus loading  $P$  is linearly related to the input of phosphorus  $P_{in}$ . However, experiment and theory suggest that the sedimentation rate of phosphorus in general depends on  $P$  nonlinearly, through a nonlinear sedimentation coefficient  $\sigma$ . In this case the steady state solutions of Eq. 1.11 are no longer linearly related to  $P_{in}$ . Since at steady state the total phosphorus input must equal the phosphorus sedimented plus that discharged, i.e.  $M_{in} = M_s + M_{out}$ , the nonlinear dependence of  $M_s$  on  $P$  results in more complex behaviour of steady state concentration  $P_{\infty}$  (see Fig. 1.8). Note that Fig. 7c indicate a "hysteresis effect": the steady state concentration  $P_{in}$  is not unique and depends on how it is reached. Increasing the inflow concentration above **A** results in an abrupt jump to **B**, and corresponding increase in  $P_{\infty}$ . If now the inflow concentration is reduced below **B**, the steady state concentration does not return to **A** but instead move to **C**. Only after  $M_{in}$  is reduced below **D** does  $P_{\infty}$  return to the original branch of **A**.



Nitrogen submodel, horizontal flow in one direction. Vertical flow upwards and downwards. The flows are obtained from the hydrological submodel about the processes (1)-(10), see text.

Phosphorus submodel. Flows as for nitrogen. Processes (12)-(17), see text.



Hydrological model (H-model). 18-21 are horizontal inflows to parcel; 26-28 are exchange of water between zones; 30 is evapotranspiration at surface; 29 is precipitation; 31 is water uptake by plants; 32 is evapotranspiration from plants; 22-25 are outflows from parcel.

The model uses differential equations to express the changes in the state variables. Mineralization, process (1) is described by use of a first order reaction scheme, where the rate constant,  $K$ , is dependent on the temperature,  $T$ , and the moisture,  $\Omega$ , content:

$$K = K_{\max} f(T) f(\Omega), \quad (1)$$

where  $f(T)$  is  $K_T \cdot (T - 20)$  (Bowie et al (1985)) and  $K_T$  is 1.02 - 1.08, averagely 1.05, while  $f(\Omega)$  is

Figure 1.9: Wetland model

This discussion shows that nonlinearities in open systems are not just of academic interest but also of potential practical importance, especially if steady state concentrations in an ecosystem are being controlled by adjusting inflow rates. *It is my belief that the neglect of nonlinearities in ecosystem modelling is the main reason why many models do not always fit the observations.* The problem is not that models are not sufficiently complex (this often makes them more unreliable) but rather that the key processes identified are modelled as linear processes. A great discovery recently in physics is that simple nonlinear models can produce a plethora of complex behaviour—the theory of self-organization. Nonlinearities are expected to play a major role in any biogeochemical system, since many biochemical reactions involving enzyme catalysis have cubic nonlinearities—a prerequisite for complex behaviour (for example, the Michaelis-Menten equation of enzyme kinetics).

### 1.4.3 Modelling ARUM

*The first step in modelling tailing ponds, open pits, polishing ponds etc. is to draw on the expertise of the Boojum research team to aid in constructing a conceptual diagram, reducing the large number of potential factors which influence acidity and microbial alkalinity generation to a manageable set of 15 to 20 state variables. The second step is to write down kinetic equations for each state variable (ordinary differential equations), drawing on the Boojum data base, laboratory results, and literature. The third step is to numerically solve the resulting coupled set of differential equations on the computer, and to investigate the stability of the steady states.*

Important processes in the ARUM (Acid Reduction Using Microbiology) process include:

- (i) Physical processes: transport processes (diffusion and convection), sorption, temperature dependence, and evaporation.
- (ii) Chemical processes: chemical oxidation and reduction, acid-base reactions, photolysis, ionization, complexation, and precipitation, and geochemical aspects of diagenesis.
- (iii) Biological processes: photosynthesis, decomposition, uptake by plants, microbial metabolic reactions, enzyme kinetics, and biological aspects of diagenesis.

It is the case that in a wetland the hydrology and biogeochemistry are to good approximation weakly coupled. For the systems Boojum works with, the conceptual diagram should consist of a hydrological submodel coupled "one way" to a biogeochemical submodel since the hydrological flows transport chemicals, biota, sediments etc., but are not largely influenced by them.

As a final example of a multi-unit model, consider the conceptual wetland model in Fig. 1.9 [5]: There are 14 state variables in the nitrogen submodel, 11 in the phosphorus submodel, and 5 in the hydrological submodel. There are a total of 11 forcing functions.

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