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Cover photograph of a high rate algal pond by Rupert Craggs

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Abstract

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This report considers various issues relating to the development of mathematical models for waste stabilisation ponds (WSPs) and biofilms used for the treatment of sewage and other organic effluents before release into the environment. Initially, we focus on WSPs and a previous model of a pond, considering the processes used, and highlighting a number of uncertainties and problems in the approach taken. We then consider further issues relating to the modelling of a simpler pond system, the High Rate Algal Pond (HRAP), in which there exists a more uniform, controlled environment than in a conventional pond. We conclude that the most significant obstacle in development a reasonable model of any kind lies in the formulation of mathematical models of the basic biological and biologically mediated processes that occur in the pond environment.

A model for a microbial biofilm was also considered, however we found that the existing literature on the subject is confusing and inconsistent. Moreover, a reformulation of the model will be dependent on first understanding the basic biological processes involved, as discussed for the WSP model.

Modelling waste stabilisation ponds

An initial effort was made to formulate a model of some of the biological and chemical processes occurring in waste stabilisation ponds (WSPs), with a view to providing a general tool for the exploration of hypotheses on their operation and behaviour.

To begin with work was based upon two previous models. The first was described by Fritz *et al.* (1979) and Fritz (1985). The second, a modification of the first, was described by Colomer & Rico (1993) and Prats & LLavador (1994)[1]. Both models appear to contain conceptual errors in their construction, in addition to many typographical errors in their presentation. We shall base our discussion on the model of Fritz *et al.* (1979) and Fritz (1985), referring to this as the "Fritz model", as the most fundamental errors appear in these papers.

Basic assumptions and equations

The basic assumptions in the models of Fritz *et al.* (1979) and Colomer & Rico (1993) are as follows.

- The pond is fully mixed, without stratification.
- Hydraulic conditions are steady state (constant volume, inflow = outflow, no evaporation).
- There exists a detrital layer at the pond bottom, which acts as a source and sink of materials. This is modelled as a "black box".
- Pond dynamics can be modelled as an interplay between influent waste, N, P, algae, bacteria (heterotrophs), inorganic C, dissolved O, detritus, pH, and the atmosphere. Autotrophs (nitrifiers) are not explicitly modelled in the Fritz model, although the nitrification process itself is included.

[1]These papers are apparently by the same authors. Their names are F. LLavador Colomer and D. Prats Rico.

For each concentration (e.g., of DO, algal biomass, NH_4-N, or total inorganic carbon) the main equation is

$$\frac{dC}{dt} = \frac{C_i - C}{T} + \sum_{j=1}^{J} (r_C)_j \tag{1}$$

where C denotes the appropriate concentration variable, C_i is its inflow value, T is the residence time, and the quantities $(r_C)_j$, $j = 1,\mathrm{K},J$ (J being the number of processes that affect C) are the rates at which C is lost or gained, via the various transformation processes, sources, and sinks. It is the formulation and quantification of these rates in which the complexity of the problem lies. Once the terms $(r_C)_j$ have been determined for each species, the simultaneous equations (1) can be solved by writing a relatively simple program, or for convenience, using a simulation package (for solving systems of nonlinear ordinary differential equations).

The hydraulic conditions can be made more general (given sufficient data to allow for program runs, but program runs may not be totally clear to a novice reader). A mass balance on a fully mixed, unstratified pond yields:

$$\frac{d(CV)}{dt} = Q_i C_i - Q_o C + V \sum_{j=1}^{J} (r_C)_j$$

from which we obtain

$$\frac{dC}{dt} = \frac{Q_i C_i - (Q_o + dV/dt)C}{V} + \sum_{j=1}^{J} (r_C)_j \tag{2}$$

where V is the instantaneous pond volume, Q_i is the pond influent flow rate, and Q_o the pond discharge flow rate. The pond volume balance gives

$$\frac{dV}{dt} = Q_i - Q_o + \sum_{k=1}^{K} (r_V)_k \tag{3}$$

where $(r_V)_k$ are the various rates affecting the pond volume. Accurate description and measurement of these rates can lead to the solution of (3), and hence to (2).

A special case of (2) and (3) is where the pond volume is kept constant. In this case, we obtain:

$$\frac{dC}{dt} = \frac{Q_i C_i - Q_o C}{V} + \sum_{j=1}^{J} (r_C)_j \tag{4}$$

and

$$Q_o = Q_i + \sum_{k=1}^{K} (r_V)_k \tag{5}$$

The state variables that are included in the Fritz model are:

- soluble organic substrate ("waste") concentration measured as BOD (mg L^{-1})
- algal biomass concentration (mg L^{-1}). Separate algal species are not considered
- bacterial biomass concentration (mg L^{-1}). Only aerobic heterotrophs are modelled explicitly
- dissolved oxygen (DO) concentration (mg(O) L^{-1})
- total inorganic carbon (mg(C) L^{-1})
- organic nitrogen (mg(N) L^{-1})
- ammoniacal nitrogen (mg(N) L^{-1})
- nitrate nitrogen (mg(N) L^{-1})
- organic phosphorus (mg(N) L^{-1})
- inorganic phosphorus (mg(P) L^{-1})
- alkalinity (mg($CaCO_3$) L^{-1})
- detrital mass (mg cm^{-2})

"Ammoniacal nitrogen" represents the sum of the concentrations of ammonium (NH_4^+) and ammonia (NH_3) in solution, both expressed as N.

Algae and bacteria are each modelled as a uniform "biomass concentration", instead of modelling individual numbers. Algal and bacterial biomass and the sediments (detritus) represent reservoirs of nutrients that interact with the nutrients and organic matter in solution. The sizes of these reservoirs are affected largely by temperature, light (algae), and nutrient/organic matter availability.

The processes by which nutrients are transformed in the Fritz model are:

- photosynthesis (algae)
- aerobic heterotroph growth
- "decay" (algae and bacteria)
- nitrification
- mineralisation
- benthic regeneration
- sedimentation (settling)
- interfacial transfer of oxygen and carbon dioxide (re/deaeration), and ammonia (volatilisation).

The first six of these processes are biologically mediated and hence represent the greatest challenge to describe. We consider a number of these state variables and transformations in more detail.

Algal growth (photosynthesis)

In photosynthesis, carbon dioxide, ammonia (or nitrate, if ammonia is deficient), inorganic phosphate, and water are transformed into algal biomass. Oxygen is also released as a waste product. The Fritz model adopts a "constant stoichiometry" approach, in which a chemical equation for algal growth (photosynthesis) is derived from a determination of an "average" chemical composition of algae. Given some average algal composition (such as the commonly used $C_{106}H_{263}O_{110}N_{16}P$), and assumptions regarding the sources and sinks of various elements, one may form a chemical equation by balancing the number of moles of

each element and charge on each side of the chemical reaction. The results are equations like the Redfield equations (Stumm & Morgan 1981, table 4.5):

$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2 \qquad (6)$$

for nitrate uptake, and

$$106CO_2 + 16NH_4^+ + HPO_4^{2-} + 106H_2O \rightarrow C_{106}H_{263}O_{110}N_{16}P + 106O_2 + 14H^+ \qquad (7)$$

for ammonia uptake (it is generally assumed that ammonia, if present, will be consumed in preference to nitrate). The equation for ammonia presented here differs from that presented by Stumm & Morgan (1981), which does not preserve charge.

We can see that such equations, if "correct", provide a way to link the rates of uptake and release of various nutrient sources and alkalinity to the rate of increase in algal biomass. For lack of any better description, these equations can also be applied in reverse, to represent the processes of "respiration", "death" or the general process "decay" (more on these processes will be presented later).

Note that the formula $C_{106}H_{263}O_{110}N_{16}P$ for algal composition appears to have been derived from the "Redfield ratio" (Redfield *et al.* 1966), which simply relates the quantities of carbon, nitrogen, and phosphorus in algal biomass. I do not know the method by which the quantities of hydrogen and oxygen in the above formulation were obtained. There is some knowledge of the variability of the nutrients C, N, and P in algal biomass, but there does not appear to be much information on the variability of O and H. Consequently, the Redfield equations may be more reliable at predicting changes in C, N, and P nutrient pools than on O and in particular, H (and its effect on alkalinity).

The Redfield ratio relates to a marine alga (not a freshwater one). Algal populations in ponds generally consist of a wide variety of species of different average stoichiometry. In addition, it is well recognised that algal composition is not constant over time. Algae have the capacity to take up and store nutrients when they are available in excess, or grow with a deficiency when a nutrient is limiting.

There are generally uncertainties as to the exact sources and sinks of the nutrients required for growth. Algal photosynthesis in ponds can increase the pond pH. As pH increases, dissolved carbon dioxide (CO_2) is converted to bicarbonate (HCO_3^-), then carbonate (CO_3^{2-}). In this situation, algae must either stop growth, or take up either or both of bicarbonate and carbonate. There is evidence to suggest that this is indeed what happens, for at least some algal species (Goldman *et al.* 1972). Consequently, new stoichiometric equations are to be derived for them.

It has also been proposed that a significant amount (25–50%) of algal growth may be heterotrophic (Richmond 1986). Equations (6) and (7) do not apply for this form of growth. It is possible, however, that the net result of the modelled microbial breakdown of substrate and algal growth on the inorganic products of this breakdown may be roughly equivalent to heterotrophic algal growth on the substrate, assuming steady state conditions.

Beyond the determination of C:N:P ratios in algal biomass, there does not appear to have been much research specifically considering the accuracy of the Redfield equations in predicting the effects of algal growth on all the species concerned. Consequently, the assumption that the Redfield equations are an accurate representation of algal growth is a very strong one, which is often made regardless.

