PARAMETER DETERMINATION IN COMPOSTING – Part II

Incorporating substrate diffusion and substrate solubilisation

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1 Introduction

In an earlier paper (Chapman, Parameter determination in composting - Part I: The use of overlaying, interdependent sets of equations as a solution to the over parameterization problem, 2009a) high precision microbial kinetic parameter determination was shown to be possible, but only for a single electron acceptor/substrate combination. This paper looks at the substrate side of this combination to see if the single substrate constraint, required for high precision parameter determination, can survive given that the substrate 'pool' will also contain diffused and solubilised substrate. Part III of this series (Chapman, 2009b) addresses questions arising from the application of diffusion laws at sub-particle scales.

It will be argued here that several elements of compost theory are automatically incorporated into parameters that are determined using a simple microbial kinetics, in particular:

- The net effect of substrate diffusion at sub-particle scales.
- Continuous addition of soluble substrate to the 'pool' from solubilisation of insoluble substrate.

It is further argued that for most composting applications, keeping these elements outside the modelling environment (incorporating them automatically as a combined parameter) is sufficient for three reasons:

- The vast majority of composting particles will have an anaerobic core and hence substrate diffusion can be expected. Consequently they will all behave similarly.
- The vast majority will have an insoluble fraction (albeit possibly different types and quantities of compounds) which will be solubilised. This source can be shown to have computational space in a simple kinetic, and hence can be incorporated automatically.
- It is possible that any increased precision that may theoretically accrue from adding additional substrate parameters (which would occur if solubilisation and substrate diffusion were incorporated as model parameters), may be negated if high precision determination of the basic microbial kinetic parameters is compromised when these additional substrate parameters are made explicit.

2 Method

Consider two points on a composting time course, t_1 and t_2. Each of these points will have two associated composting rates:

- An experimentally determinable composting rate ($Q_{data}(t_1)$ and $Q_{data}(t_2)$).
- A model descriptor of the composting rate ($Q_{model}(t_1)$ and $Q_{model}(t_2)$).

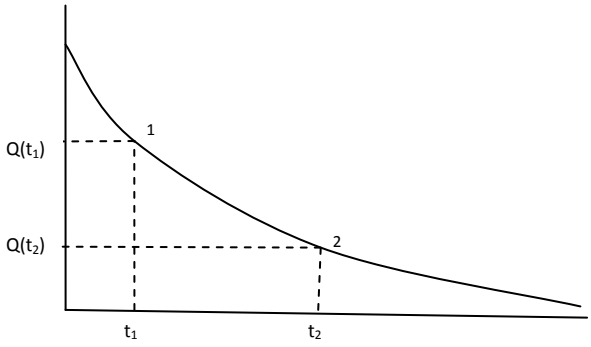

Figure 1 – Two points on a hypothetical composting time course. Each point in time (t) will have an associated composting rate (Q).

Two questions can be asked of the model descriptor:

1) The adequacy of the model description of the experimentally determined composting time course – i.e. what is its statistical fit? This is the subject of part I.
2) The scientific basis of each parameter that is determined (subject of this paper - part II).

In terms of question 1, first-order kinetics with a normalised biomass (NB) function was used to describe two different composting time courses with an r^2 better than 0.94 in part I of Chapman (2009a). With such a high r^2 this descriptor could therefore be considered adequate for the purposes of question 1.

To consider question 2, the *scientific basis* of the parameters used in question 1 needs scrutiny. The question here is a more fundamental one than that argued for the rate constant base in Part I of this series. The scientific basis arises from the assumptions in the model (which could be any equation of any order in the case of a curve fitted without consideration of microbial kinetics – but is first-order kinetics operating within a non-diffusible substrate solution of diffusion laws and a spherical geometry in the case of Chapman, Part I). A composting model with good roots in microbial kinetics and a high r^2 will have a wider application than one which has no roots in microbial kinetics.

The first-order kinetics model of Chapman (2008) was well rooted in microbial kinetics and diffusion laws while the starting substrate concentration was determined using the experimental data. However, two elements ignored in the model assumptions were substrate diffusion (a non-diffusible substrate solution was chosen) and solubilisation of insoluble substrate (this is implicit in the nature of substrate fractions). The adequacy of this stance is addressed here.

2.1 Derivation

From first-order kinetics the nature of the relationship between the experimentally observed composting rate and substrate concentration is:

Equation 1

$$Q_{model}\,(t) = k \times E(t) \times NB(t)$$

With a high r^2 then Q_{model} closely approximates Q_{data} at all t's and the ratio of the substrate concentration (E) at points 1 and 2 in Figure 1 can be written as:

Equation 2

$$\frac{Q_{data}\,(t_1)}{Q_{data}\,(t_2)} = \frac{Q_{model}\,(t_1)}{Q_{model}\,(t_2)} = \frac{E(t_1) \times NB(t_1)}{E(t_2) \times NB(t_2)}$$

Where the equality between $Q_{data}(t)$ and $Q_{model}(t)$ is only exact if r^2 =1.