Apart from the many uncertainties regarding the accuracy of the Redfield equations, they do have advantages. They are simple to derive (assuming some chemical composition like $C_{106}H_{263}O_{110}N_{16}P$ for biomass) and use, and they provide much information, including the effects of algal growth on alkalinity, via the inclusion of H^+ ions in the equations.

In the Fritz model, algae are represented by a biomass concentration X_a (mg L^{-1}). Under the assumption of constant stoichiometry, the rate (r_{ag}) at which X_a is increasing (due to photosynthesis) is assumed to be proportional X_a itself:

$$r_{ag} = k_{ag} X_a \tag{8}$$

(Fritz *et al.* (1979) call this term r_{xal}, and include "decay" in the definition.) This looks like an exponential growth term but is not, because the coefficient k_{ag} is defined to reflect the dependence of photosynthesis on other factors, like light (L) availability, temperature (T), and the availability of nutrients (CO_2, inorganic N, and inorganic P) needed for growth:

$$k_{ag} = \mu_a f_1(L) f_2(T) \left[\frac{CO_2}{K_{CO_2} + CO_2}\right]\left[\frac{N_i}{K_{N_i} + N_i}\right]\left[\frac{P_i}{K_{P_i} + P_i}\right] \tag{9}$$

Here, μ_a is an algal specific growth parameter, for which a suitable value (relevant to the algal species found in ponds) is required. The light and temperature dependent functions $f_1(L)$ and $f_2(T)$ also generally involve one or more parameters that must also be determined. The final three bracketed factors in the expression for k_{ag} are termed "Michaelis-Menten" or "Monod" factors, after the various authors who proposed such descriptions. They are essentially smooth "switches" that turn off growth when sources of nutrients (in this case carbon, nitrogen, and phosphorus) are limiting.

The Fritz description of the algal growth rate given by (8) and (9) requires some modification to account for possible bicarbonate, then carbonate uptake as pH increases, as well as possible inhibition of growth at higher pH.

Given (8) and (9), we can obtain rates of increase/decrease of nutrient sinks/sources by relating the masses of each component in equations (6) and (7) as appropriate. As an example, we express the rate of dissolved oxygen concentration production due to photosynthesis as

$$r_{O_2,ag} = a_{O_2,ag} r_{ag} \tag{10}$$

where $a_{O_2,ag}$ represents the ratio (mass of oxygen produced)/(mass of algae produced). Assuming the validity of (6) and (7), we have that the mass of one mole of algae is

$$12\times106 + 1\times263 + 16\times110 + 14\times16 + 31\times1 = 3550$$

Consequently, assuming growth on ammonium (equation 7), we have:

$$a_{O_2,ag} = \frac{106\times16}{1\times3550} = 0.478$$

An alternative to using (6) or (7) to determine $a_{O_2,ag}$ is to measure this quantity experimentally. Similar stoichiometric ratios for the uptake of carbon dioxide, bicarbonate, carbonate, ammonium, nitrate, and phosphate could in theory be determined experimentally. However, in practice this is unlikely to be feasible, due to the expense, the difficulty in reproducing pond conditions in the laboratory, and the presence of confounding effects such as microbial activity or algal respiration and decay.

The constant stoichiometry approach may be applicable in steady state or slowly varying conditions to provide rough estimates of the rates of production (and release) of nutrients as a result of algal growth and decay processes. They are likely to provide more accuracy when applied over longer periods of time. For shorter periods of time and non-steady-state situations, a non-constant stoichiometry approach may be required. We now briefly consider this.

A widely accepted and used alternative to the constant stoichiometry approach is "Droop kinetics". Droop (1968) proposed that nutrient uptake was not directly proportional to the growth rate and that Monod factors may not accurately represent the limitation of growth by nutrient availability. Instead Droop proposed the "cell quota model" of nutrient uptake in algae. The cell quota (Q) of a given nutrient can be defined as the mass (or moles) of nutrient per cell. In the cell quota model, nutrient uptake is still regarded as proportional to the amount of algae present, but the cell growth rate (μ) is assumed to be related to the cell quota by the equation:

$$\mu = \mu'_m\left(1-\frac{k_Q}{Q}\right)$$

where μ'_m is a maximum growth rate and k_Q is a "subsistence quota" of the appropriate nutrient. The subsistence quota is the minimum quota necessary for life, and may sometimes be interpreted as representing a structural component of the algal biomass. The cell quota model allows us to incorporate into our modelling a recognised phenomenon known as "luxury uptake", where an organism in an environment rich in a given nutrient absorbs and stores more of that nutrient than is immediately needed for growth.

The cell quota model provides a representation of cell growth and nutrient content that is widely regarded as more realistic than the constant stoichiometry model, and can better simulate nutrient dynamics in non-steady-state environments, over shorter periods of time.

However, the cell quota model has its limitations. It tends to focus on a single nutrient at a time, and does not provide full information on a range of nutrients, as well as alkalinity. Legovic & Cruzado (1997) presented a model of growth on multiple nutrients with Droop mechanics, but it neglected alkalinity. The cell quota model also focuses only on uptake/growth, and does not deal with any release of nutrients as a result of any "decay" processes, or the release on oxygen in photosynthesis. Consequently, it has tended to be used in modelling situations that focus on a single nutrient, where other complicating issues can be ignored. The cell quota model is also more parameter-intensive. Although parameter values for many species exist in the literature, there remmains the problem of applying parameter values for a specific species to a mixed population.

Generally the cell quota and more sophisticated models for algae-nutrient interactions have been successfully used in situations which tend to simplify the environment description. pH issues are ignored, and nutrient sources are defined only loosely. For example, such models may represent carbon in terms of organic carbon and total inorganic carbon (TIC), instead of

attempting to consider any detailed stoichiometric formulation for the organic carbon sources, or the CO_2 - HCO_3^- - CO_3^{2-} subsystem of TIC.

Algal "decay"

Algal growth occurs through the process of photosynthesis (neglecting for now the issue of heterotrophy) and leads to an increase of algal biomass. There are also a number of mechanisms that lead to a decrease in biomass. Some of the more significant of these include:

- respiration
- lysis (death)
- settling
- grazing by zooplankton
- excretion
- leakage

Settling can be represented as a rate that is linearly proportional to the algal biomass concentration, and represents a contribution of algal biomass to the detrital layer. The remaining processes (including grazing, when grazers are not modelled explicitly) are generally regarded as representing conversion of algal biomass back into nutrients, or into non-living organic matter in solution.

There is much uncertainty in describing many of the processes that reduce biomass, especially when one tries to track the nutrient transformations that result. This is further complicated by the various definitions in the literature of terms like "growth", "death", "respiration", and "decay". In this discussion, "growth" refers specifically to the production of new cell material from nutrient and energy sources. "Respiration" refers to the consumption of either cell material or organic substrate to provide energy distinct from that required for synthesis of new biomass during growth. "Death" refers to the process by which a cell ceases to function, releasing its organic material for further heterotrophic growth. "Decay" is used when we wish to lump together some or all of the biomass loss factors (potentially including death, respiration, grazing, etc).

In algae, respiration is assumed to represent the consumption of algal biomass for energy purposes. There are various energy requirements in the algal cell — for our purposes we split them into "synthesis" (or "growth") energy and "maintenance" energy. Synthesis energy is that required for the conversion of inorganic material into algal biomass; maintenance energy is that required for continued existence. In photosynthetic growth, it appears to be assumed that the energy for synthesis is provided directly from sunlight, while maintenance energy (often equated with "respiration") results from the consumption of biomass (which is what we assume in this work). Naturally, the real situation is not this simple: however, we are mainly concerned at this stage with suitable "black box" representations of these processes which suffice to approximate the net result. Under these assumptions, we can neglect growth energy, and simply regard respiration as the consumption of biomass for maintenance energy, represented by the reverse of either equation (6) or (7). Which equation to use is not known to me.

The biomass consumed for energy purposes is unlikely to be accurately represented by the average biomass chemical composition. Energy stores are usually carbohydrates and the average composition of the cell can be expected to change when said stores are consumed without being replenished.

Some authors describe population dynamics quite simply in terms of "growth" representing an increase in algal biomass, and "decay", representing any process that results in a loss of

biomass (sometimes even including settling). For decay, equations like (6) and (7) are again applied in reverse, representing the (eventual) production of nutrients as a result of the unknown processes involved in "decay". Other reservoirs of nutrients from algal biomass are either accounted for by other terms in the model or assumed to be negligible. These approximations seem more appropriate for the longer term, and regarded as a representation of the "steady state". Once defined in this way, the problem is then to determine suitable parameter values for the rates of growth and decay from experiment, the literature, or by model calibration. This in itself may be complicated by the vague nature of the "growth" and "death" definitions, the difficulty in simulating a realistic growth environment in the laboratory, and the problem of determining the desired values from what little can actually be measured.

The Fritz model attempts to use the "growth vs. decay" approach. "Decay" appears to imply any loss of cell material. In order to keep track of the nitrogen and phosphorus released by decay processes, the Fritz model includes the variables "organic nitrogen" and "organic phosphorus". Algal and bacterial nitrogen and phosphorus released by decay processes are fed by the model into these pools. They are then eventually released as ammoniacal nitrogen and phosphate as a result of "mineralisation" processes, which are described as simple first order rates, proportional to the amounts of organic N and P present.

In some ways this seems a reasonable way to handle the release of nitrogen and phosphorus as a result of decay processes. The approach avoids formulating stoichiometric equations for "decay", instead focussing on conserving the total N and P in the system. However, the effects of decay and mineralisation processes on other factors such as oxygen are neglected. (The Fritz model includes a term for the influence of bacterial "decay" on oxygen, but it is not at all clear how this term has been derived, or what sense it makes.) Carbon is not handled in a similar manner — instead, bacterial carbon is immediately released as dissolved carbon dioxide by "decay". It is unclear what the reasoning for this is.

Another problem with the Fritz model approach to "decay" is that the concept of "mineralisation" represents the net effects of microbial activity, including heterotrophic growth on decay products and respiration. "Organic N" and "organic P" in the Fritz model appear to be regarded as separate from the organic N and P content of the main substrate (effluent). Quite apart from the impossibility of separating these different types of organic materials in water quality measurements, it does not seem sensible to separate bacterial growth on substrate from bacterial growth on decay products in this way. Indeed, the Fritz model does not explicitly model bacterial growth on anything other than the main substrate. Growth on lysis products is not directly modelled — yet if lysis products represent a significant source of substrate for growth, then bacterial growth on these products should be explicitly described. However, it is not known what a suitable chemical formulation for lysis products would be, so the use of stoichiometric equations for bacterial growth (see below) on this alternative substrate may not be feasible.

The inclusion of grazing in "decay" may not be a very realistic assumption to make, as the interaction between grazer and prey populations is well known to be a dynamic nonlinear one. However, the nature of the grazer/prey interactions is heavily dependent on the species considered. In a pond there may be any number of grazers of potential significance, and it is not clear which one(s) will predominate, or whether the appropriate parameter values exist for these in the literature. Grazer/prey modelling is usually either applied to a specific interaction (between particular species), or is used only to elucidate the general properties of such interactions and is not intended to predict the behaviour of any particular system. Inclusion of a detailed grazing submodel into the pond model should probably be deferred until the purpose of such a submodel is clarified.

Speciation of algae types may also represent a problem in modelling a pond system. The Fritz model assumes a single "average" algal population, which can be described using a single set of parameters. In reality, pond performance may vary over the longer term simply due to changes in the dominant algal species.

Bacterial growth

We now turn our attention to the general issue of heterotrophic growth, in which an organic substrate is used for both biomass and energy. We defer for the moment any discussion of maintenance energy, and focus on growth (synthesis). We also concentrate on bacterial growth, rather than heterotrophic growth of algae, although we may assume that heterotrophic algal growth may be described by similar means (in the Fritz model, only bacteria are assumed to grow heterotrophically). The interaction between algal heterotrophic growth and photosynthesis remains to be considered, however.

Heterotrophic growth (excluding basal or maintenance respiration) has a synthesis component and an energy component. The synthesis component represents the direct conversion of substrate (soluble organic waste, represented by $C_{18}H_{19}O_9N$ in the Fritz model) to cell biomass (represented by $C_5H_7NO_2$). The energy component consists of the oxidation of substrate to provide energy for the growth process. Thus, not all of the carbon consumed by a cell will appear in the cell biomass. The difference is accounted for by a yield factor, Y, defined for now as the ratio of bacterial biomass produced to the substrate consumed during growth (the exact definition of the yield constant depends on the selected units of measurement used for biomass and substrate). Given average compositions of substrate and bacterial biomass, assumptions regarding the sources and sinks of nutrients, a value for the yield, and the assumption of constant stoichiometry, one may derive stoichiometric equations representing heterotrophic growth, similar to the Redfield equations for photosynthesis. Here is an example, taken from Henze *et al.* (1995, p. 68):

$$100C_{18}H_{19}O_9N + 74NH_3 + 880O_2 \rightarrow 174C_5H_7NO_2 + 930CO_2 + 452H_2O \qquad (11)$$

From this equation one may calculate that the yield used to construct this equation is 0.5mg(biomass)/mg(substrate). One may also separate this equation into the components

$$\frac{145}{3}C_{18}H_{19}O_9N + \frac{377}{3}NH_3 \rightarrow 174C_5H_7NO_2 + \frac{145}{6}O_2 + \frac{116}{3}H_2O$$

$$\frac{155}{3}C_{18}H_{19}O_9N + \frac{5425}{6}O_2 \rightarrow 930CO_2 + \frac{155}{3}NH_3 + \frac{1240}{3}H_2O$$

with the first representing the synthesis component, and the second representing the growth energy component. The second component may sometimes be termed "exogenous" respiration — substrate is assumed to be immediately "burned" for energy purposes, without first being incorporated into biomass.

Given an equation such as (11), the rate of bacterial growth (r_{bg}) is then represented by an expression of the form

$$r_{bg} = \mu_m X_b \left[\frac{S}{K_S + S}\right]\left[\frac{O_2}{K_{O_2} + O_2}\right]\left[\frac{N_i}{K_{N_i} + N_i}\right]\left[\frac{P_i}{K_{P_i} + P_i}\right]$$

representing the gain in bacterial biomass concentration per unit time, where μ_m is a bacterial maximum specific growth parameter, X_b is the bacterial biomass concentration, and the final four bracketed terms implement growth limitation by substrate (S), dissolved oxygen (O_2), inorganic N (N_i), and inorganic P (P_i). Rates of nutrient consumption and product formation are then expressed in terms of the growth rate using (11).

Equations like (11) are subject to many of the uncertainties that apply to the Redfield equations. We require that $C_{18}H_{19}O_9N$ and $C_5H_7NO_2$ are accurate average representations for organic wastes and bacterial biomass respectively, which do not vary significantly over the timescales to which the modelling is to be applied. We also require that the yield be known and fixed. These requirements are unlikely to be satisfied in a natural environment. A further complication is that, in general, organic waste will consist of a mixture of fats, carbohydrates, and proteins, which may have different rates of consumption by bacteria.

Note the assumption in (11) of free ammonia as the source of extra nitrogen. This differs from the Redfield equations where ammonium is assumed to be the nitrogen source. The choice of nitrogen source will affect the predictions of alkalinity changes that result from the equations used (equation 11 is neutral, suggesting no affect on alkalinity). I have not determined the reasons for particular choices of nitrogen, and hence again, the issue of alkalinity changes predicted by the equations is in doubt. It remains uncertain whether the lack of an alkalinity change by the net growth of bacteria on substrate is indeed realistic, or whether (11) was simply derived under this assumption, because alkalinity and pH changes were regarded as being of no interest.

Henze *et al.* (1995) do not provide any equation similar to (11) for the uptake of nitrate as a nitrogen source, instead of ammonia. It is not clear whether this should be an issue.

Equations like (11) have been applied in environmentally controlled situations such as activated sludge treatment plants. Here, there is less overall variability in conditions, hence stoichiometric equations like (11) may have more applicability, and may be successfully used in models to predict the behaviour of such a system.

Although it is tempting to simply apply equations like (11) to represent bacterial growth in any model, it is important to remember that the equations must be formulated for a given organic waste (average formulation), bacterial population (average formulation), assumptions regarding sources and sinks, and bacterial yield. All of these are subject to various degrees of variability/uncertainty, especially in natural environments. Equation (11) is an *example*, and ideally should not be accepted as "the equation for bacterial growth" without some sort of confirmation of its applicability.

Bacterial "decay"

If the substrate concentration is reduced, a point will be reached at which substrate is consumed, but no net growth occurs. At this point, the substrate consumed is being used to maintain the basic cell processes, rather than contributing to cell growth. This is what is termed "cell maintenance" or "basal respiration". There are two paths by which the energy required for cell maintenance can be obtained — first, by direct oxidation of external substrate (exogenous respiration) and second, by degradation of cell biomass (endogenous respiration). It is not clear which path occurs in practice, but it is convenient to assume that maintenance energy is obtained by endogenous respiration, represented by the reaction

$$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 \quad (12)$$

This approach has the advantage of more accurately modelling what happens when substrate concentration is limiting.

The endogenous respiration rate is given as a first order term

$$r_{br} = k_{br} X_b$$

representing a loss in bacterial biomass concentration per unit time, where k_{br} is the respiration coefficient. Rates of oxygen consumption and product formation are expressed in terms of r_{br} using equation (12). Note that in this formulation, growth can slow or stop (due to substrate or nutrient limitation), but respiration continues, as one might expect.

One problem is that we would expect endogenous respiration to be limited by oxygen availability, as is growth. This could be addressed by including a typical Michaelis-Menten factor $O_2/(K_{rO_2} + O_2)$ in the definition of r_{br}, thus requiring a suitable value for the half saturation constant K_{rO_2}. If respiration slows or stops due to oxygen limitation, one would also expect bacterial death rates to increase, but it is not clear how this may be modelled. Thus, we cannot expect the model to accurately represent situations in which a pond is oxygen deficient for an extended period of time. Similarly, when growth stops due to nutrient limitation but respiration continues, we would expect death rates to increase, but there is no information known to me on this issue.

Apart from respiration discussed above, bacteria are subject to other "decay" processes, similar to those mentioned for algae. We may also wish to model these, but again there are difficulties in representing the flow of nutrients through such processes.

Of course, the constant stoichiometry assumption remains a problem. Suitable time (and space) averages for the chemical composition of both heterotroph biomass and organic waste are required in order to formulate equations like (11). A value for the yield is also required, and although the procedure for determining this is well established, the values obtained in the laboratory are unlikely to reflect the situation in a highly variable field environment. In addition, in obtaining values of growth yields and respiration rates from the literature, there is usually uncertainty as to the meanings of the values, especially with regard to respiration. Depending upon the nature of the experimental set up, values for respiration may include the effects of death and predation, as well as cell maintenance. Hence there is often confusion between the concept of "respiration" and the more general concept of "decay". This tends to make literature values for "respiration" harder to interpret and less trustworthy.