From first-order kinetics the nature of the relationship between $E(t_1)$ and $E(t_2)$ is:

Equation 3

$$\frac{E(t_1)}{E(t_2)} = \frac{1}{\exp(-k \times t_{1\to2} \times NB(t_1))} = \exp(k \times t_{1\to2} \times NB(t_1))$$

Where: t is in days and k is in d^{-1} form. For the thermodynamic form of the rate constant used in part I divide the d^{-1} form by 0.0864.

Combining Equation 2 with Equation 3 it can be seen that for data with a high r^2, the same parameters that are determined from the experimental data also describe the time course of substrate concentration. Therefore, $E(t_2)$ must be the 'actual' $E(t_2)$ – otherwise the r^2 would reflect the miss-fit. It follows that if substrate diffusion and solubilisation have occurred in the time period $t_1 \rightarrow t_2$ then these must be included in $E(t_2)$ in Equation 3.

Therefore $E(t_2)$ could be written in more expanded form as:

Equation 4

$$E(t_2) = E_{resident}\,(t_2) + E_{diffused}\,(t_2) + E_{released}\,(t_2)$$

There are two cases that can be made to argue that this complexity is automatically incorporated into first-order kinetics:

2.1.1 Case 1 – Experimental and derivational

For simplicity, consider that Figure 1 covers that segment of the composting time course when biomass is not limiting the composting rate i.e. the NB function equals 1 – this simplifies the mathematics so the arguments become clearer, the same logic would also apply if NB < 1 although the mathematics would be more complicated. For this segment, the rate constant can be determined from the composting rate at t_1 and t_2 by rearranging Equation 3 and substituting Equation 2:

Equation 5

$$k = \frac{\ln(\frac{E(t_1)}{E(t_2)})}{t_{1\to2}} = \frac{\ln(\frac{Q(t_1)}{Q(t_2)})}{t_{1\to2}}$$

It becomes apparent that the rate constant determined using experimental data and Equation 5, (or its more complex version in Chapman (2009a)) is net of all the influences on E, so long as the r^2 is

sufficiently high. That is, if a simple model is a good descriptor of the composting time course then the rate constant that is determined must include diffused substrate and substrate released from insoluble sources.

Leading to the question as to why bother to add computational complexity (and additional parameters) unless:

- The simple kinetic fails to adequately describe the composting time course or
- It is necessary to know each of the components separately. Such as if an experiment required using particle sizes that straddled the critical radius. In this case the rate constant for a fully aerobic particle (one smaller than the critical radius) may differ from the rate constant for particles with an anaerobic core.
- It is important to know E(0) accurately.

Note: that the value of E(0) is dependent on the value of the rate constant. The experimentally observed composting rate is modelled by these two parameters hence change one and the other must change for the model to explain the composting time course.

2.1.2 Case 2 - Theoretical

A theoretical test can be applied to gain insights into the adequacy of using first-order kinetics as a descriptor of the composting time course. If incorporating these other sources of substrate results in an equation where E(t) is described by Equation 3, then the combined parameter will behave as a single one over the entire time course. Such a state could exist if the proportion of these other contributions remains fixed to the resident substrate. In this case let α represent this fixed proportion then Equation 4 can be written as:

Equation 6

$$E(t_2) = E_{resident}\ (t_2) \times \left(1 + \alpha_{diffused}\ + \alpha_{released}\ \right)$$

Then as long as $E_{resident}$ is described by Equation 3, and the proportions remain constant, a valid first-order kinetics descriptor of a composting time course arises which incorporates these other sources of substrate.

A requirement arising from Equation 6 is that the added substrates need to be a *fixed* proportion of the resident substrate.

The question as to whether each component remains a fixed proportion over time can be addressed for each component independently of the other. A superficial look at each of these components follows:

2.1.2.1 The diffused substrate component

The diffused substrate component of Equation 6 is net of addition and consumption. The resulting dynamic balance introduces an added level of complexity in that a rigorous analysis would need to account for:

- Diffusion coefficients being affected by molecular weights. High molecular weight compounds would therefore move differently from low molecular weight compounds.
- Consequently, each compound may need a specific rate constant.

This level of complexity can be reduced by considering that for each compound the diffusion driver is concentration difference with the flux determined by Fick's first law of diffusion. Fick's first law states that the flux of a substance is equal to a constant times concentration difference divided by distance ($J = -D * dC/dx$). Considering that for the composting situation being discussed here, the concentration difference leading to substrate diffusion arises from substrate degradation, then for any compound at any time (t) this difference (and consequently the diffusion flux) is likely to be explained to a large degree by Equation 3.

While a full analysis should await a larger study meshing diffusion laws with microbial kinetics (as it also involves moving boundaries), it would seem reasonable to expect the net effect of the diffusion flux to be a fixed proportion of the resident substrate, with the common element linking the two being the rate constant.