Phosphorus does not appear explicitly in equations (11) and (12), but its interaction with bacterial growth and respiration is still included in the Fritz model. Fritz *et al.* (1979) appeared to assume that phosphorus is obtained from inorganic P, not from any P component of the organic waste, but it is not clear what the motivation for this is. If this assumption is not correct, then it means that the flow of P through the system is not correctly modelled. However, given this assumption, the rate of decrease of inorganic P due to bacterial growth is expressed in terms of the bacterial growth rate using the observation that the mass of P is generally about one-fifth the mass of N in bacterial biomass. There is no attempt to model different chemical forms of inorganic P in the Fritz model.

It seems that the actual bacterial concentration in a pond is not an easy thing to measure. Consequently, the bacterial component in a pond model is likely to represent an unknown

pool whose size cannot be validated readily. A possible simplification in modelling a pond lies in the general assumption that bacterial processes are "fast", with regard to other processes in the pond. Under this assumption, bacterial activity is itself unlikely to represent a significant limiting step in pond performance. The bacterial population represents a reservoir of nutrients which, it is assumed, responds so quickly to changes in the environment that its effects on the system are negligible. In consequence, we regard bacteria as a process, rather than a model component. The net effect of all the unknown bacterial activity is a simple conversion of organic substrate and oxygen to carbon dioxide, ammonia, and phosphate, whose rate can, it is assumed, be measured without needing to determine the rates of the various processes affecting the bacterial population itself. In making these assumptions, we are stepping back from the complexity of the bacterial processes, wrapping them up in a "black box". We hope that by this approach we are applying a suitable averaging to the bacterial processes, which will provide a reasonable description, sufficient for our purposes.

Pond sediments

The pond sediments represent a reservoir in which nutrients are stored for later release by the bacterial activity. Sediments are built up from the settling of particulate matter in the overlying water, most notably organic (non-living) suspended solids and non-motile algae.

Due to the complexity of and uncertainty surrounding the exact nature of the reactions occurring in the sediments, the Fritz model regards the sediments as a "black box". In this model, sediments are assumed to comprise settled algal and bacterial biomass only. In reality, there should be a significant contribution from suspended organic solids in the influent, which is neglected from the Fritz model. The model tracks the total sediment (area) concentration D_m (mg cm^{-2}) as a function of the settling of biomass and release of nutrients. The rate of increase of the sediment layer r_{1d} (mg cm^{-2} day^{-1}) is calculated from the algal and bacterial settling rates as:

$$r_{1d} = \frac{(s_a X_a + s_b X_b)d}{10}$$

where d is the pond depth (m), s_a and s_b are algal and bacterial settling rate parameters (day^{-1}), and X_a and X_b are the algal and bacterial biomass concentrations (mg L^{-1}). (The expression given above for r_{1d} differs from that given in Fritz *et al.* (1979). They appear to be in some confusion over maintaining the correct units of measurements when transferring from volumetric measures to areal measures.)

Organic matter in the sediments is assumed to be converted into nutrients by unspecified processes occurring in the sediments. Sediment mass is assumed to be lost at a rate r_{2d} proportional to the amount of sediment:

$$r_{2d} = U_r D_m$$

where U_r is a regeneration rate (day^{-1}) coefficient. U_r is expressed as a function of temperature using the Arrhenius form,

$$U_r = U_{r20} \beta^{T-20}$$

where U_{r20} is the regeneration rate at 20 °C (day^{-1}), T is the temperature in degrees Celsius, and β is a dimensionless parameter. Since regeneration of nutrients in the Fritz model is assumed to be the result of bacterial processes, the value for β used is the same as that used for bacterial growth in the overlying waters.

Algal and bacterial carbon, nitrogen, and phosphorus in the sediments are assumed to be mineralised by undescribed processes and released as carbon dioxide, methane, ammoniacal nitrogen, and phosphate. The expression used for the release rate of say, ammoniacal nitrogen, is

$$R_N = U_r D_m (0.063 S_a + 0.124 S_b)$$

where R_N is the rate of release of nitrogen from the benthos (mg cm^{-2} day^{-1}), U_r is a (temperature dependent) regeneration rate coefficient (day^{-1}), and S_a and S_b are the algal and bacterial biomasses as a function of the total settling mass. The constants 0.063 and 0.124 are the stoichiometric ratios of nitrogen to total (dry weight) biomass in algae and bacteria, calculated from the assumed biomass formulations. S_a and S_b are given by:

$$S_a = \frac{s_a X_a}{s_a X_a + s_b X_b}, \qquad S_b = \frac{s_b X_b}{s_a X_a + s_b X_b}$$

where s_a and s_b are the algal and bacterial settling velocities, and X_a and X_b are the algal and bacterial concentrations in the water column.

The resulting rate of increase of ammoniacal nitrogen r_{4am} (mg L^{-1} day^{-1}) in the water body is then given by

$$r_{4am} = \frac{10 R_N}{d}$$

Again, this differs from the formulation of Fritz *et al.* (1979), which does not preserve the correct units of measurement.

Of the released carbon, a proportion (50%) is assumed to be released as methane, which is lost to the atmosphere without further interaction with the system.

We see from the above formulation that the proportions of organic C, N, and P in the sediments are estimated from the rates at which they enter the sediments (S_a and S_b). A better method would be to track the total amounts of organic C, N, and P in the sediments so that their proportions can be calculated exactly.

However, rather than go into how this might be done, we should instead point out that the Fritz formulation of sediment processes suffers from a number of other uncertainties. It seems likely that influent organic matter (suspended solids) is a significant contribution to the sediment layer, which has been neglected from the Fritz model. The Fritz model does allow for a refractory component of influent COD or for a component that is stored in the sediment at lower water temperatures. Curiously, however, there is no actual link between these two components and the pond sediment model. The stored component is described by an

empirical relation of uncertain origin, and the actual amount of COD being stored is not accounted for.

In reality, the processes occurring in the sediments are complex and depend upon temperature and oxygen availability, thus the assumptions regarding the products of sediment regeneration may well be invalid. Van Luijn *et al.* (1999) presented results from measurements on lake sediments that indicate nitrogen can be released from the sediments as nitrate, ammonia, and nitrogen gas in relative proportions that vary with time and environmental conditions.

The value of U_{r20} quoted by Fritz *et al.* (1979) appears to have been obtained from the decomposition of algal biomass alone, and its applicability to an unknown mixture of algal, bacterial, and general organic matter in a pond environment may be an overly strong assumption.

Finally, the Fritz model does not appear to allow for the permanent binding of nutrients in the sediments.

Without further data, it is unclear whether the formulation of sediment processes in the Fritz model provides a reasonable representation or not. Further investigation may be required before such a model is accepted as part of a larger model.

Nitrification and denitrification

The process of nitrification has been included only crudely in the Fritz model, as a rate of ammonium to nitrate conversion which depends upon the nitrifier growth rate, but not upon the size of the nitrifier population itself, which is not modelled. Explicitly modelling the nitrifier population is subject to the same difficulties as in modelling the wider bacterial population. Including nitrifiers as a black box as in the Fritz model is likely to be less realistic than "black boxing" the heterotrophic bacteria, since nitrifiers are slower growing, and hence may represent a limiting factor in the nitrogen transformations occurring in a pond.

Denitrifiers are also modelled in Colomer & Rico (1993) as a simple rate of loss of nitrate due to conversion to dinitrogen (N_2) gas (which is not modelled), without explicitly modelling the denitrifier population. In fact, denitrification is generally carried out by facultative bacteria, which are able to transfer from normal aerobic growth to denitrification under conditions of anoxia. Thus the proportion of bacteria operating as denitrifiers may vary with varying pond conditions, especially when stratification occurs. In a pond that is indeed well-mixed by wind or machinery, denitrification can still occur near the bottom of a pond, or possibly in many small anoxic pockets within the pond. Under these conditions, the assumption of an essentially constant conversion of nitrate to dinitrogen by an insignificant bacterial population may not be unreasonable. However, the magnitude of this rate needs to be determined.

Stratification

It is generally regarded that stratification has a significant effect on pond behaviour and performance in the summer months. Unlike most lakes, where stratification and mixing are seasonal occurrences, pond stratification is a daily occurrence. Unfortunately, modelling such a dynamic change in the environment does not seem feasible at this time. Even if the physics of the stratification itself can be described, there is still the problem of partitioning the various species (algae, bacteria, substrate, nutrients, etc) between the stratified layers. Little seems to be known about this aspect.

Other complications

The Fritz model includes a number of extreme simplifying assumptions, which are probably not reasonable in a general pond, such as the assumption of complete mixing. "Short circuiting", or flow of influent directly across the pond to the pond outflow, is a recognised occurrence in ponds, especially when the pond is stratified. The great simplicity of the hydraulic regime in the Fritz model seems inconsistent with the attempted detail in the microbial process descriptions, making for an unbalanced model design. In addition, the Fritz model, though in some ways detailed, may not be sufficiently general to answer many of the questions of interest, such as when a pond will cease to discharge during the summer months.

Already in the Fritz model there are numerous inadequacies and uncertainties in the process descriptions. It does not seem advisable to include any more poorly described processes into such a model. If ponds are to be modelled at all, it would probably be better to concentrate initially on a simpler system, rather than a more complicated one. Such a simpler system is provided by the High Rate Algal Pond.

The High Rate Algal Pond (HRAP)

Recently attention has been focused on the development of Advanced Integrated Wastewater Pond Systems (AIWPS). These systems are composed of several successive ponds, each designed to optimise certain processes and achieve specific results.

Effluent entering an AIWPS usually enters an Advanced Facultative Pond (AFP). These deep ponds are designed to remove most of the suspended solids in the wastewater, and obtain a significant reduction in the wastewater BOD_5. Effluent from the AFP then enters the High Rate Algal Pond (HRAP), which is optimised for the conversion of substrate and nutrients into algal biomass. Algal solids in the HRAP effluent can then be settled out in a deep settling pond. If necessary, these solids can be harvested and re-used as fertiliser or for energy production. Finally, the effluent from the settling pond enters a maturation pond, designed to allow the polishing of the effluent by disinfection and grazing on the remaining algae.

The HRAP is designed to optimise the symbiosis between algae and bacteria. The pond is shallow to maximise light penetration, improving photosynthesis and disinfection (light attenuation by algae and pigments in the water notwithstanding). The pond is also mixed by a paddle wheel. This ensures a uniform environment for algal growth with no stratification and prevents buildup of any significant sediment layer on the pond bottom. HRAP hydraulic conditions are usually controlled to maintain uniform volume and residence time.

HRAPs are much simpler to model than other pond designs, though it is still subject to significant uncertainties in modelling the biological compartments. The deliberate mixing in the HRAP strongly justifies the application of a well mixed model—certainly there is no need to concern ourselves with stratification. The mixing also prevents settling and the buildup of any significant sediment layer on the pond bottom. There may still be significant effects from biofilm buildup on the pond walls; without further information, we must neglect this aspect. Due to the action of algae, the pond can be regarded as always aerobic. Thus, denitrification is less likely to have a significant effect on pond behaviour (denitrifier activity in localised anaerobic pockets notwithstanding).

We propose, therefore, that the HRAP model will be much more accurately represented by equations (1)–(5) than a general pond, provided suitable choices for the concentration variables C and the rates $(r_C)_j$ can be obtained.

Algae

Clearly algae play a dominant role in the behaviour of an HRAP, so it seems likely that the HRAP model will need to retain some representation of algae and their interactions with any nutrients of interest. Indeed, it is probably desirable to have a detailed algal model. However, we propose to begin with the simple constant stoichiometry model described so far, in which the Redfield equations are used.

Aerobic heterotrophic bacteria

Aerobic heterotrophs are commonly regarded as "fast" with respect to other pond processes, and we propose that in a highly oxygenated HRAP bacterial activity is unlikely to be limited, and that bacterial population size will adjust to external conditions (such as the availability of substrate) quickly. Under this assumption, we neglect the presence of bacteria as a separate reservoir store and limiting step, instead regarding substrate and bacteria together as a source/sink of the appropriate nutrients. Rates of uptake/release of inputs/products are related to the rate of decrease of substrate by an effective stoichiometric equation like

$$(\text{Waste}) + a\text{O}_2 \rightarrow b\text{H}_2\text{O} + c\text{NH}_3 + d\text{CO}_2$$

where a, b, c, and d are the required stoichiometric coefficients: bacteria are not included in the above stoichiometric equation.

The decay rate of substrate can be represented by :

$$r_{bg} = -k_S \left[\frac{\text{O}_2}{K_{\text{O}_2} + \text{O}_2} \right] \left[\frac{\text{N}_i}{K_{\text{N}_i} + \text{N}_i} \right] \left[\frac{\text{P}_i}{K_{\text{P}_i} + \text{P}_i} \right]$$

where $k_S = k_{S,20}\theta^{T-20}$ is the substrate decay rate (related to the pond temperature by an Arrhenius formulation). Since substrate decay is due to microbial activity, the parameter θ can be assumed to take values associated with the temperature dependence of microbial activity in waste stabilisation ponds, typically in the range 1.05–1.09 (Mara 1976).

We need to determine values for the stoichiometric coefficients a, b, , and d, as well as a value for the substrate decay rate coefficient, $k_{S,20}$. This will require either designed experiments, or some assumption of an average stoichiometric formulation of the substrate/bacteria mix.

However, experimentally, there are difficulties in separating bacteria and substrate from algae. In any BOD test, for example, the determination of the rate of decay of substrate will be distorted by the presence of algal respiration. Filtering the mixture to remove the algae will also remove the bacteria as well as any biodegradable solids. It is possible to measure chlorophyll *a* concentration, but unfortunately chlorophyll *a* is fairly loosely correlated with algal biomass. These difficulties would need to be addressed in order to obtain parameter values for a model.

In modelling, it may be desirable to separate the influent substrate into different components, with separate degradation reactions for each. One possible partitioning is refractory, biodegradable (suspended) solid, and biodegradable organic solute. We may further wish to distinguish between quickly and slowly degradable solutes. McCarty (1975) suggested that an

approximate chemical formulation for organic waste can be obtained from knowledge of the proportions of fats, proteins, and carbohydrates in the waste. This is based on the assumption that the chemical formulations of different proteins, different carbohydrates, and different fats are similar. This approach suggests the possibility of partitioning the waste into fats, proteins, and carbohydrates.

If we neglect explicit modelling of the bacterial population, there should be no great mathematical difficulty in separately modelling each compartment of the influent waste. The difficulty, however, will lie in the experimental determination of reaction inputs/products and the rates of their uptake/production.

Carbonate equilibria and pH

Algae are a strong driving force in an HRAP, leading to large diurnal swings in CO_2 and O_2 concentrations and pond pH.

As pond pH rises, the carbonate equilibria shift, converting dissolved carbon dioxide to bicarbonate, and then to carbonate. The algal carbon source may therefore change — the assumption in the Redfield equations that algal carbon comes solely from carbon dioxide may not be correct. In addition, algal growth is inhibited at high pH (and uptake of carbonate may never occur because of this). The pond pH also influences the rate of ammonia volatilisation by determining the proportion of ammoniacal N in the volatile free ammonia form.

For these reasons, it may well be of interest to model the pond pH. pH models have been developed for use in streams (Chapra 1997, McBride unpublished results). The description below is largely derived on these two works.

Note that the symbol [A] is understood to denote the molar concentration of A, i.e., mol (A) L^{-1}.

The carbonate system is characterised by the following equilibria (Stumm & Morgan 1981, Yeasted & Shane 1976):

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{13}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{14}$$

$$H_2O \leftrightarrow H^+ + OH^- \tag{15}$$

The respective points of equilibria are determined by the conditions:

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \tag{16}$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{17}$$

$$K_w = [H^+][OH^-] \tag{18}$$

The quantities K_1, K_2, and K_w as defined above are not independent of the activities of the species, and will therefore vary with the ionic strength of the solution. Consequently it is more accurate to use the equilibrium constants defined by:

$$K_1^0 = \frac{\{H^+\}\{HCO_3^-\}}{\{CO_2\}} \tag{19}$$

$$K_2^0 = \frac{\{H^+\}\{CO_3^{2-}\}}{\{HCO_3^-\}} \tag{20}$$

$$K_w^0 = \{H^+\}\{OH^-\} \tag{21}$$

where $\{A\} = \gamma_A[A]$ denotes the activity of substance A, and γ_A (dimensionless) is the activity coefficient of A. The constants K_1^0, K_2^0, and K_w^0 are the first and second ionization constants of carbonic acid, and the ionization constant of water, respectively. Here we are following the notation of Butler (1991). The definition of K_*^0 ("*" is used here to denote any one of "1", "2", or "w") in terms of the activities of the species in solution means that K_*^0 is independent of the solution's ionic strength (making it the more natural quantity to use). The meaning of the zero superscript is that K_*^0 is equal to K_* in the limit of zero ionic strength.

Much of the literature on the subject can be confusing on this issue because most authors do not make an explicit distinction between K_*^0 and K_*. The standard seems to be to use K_* to denote K_*^0 in solutions of non-zero ionic strength. This makes a lot of sense, since the K_* quantities as defined in (16)–(18) are of limited use, being dependent upon the solution's ionic strength. Thus we may as well dispose of them and simply use K_* to denote the activity independent quantities defined as K_*^0 in (19)–(21). However, the situation may be confused by authors who assume the zero ionic strength limit, in which concentrations and activities are equal. In this limiting case, $K_*^0 = K_*$ and expressions like (16)–(18) really define K_*^0 and not K_*.

Temperature dependencies for these equilibrium constants are provided in Chapter 4 of Bowie *et al.* (1985) (K_1^0 and K_2^0, 0–50 °C only); or in Plummer & Busenberg (1982) (K_1^0 and K_2^0, 0–90 °C) and Harned & Owen (1958) (K_w^0).

Plummer & Busenburg (1982) define K_1^0 as

$$K_1^0 = \frac{a_{H^+} a_{HCO_3^-}}{a_{CO_2} a_{H_2O}}$$

where a_A denotes the activity of species A, i.e., the activity of water (being nearly constant) has not been incorporated into their definition of K_1^0. However, Plummer & Busenburg's empirical expression for pK_1^0 gives values which agree with those quoted by Butler (1991). This means either that Plummer & Busenburg's definition of activity (i.e., concentration) is

such that $a_{H_2O} \approx 1$, or that Plummer & Busenburg have applied the wrong definition for K_1^0. The activity a_{H_2O} could be near unity if measured in mole fractions, but it is (strongly) implied (but not clearly stated) that Plummer & Busenburg used units of molality for activity, and hence a_{H_2O} cannot be near unity because the molality of water is about 55.6 mol(H_2O)/1000g(H_2O).

In any case, Plummer & Busenburg's actual formulae for pK_1^0 and pK_2^0 appear to give the right results, assuming the definitions (19)–(21) and assuming units of molarity (approximately the same as molality for water) for concentration.

It is convenient to write (19)–(21) in the form

$$K_1' = \frac{\{H^+\}[HCO_3^-]}{[CO_2]} \tag{22}$$

$$K_2' = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]} \tag{23}$$

$$K_w' = \{H^+\}[OH^-] \tag{24}$$

where

$$K_1' = \frac{K_1^0 \gamma_{CO_2}}{\gamma_{HCO_3^-}} \tag{25}$$

$$K_2' = \frac{K_2^0 \gamma_{HCO_3^-}}{\gamma_{CO_3^{2-}}} \tag{26}$$

$$K_w' = \frac{K_w^0}{\gamma_{OH^-}} \tag{27}$$

(*see* Stumm & Morgan, 1981, p. 134 — we have just defined the "mixed acidity constants").

From this point on, it will be understood that we are considering high ionic strength solutions, and hence will use activities where they are required (these are more general anyway). In low ionic strength solutions, $\gamma_A \to 1$, so $\{A\} \to [A]$ for all species A and $K_*' \to K_*^0$ ("$\to$" meaning "tends toward"). Thus, results for low ionic fluids can be obtained from the results that follow by making these substitutions.

Rather than deal with CO_2, HCO_3^-, and CO_3^{2-} concentrations (or activities) directly, it is more convenient to introduce the quantities total inorganic carbon (TiC) C_T, alkalinity Alk, and CO_2 acidity CO_2 - Acy, such that:

$$[C_T] = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \tag{28}$$

$$[\text{Alk}] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{29}$$

$$[CO_2 - \text{Acy}] = [CO_2] + [H^+] - [OH^-] - [CO_3^{2-}] \tag{30}$$

These are termed "conserved" quantities. The issue of (say) determining the rate of change of aqueous CO_2 due to plant photosynthesis is complicated because, as CO_2 is taken up from solution, the carbonate equilibria shift to maintain the same proportions of CO_2, HCO_3, and CO_3^{2-} (assuming all other factors affecting the equilibria remain constant). The time behaviour of each species is determined by:

$$\frac{d[CO_2]}{dt} = -r_1 + S_{CO_2} \tag{31}$$

$$\frac{d[HCO_3^-]}{dt} = r_1 - r_2 + S_{HCO_3^-} \tag{32}$$

$$\frac{d[CO_3^{2-}]}{dt} = r_2 + S_{CO_3^{2-}} \tag{33}$$

where r_1, and r_2 are the rates at which the forward reactions in (13) and (14) occur (respectively), and S_{CO_2}, $S_{HCO_3^-}$, and $S_{CO_3^{2-}}$ are the rates of production/loss of each carbonate species due to external sources and sinks (such as photosynthesis and respiration). If we add (31)–(33) and invoke the definition of $[C_T]$ in (28), we obtain:

$$\frac{d[C_T]}{dt} = S_{CO_2} + S_{HCO_3^-} + S_{CO_3^{2-}} \tag{34}$$

Thus the advantage in using C_T is that its concentration is unaffected by internal shifts in the carbonate equilibria, depending only upon external sources and sinks of any of its components. Similar equations and a rate can be introduced for $[H^+]$ and $[OH^-]$, and used to show that alkalinity and CO_2-acidity as defined above are also conserved quantities, (for further details, *see* Di Toro (1976)).

Consequently, in dealing with the carbonate equilibria, we consider the influences of external sources and sinks on the conserved quantities, not on the individual species that comprise conserved quantities. The individual species are then calculated from the conserved quantities using the equilibrium conditions (16)–(18) or (19)–(21) as appropriate. This last step is an approximation, based upon the assumption that rates like r_1 and r_2 are "fast" when compared to source/sink rates like S_{CO_2}, $S_{HCO_3^-}$, and $S_{CO_3^{2-}}$, i.e., we are assuming that the carbonate equilibria are always "in equilibrium" with the external sources and sinks.

Note that the conserved quantities are defined in terms of concentrations (molarities), not activities. The following relationship holds between these quantities:

$$[C_T] = [\text{Alk}] + [CO_2 - \text{Acy}] \tag{35}$$

This relationship is important because $[C_T]$ is generally difficult to determine directly (Yeasted & Shane 1976). Therefore, $[C_T]$ can be obtained indirectly through measurements of $[\text{Alk}]$ and $[CO_2 - \text{Acy}]$.

Equations (19), (20), and (28) can be used to obtain $[CO_2]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ in terms of $[C_T]$, $\{H^+\}$ and the mixed acidity constants K_1' and K_2' (Stumm & Morgan 1981):

$$[CO_2] = \alpha_0 [C_T], \qquad [HCO_3^-] = \alpha_1 [C_T], \qquad [CO_3^{2-}] = \alpha_2 [C_T] \tag{36}$$

where

$$\alpha_0 = \left(1 + \frac{K_1'}{\{H^+\}} + \frac{K_1' K_2'}{\{H^+\}^2} \right)^{-1} \tag{37}$$

$$\alpha_1 = \left(1 + \frac{\{H^+\}}{K_1'} + \frac{K_2'}{\{H^+\}} \right)^{-1} \tag{38}$$

$$\alpha_2 = \left(1 + \frac{\{H^+\}}{K_2'} + \frac{\{H^+\}^2}{K_1' K_2'} \right)^{-1} \tag{39}$$

Thus, if the TiC concentration and pH are known, the quantities of the individual carbonate species can be obtained. Note also that

$$\alpha_1 = \frac{K_1'}{\{H^+\}} \alpha_0 \quad \text{and} \quad \alpha_2 = \frac{K_2'}{\{H^+\}} \alpha_1$$

Elimination of the unknowns $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[OH^-]$ from equations (22)–(24) and (29)–(30), and noting that

$$[H^+] = \{H^+\} / \gamma_{H^+} \tag{40}$$

leads to a fourth order polynomial for $\{H^+\}$:

$$\{H^+\}^4 + A_3 \{H^+\}^3 + A_2 \{H^+\}^2 + A_1 \{H^+\} + A_0 = 0 \tag{41}$$

where

$$A_3 = K_1' + [\text{Alk}] \gamma_{H^+}$$

$$A_2 = K_1' K_2' - K_1' [CO_2 - \text{Acy}] \gamma_{H^+} - K_w' \gamma_{H^+}$$

$$A_1 = -K_1'\gamma_{H^+}\left(K_2'[\text{Alk}] + 2K_2'[CO_2 - \text{Acy}] + K_w'\right)$$

$$A_0 = -K_1'K_2'K_w'\gamma_{H^+}$$

Given K_1', K_2', K_w', $[\text{Alk}]$, and $[CO_2 - \text{Acy}] = [C_T] - [\text{Alk}]$, the value of $\{H^+\}$ is obtained by solving for the appropriate root of (41).

There is an alternative method to determine pH, which does not require the solution to (41). Combining (29) with (36) and (37)–(39) gives

$$[C_T] = \left(1 + \frac{\{H^+\}}{K_1'} + \frac{K_2'}{\{H^+\}}\right)\frac{[\text{Alk}] - \frac{K_w'}{\{H^+\}} + \frac{\{H^+\}}{\gamma_{H^+}}}{1 + \frac{2K_2'}{\{H^+\}}} \tag{42}$$

Equation (42) implicitly defines $\{H^+\}$ in terms of $[C_t]$ and $[\text{Alk}]$, which in our model are assumed to be independently determined functions of time. We wish to determine the rate of change of pH. We have:

$$\frac{d[C_T]}{dt} = \frac{\partial[C_T]}{\partial\{H^+\}}\frac{d\{H^+\}}{dt} + \frac{\partial[C_T]}{\partial[\text{Alk}]}\frac{d[\text{Alk}]}{dt} = f \tag{43}$$

where f is a function either of time or of other quantities that depend upon time. Then upon rearranging, we have:

$$\frac{d\{H^+\}}{dt} = \frac{f - \frac{\partial[C_T]}{\partial[\text{Alk}]}\frac{d[\text{Alk}]}{dt}}{\frac{\partial[C_T]}{\partial\{H^+\}}}$$

where $\partial[C_T]/\partial[\text{Alk}]$ and $\partial[C_T]/\partial\{H^+\}$ can be obtained by partial differentiation of (30), and $d[\text{Alk}]/dt$ is assumed to be known. All that is required now is to specify f, and to ensure that all the dependencies of f are explicitly determined. Due to equation (42), we can write any terms in f that are dependent on $[C_T]$ in terms of $\{H^+\}$ and $[\text{Alk}]$. Thus we can write $f = \bar{f}(\{H^+\}, [\text{Alk}])$, and so

$$\frac{d\{H^+\}}{dt} = \frac{\bar{f}(\{H^+\}, [\text{Alk}]) - \frac{\partial[C_T]}{\partial[\text{Alk}]}\frac{d[\text{Alk}]}{dt}}{\frac{\partial[C_T]}{\partial\{H^+\}}} \tag{44}$$

Note that external sources/sinks of $\{H^+\}$ such as the influent, effluent, or photosynthesis do not appear explicitly in this equation. These sources and sinks instead affect the conserved quantities $[C_T]$ and $[Alk]$ from which $\{H^+\}$ is determined.

From (42) and the forms of α_0 and α_1 we also have that:

$$[CO_2] = \frac{\{H^+\}}{K_1'} \frac{[Alk] - \frac{K_w'}{\{H^+\}} + \frac{\{H^+\}}{\gamma_{H^+}}}{1 + \frac{2K_2'}{\{H^+\}}} \tag{45}$$

To summarise, the system is solved by formulating differential equations like (2) for total inorganic carbon (equation 43, with f specified explicitly) and alkalinity. These two equations are solved simultaneously with (44), to obtain the pond TiC, alkalinity, and H^+ activity. Pond pH is then calculated from its definition, $pH = -\log_{10}\{H^+\}$.

Interfacial transfer and saturation CO_2 concentration

From Banks & Herrara (1977), we have, for dissolved oxygen:

$$M = \overline{K}A(C_s - C)$$

where M is the rate of oxygen transfer across an air-water interface of area A (amount/time), C_s is the equilibrium (saturation) concentration of oxygen (amount/volume), and C is the concentration of oxygen (amount/volume) in a well mixed column of water of depth H. Consequently, $\overline{K}$ has units of velocity (length/time) and is termed the oxygen transfer coefficient. (The "bar" on $\overline{K}$ is to avoid confusion between Banks & Herrara's oxygen transfer coefficients and the chemical equilibrium constants used in the previous section).

The surface reaeration coefficient, which Banks & Herrara called $\overline{K}_2$, is defined by the expression

$$M = \overline{K}_2 HA(C_s - C)$$

i.e, $\overline{K}_2 = \overline{K}/H$, and has units of reciprocal time. Consequently, noting that M/V is the rate of change of concentration of oxygen due to interfacial transfer and $V = HA$, we have:

$$r_{1do} = \frac{M}{V} = \overline{K}_2(C_s - C)$$

This form is almost identical to that quoted by Fritz *et al.* (1979), except they used K_{IO_2} for $\overline{K}_2$ and they erroneously included an extra factor of A/V in their formulation (which is not dimensionally correct, given the definition of Banks and Herrara's surface reaeration coefficient).

Banks & Herrara (1977) then provided an empirically determined expression for the surface reaeration coefficient:

$$\overline{K}_{0,2} = K_{1O_2} = \frac{\left(0.384U^{1/2} - 0.088U + 0.0029U^2\right)}{H} \tag{46}$$

This is measured in units of reciprocal days.

Consequently, r_{1do} as defined above has units of mg(O) L^{-1} day^{-1}, given the assumption of units of mg(O) L^{-1} for oxygen concentration.

The saturation DO can be obtained from the formula of Benson & Krause (1984).

We now derive the appropriate form for the interfacial transfer rate of CO_2. First, we obtain the surface reaeration coefficient for carbon dioxide from that for oxygen. The surface reaeration coefficient for species X (K_{1X}), is proportional to the inverse square root of the Schmidt number for species X. The Schmidt number is defined as $S_c = \nu / D$, where ν is the kinematic viscosity of the fluid (water) and D is the diffusion coefficient for species X. Consequently,

$$\frac{K_{1CO_2}}{K_{1O_2}} = \frac{\left(\frac{\nu}{D_{CO_2}}\right)^{-1/2}}{\left(\frac{\nu}{D_{O_2}}\right)^{-1/2}} = \left(\frac{D_{CO_2}}{D_{O_2}}\right)^{1/2}$$

We have that $D_{CO_2}/D_{O_2} = 0.840$, thus $K_{1CO_2} = \sqrt{0.84}K_{1O_2} = 0.9165K_{1O_2}$

Therefore, given this definition of K_{1CO_2}, the rate of change of CO_2 due to interfacial transfer is given by $K_{1CO_2}(CO_{2s} - CO_2)$. The units of this expression depend upon the chosen units of the CO_{2s} and CO_2 concentrations.

First, we obtain the saturation carbon dioxide concentration, CO_{2s} and its units of measurement. This is given by $CO_{2s} = p_{CO_2}K_H$, where $p_{CO_2} = 10^{-3.456}$ atm is the partial pressure of CO_2 and K_H is the Henry's law constant for CO_2. K_H is given by Plummer & Busenberg (1982) as

$$\log_{10}(K_H) = 108.3865 + 0.01985076T_k - \frac{6919.53}{T_K} - 40.45154\log(T_K) + \frac{669365.0}{T_K^2}$$

Plummer & Busenberg do not mention the units of K_H, despite noting that "the problem of defining K_H is complicated by the varied units used in reporting gas solubility...". However, they quote K_H as defined by

$$\frac{m_{CO_2(aq)}\gamma_{CO_2(aq)}}{PCO_2\gamma_{CO_2(g)}}$$

where they claim the γ s denote activity coefficients and the m is a *molality* (having units of mol(solute)/1000g(solvent)). At lower solute concentrations in water, this last measure is almost equivalent to the *molarity* (units mol(solute) L^{-1}). We assume that "PCO_2" (their notation) in Plummer & Busenberg's formula denotes the partial pressure of CO_2 in atmosphere (it is not defined, but this is the most obvious assumption — units of atmosphere are used for PCO_2 elsewhere in the paper). The activity coefficients are both dimensionless (in fact $\gamma_{CO_2(g)}$ is really called a coefficient of fugacity, but presumably it is still dimensionless). Then, we have that K_H has units of mol(CO_2)/1000g(water)/atm, or in other words, mol(CO_2) L^{-1} atm^{-1}.

So, the saturation carbon dioxide concentration is then given by $CO_{2s} = p_{CO_2} K_H$, where the partial pressure is measured in atmospheres, the Henry's law constant given by Plummer & Busenberg's expression is measured in mol(CO_2) L^{-1} atm^{-1}, and hence the resulting units for CO_{2s} are mol(CO_2) L^{-1} i.e., we really have $[CO_2]_s = p_{CO_2} K_H$

To summarise then, the expression

$$K_{1CO_2}([CO_2]_s - [CO_2]) \tag{47}$$

is the rate of transfer of aqueous CO_2 across the fluid interface, measured in mol(CO_2) L^{-1} day^{-1}, where

$$[CO_2]_s = p_{CO_2} K_H \tag{48}$$

and

$$[CO_2] = \alpha_0 [C_T] = \frac{\{H^+\}}{K_1'} \frac{[Alk] - \frac{K_w'}{\{H^+\}} + \frac{\{H^+\}}{\gamma_{H^+}}}{1 + \frac{2K_2'}{\{H^+\}}} \tag{49}$$

Note that (47)–(49) are used in the ODE for the conserved quantity $[C_T]$ (equation 36a), and are not applied directly to CO_2.

It is important to remember that CO_2, and C_T concentrations in these formulas are **molarities**, i.e., expressed in units of mol L^{-1}, and not mg(C) L^{-1} as may be used by the model. Multiplying the molar rate by 1200 will yield the same rate in mg(C) L^{-1} units. Alkalinity in these formulas is similarly measured as a molarity, and not as mg($CaCO_3$) L^{-1}, as it is commonly reported in the engineering literature. As the charge on the carbonate ion is –2, each mole of alkalinity corresponds to two moles of $CaCO_3$.

Chapra (1997) corrected the surface reaeration coefficients for both oxygen and CO_2 via an Arrhenius factor, θ^{T-20}, where T is temperature in degrees celsius and $\theta = 1.024$. Chapra used the oxygen saturation formula given by Bensen & Krause (1984), which he clearly assumed applied to conditions at 20 °C. Similarly he assumed the saturation CO_2

concentration given by Henry's law and the K_H of Plummer & Busenberg (1982) applied at a temperature of 20 °C. Chapra (1997) also included an elevation correction for the oxygen saturation.

Determination of activity coefficients

A number of approximate expressions for the activity coefficient exist (*see* p. 135 of Stumm & Morgan 1981), applicable for different ranges of ionic strengths. The most general expression appears to be the Davies equation:

$$\log_{10}(\gamma_i) = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.24I\right)$$

where I is the ionic strength of the solution, z is the charge on the ion considered,

$$A = 1.82\times10^6(\varepsilon T)^{-3/2}$$

where T is temperature in Kelvins, and ε is the dielectric constant of water (Chapra 1997 claims this is approximately equal to 78, but generally it is temperature and pressure dependent — *see* Uematsu & Franck 1980, Malmberg & Maryot, 1956).

There is some uncertainty about the value of 0.24 in the last term of the Davies equation. This value comes from Allison *et al.* (1991), but the actual value may range between 0.2 and 0.3 (Stumm & Morgan 1981, p. 135). A value of 0.24 certainly seems to be a reasonable compromise.

The ionic strength of the solution can be estimated via

$$I \approx 1.6\times10^{-5}\Lambda$$

where Λ is the specific conductance of the solution, in μmho cm^{-1}.

For the activity coefficient of CO_2, we use

$$\log_{10}(\gamma) = -0.1I$$

from Helgeson (1969), as quoted by Allison *et al.* (1991).

Ammonia volatilisation

For the interfacial transfer of ammonia, we first calculate the proportion of ammoniacal nitrogen that appears as ammonia. Bowie *et al.* (1985) presented this calculation, apparently neglecting activity considerations and using different definitions for the equilibrium constants from the convention used in this report. Here we define equilibrium constants in terms of activities, and absorb the concentration of water into the equilibrium constants. The equilibrium constant for the ammonia-ammonium reaction is then given by:

$$K_i^0 = \frac{\{NH_4^+\}\{OH^-\}}{\{NH_3\}} = \frac{\{NH_4^+\}K_w^0}{\{NH_3\}\{H^+\}}$$

where we have used equation (21). Recalling the notation $pA = -\log_{10}\{A\}$ and that $\{A\} = \gamma_A[A]$, we obtain

$$\frac{\gamma_{NH_4^+}[NH_4^+]}{\gamma_{NH_3}[NH_3]} = 10^{pK_w^0 - pK_i^0 - pH} \tag{50}$$

We now define the hydrolysis constant $pK_h = pK_w^0 - pK_i^0$, and note that $[NH_3] = [NH_4\text{–}N] - [NH_4^+]$. After substituting into (50) and solving for $[NH_3]$, we obtain

$$[NH_3] = \frac{[NH_4\text{–}N]}{1+R}, \text{ where } R = \frac{\gamma_{NH_3} 10^{pK_h - pH}}{\gamma_{NH_4^+}}$$

The hydrolysis constant pK_h is specified in terms of the temperature ($^\circ$C) as

$$pK_h = 0.09018 + \frac{2729.92}{T + 273.16}$$

which is obtained from Thurston *et al.* (1974). Note that the definition of pK_h is unaffected by whether the concentration of water is absorbed into K_i^0 and K_w^0 or not.

The volatilisation rate coefficient quoted by Colomer & Rico (1993) is apparently based upon the content of Stratton (1968, 1969). The formula used

$$K_{am} = \frac{0.0566}{d} e^{0.13(T-20)}$$

does not appear explicitly in either of the Stratton papers, but rather in Ferrara & Avci (1982) (who Colomer & Rico do not reference), who claim it is derived from Stratton's papers. The quantity d in the formula is the pond depth, but Ferrara & Avci do not indicate clearly what the units of measurement are. In addition, the quantity 0.0566 does not appear in either of Stratton's papers, presumably because of a change in the units of measurement. Assuming Stratton uses feet and hours, and Ferrara has converted to metres and days, one may show that 0.0566 is at least of the right order of magnitude, but I was unable to match this value with any particular value quoted in Stratton's papers.

Given a form for the volatilisation rate coefficient, the resulting rate of ammonia volatilisation is then

$$K_{am}[NH_3] = K_{am}\frac{[NH_4\text{–}N]}{1+R}$$

where $[N_i]$ is the molar concentration of ammoniacal nitrogen. The model will typically represent nutrient concentrations in mass units, so the appropriate molar weights must be applied where needed to obtain the correct units of measurement.

Model implementation

Any modelling of the type discussed in this report will consist of a system of first order non-linear ordinary differential equations (ODEs). Such systems (unless they are found to be "stiff"), can be solved numerically using fairly simple integration techniques. Software packages (often known generically as "simulation" software) exist which allow easy specification, solution, and analysis of such systems. Stiff systems may often be handled by these packages also, provided the appropriate integration routine is used.

Some simulation software is more "programming language" based, such as ACSL (Advanced Continuous Simulation Language) or the Unix based Xpp. These packages may be quite powerful, but require more expert knowledge to develop models, run simulations, and conceptualise the model structure. Often the model developer wishes to pass the finished model on to inexpert users who can run simulations and test hypothesis. The language-based simulation packages may therefore be less desirable in this regard.

Other simulation packages are GUI (Graphical User Interface) oriented, with systems of ODEs built up as a (possibly hierarchical) diagram of blocks and arrows representing variables and processes. Examples of these are STELLA and Vensim.

The GUI oriented packages can often be unsuitable for the development of larger, more sophisticated models, especially when they require all variables and processes to be represented as individual components in a diagram. On the other hand, they may make it easier for non-experts to develop and/or use the models.

The ACSL Graphic Modeller (or ACSL GM) is a compromise between the two extremes. The GM provides a graphical interface to the ACSL programming language. Models can be constructed from simpler predefined building blocks (called "Powerblocks"), or user defined Powerblocks containing ACSL code. Blocks in a model diagram can also contain further model diagrams, or submodels. The ACSL programming language itself provides a good range of mathematical functions and analysis, which is an added advantage.

I encountered some difficulties in developing a large ecological model involving many equations, variables, and parameters using ACSL GM. However, ACSL GM is a product still under development, so it is likely that the package's robustness and ease of use will improve as new versions are produced. In addition, it is quite possible that my frustrations represent deficiencies in my understanding of the package, not deficiencies in the package itself. Aegis software (the current developers of the ACSL package) have plans for a World-Wide Web "chat room" to allow discussion between ACSL users (Aegis Research Corporation 1999), which may (amongst other things) provide a useful source of advice on programming protocols. This resource may provide solutions for the difficulties encountered.

Conclusions

We have considered a previously formulated model (Fritz *et al.* 1979) for the biochemical processes and nutrient transformations occurring in a waste stabilisation pond, outlining some problems and areas of uncertainty in this model which need to be addressed. Problems arise particularly in attempting to describe biological behaviours, and biologically mediated processes, due to the inherent complexity of biological systems, and the consequent difficulty in reliably describing their behaviour in terms of simple laws or mathematical models.

We have suggested a simpler system to be considered, the high rate algal pond (HRAP). Conditions in the HRAP are more rigorously controlled as a consequence of mixing by a paddle wheel, thus removing some of the uncertainties existing in a model of a general

stabilisation pond. Unfortunately, the uncertainties in describing the biological components of such systems remain.

It is clear then, that there is still much to be clarified about the fundamental processes that affect the behaviour of a waste stabilisation pond, particularly biochemical processes. Understanding and mathematically describing these processes is further complicated, not only by the complex nature of the individual processes themselves, but by the complexity of the environment in which they act. In experiments to determine the nature of the processes, environmental conditions should ideally be reproduced as accurately as possible, which may not be feasible in the laboratory.

I believe the problem should always be considered from two angles. First, that of mathematically describing the fundamental processes occurring in a pond, and second, of determining the level of mathematical description that is allowed by the empirical measurements available. I have found that what can be measured is invariably at a far cruder level of detail than that required by the mathematical modelling approaches that have been taken. Consequently, the procedure has been to look for values of unknown parameters in the literature. However, these values often pertain to different environmental situations, and even different species, hence their use in the model being developed is often suspect. Consequently, I believe that the level of mathematical description applied to a problem should be influenced by the level of detail in the data that is available and self consistent. Unfortunately, such information may not be nearly sufficient to provide an adequate description of such a complex system as a waste stabilisation pond.

Modelling biofilms

A biofilm is a form of accumulation of microbial cells on a surface submerged in an aquatic environment. Microbial cells adhering to the surface grow, reproduce, and produce a network of polymers forming a tangled external matrix of organic and inorganic material that provides structure and support to the layer. The biofilm thickness can increase by microbial growth within the layer or by adherence of bulk-water particles to the layer's upper surface. Similarly, the biofilm may decrease in thickness as sloughing or release of individual microbes occurs.

Biofilms can be beneficial or detrimental in different circumstances. Wastewater treatments such as rotating biological contactors encourage the growth of biofilms in order to remove unwanted nutrients from wastewaters. On the other hand, biofilm buildup on submerged machinery can clog mechanisms or reduce desired waste heat loss.

It is therefore desirable to understand the processes that occur within and at the boundaries of biofilms and the effects on their accumulation and nutrient uptake, either to allow greater efficiency in nutrient removal applications, or to reduce unwanted fouling by biofilm buildup.

In the simplest mathematical models, a biofilm is regarded as a planar source and sink of nutrients, adjacent to or surrounding an aquatic environment. It is typically assumed that the biofilm itself is in a steady state, and that the rates of uptake and release are limited by microbial growth rates and nutrient availability within the bulk liquid. References and a tabular overview of such simple models were presented by Wanner & Gujer (1986) and by Characklis & Marshall (1990, Chapter 9).

Attempts at more realistic models allow the biofilm to develop over time and to contain more than one microbial species. They recognise that nutrient availability in the bulk liquid and microbial growth rates may not be the correct factors limiting process rates. Instead, such

models attempt to allow for growth in biofilm volume, and include the limiting effect of diffusion of nutrients within the biofilm.

The first such model was described by Wanner & Gujer (1986) and developed further by Wanner (1989), Gujer & Boller (1990), Wanner (1994 & 1995), Wanner & Reichert (1996), and Reichart & Wanner (1997). Further discussion of modelling techniques used was provided by Wanner & Gujer in Characklis & Marshall (1990).

Unfortunately I found this series of references difficult to comprehend, an opinion supported by others (G. McBride, NIWA, pers. comm.). In part this has to do with inconsistencies and apparent typographical errors, but it also has to do with the development of fundamental concepts. While some of these concepts — and the corresponding mathematical equations — are clearly explained, others are not so clear. A biofilm is an extremely complicated system requiring careful consideration of length and time scales in order to determine which are the significant phenomena that must be modelled. The authors of the previous papers undoubtedly considered such issues before modelling, but the absence of careful discussion of these aspects in their publications makes it difficult for the reader to follow the reasoning behind what has been included in the model, and what has not. In particular, the boundary conditions at the biofilm-bulk fluid interface are a source of much confusion, and the application of a continuum approximation in deriving these boundary conditions may not be at all realistic.

Conclusions

An attempt to begin a new model from fundamental principles was hampered by our confusion over the previous work, and the scale of the problem. It was decided that as any biofilm model must include a nutrient kinetics component, there may be little to be gained in looking at the structural component of such a model until the issues in the area of nutrient kinetics have been addressed, as is discussed in the general pond model section of this report.

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