2.1.2.2 The released substrate component

The fast fraction is likely to be entirely soluble substrate therefore the slow and humification fractions can be expected to be donators of $E_{released}$. Consequently, the absolute amount of substrate released by solubilisation would be more likely to be influenced by the insoluble substrate concentration and the quantity of exo-enzymes present (i.e. the composting rate of the slow and humification fractions), rather than the resident pool of soluble substrate. The proportion $\alpha_{released}$ could change over time and the validity of first-order kinetics fail due to violation of the requirement for the proportion of the resident substrate to be constant (Equation 6).

The question is how this variability can be accommodated in the first-order kinetics formulation?

Hess's law of constant heat summation states that the net heat of a chemical reaction is equal to the algebraic sum of the heats of any intermediate reactions. That is, the existence of intermediate solubilised compounds has no influence on the overall heat loss if these intermediate compounds are further oxidised. The same heat loss would occur if the substrate were oxidised directly to CO_2 and H_2O without any intermediate products. This is the case with solubilisation where large molecules are broken into smaller ones that can then be utilised by cells.

To consider the effect of this law on parameter determination, consider the composting time course that would arise if a single insoluble substrate (such as cellulose or hemicellulose) was being composted. This author would argue that it would not be possible to distinguish the solubilisation signal from the consumption signal (in the manner that the fractions were able to be distinguished in part I). They would appear as a single fraction and a single 'combined' rate constant would be determined. If this paper were to explain this effect from a scientific perspective, then Monod kinetics could be used to determine the concentration of soluble compounds at which the consumption rate = solubilisation rate and the time course of the solubilised substrate concentration plotted against the concentration of the insoluble substrate. I would expect this plot to be linear with the slope representing the net effect of the two rate constants and the half-rate constant. In effect solubilisation becomes rate limiting and the contribution to composting from consumption of these soluble compounds is constrained by this release rate. So while, with a strictly chemical classification one may be able to identify a fast fraction (the solubilised substrate) and a slow fraction (the insoluble substrate), their interdependence would mean that they would appear to be a single fraction in their experimental time course.

So how can this complexity reduce to a form suitable for inclusion in a first-order kinetics model?

Equation 6 has been shown to be a suitable form for inclusion, leading to the consideration as to whether Equation 6 adequately accounts for solubilisation and consumption within each fraction. Firstly, Equation 6 needs to be formulated for each fraction (S) as:

Equation 7

$$E_S(t_2) = E_{(S)resident}\ (t_2) \times \left(1 + \alpha_{(S)diffused} + \alpha_{(S)released}\right)$$

With solubilisation being rate limiting, the solubilisation rate constant would determine the fraction's composting time course and hence also the time course of $E_{(S)resident}(t_2)$; while $\alpha_{(S)released}$ describes the subsequent oxidation of the solubilised products. Hence, for a fraction which requires solubilisation of its substrate (where the solubilised products are subsequently utilised), it becomes apparent that the two processes under consideration can be incorporated into Equation 7 but only when it is formulated for each fraction.

The magnitude of $\alpha_{(S)released}$ would be determined by the stoichiometric relationship between the substrate, the solubilised compounds and the final breakdown products. Consequently, it is reasonable to assume that $\alpha_{(S)released}$ will be constant. It also becomes apparent that the rate constant as determined by Equation 5 would be a 'combination' of the solubilisation rate constant (explaining the time course of $E_{(S)resident}(t_2)$) and the contribution from the solubilised compounds – the effect of this on the magnitude of the rate constant is discussed further below.

There may be a question as to whether the proportioning method advocated in Part I adequately allocates *all* the experimental time course of the soluble components to each fraction (as required for Equation 7), although the high r^2 would suggest (rather than prove) that this is happening. However, with both theoretical space in the first-order kinetics model and a high r^2 it is argued here that solubilisation *is* included in each fraction's time course and hence automatically included in the parameters.

It is therefore a different interpretation of Equation 7 that is required to account for solubilisation. If the rate limiting step determines the time course of $E_{(S)resident}\ (t_2)$, then Equation 7 explains all fractions, thus:

- For the fast fraction, the rate limit is the internal machinery of the microbes and $\alpha_{released} \rightarrow 0$. $E_{(f)resident}(t_2)$ is the pool of highly degradable substrate, which is most likely to be all soluble. It is possible that some compounds which have the kinetic characteristics of the fast fraction may need to go through an intermediate stage; hence $\alpha_{released}$ may not be 0.
- For the fractions which require solubilisation, it is the kinetics of solubilisation which is rate limiting and therefore determines $E_{resident}(t_2)$. While the contribution to the observed composting time course from degradation of the resulting solubilised compounds is incorporated into $\alpha_{released}$.

First-order kinetics is preserved as an adequate descriptor even though for the fast fraction the soluble components appear as resident substrate, while for the insoluble fractions the same compounds would appear as substrate released.

The theoretical space identified in Case 2 is supported by the experimental and derivational evidence of case 1.

If $\alpha_{released}$ did vary over time then the effect of this variation on the rate constant value should be apparent. The method for determining the rate constant detailed in part I enables determination of the rate constant at each data point. Hence we have the tools available to detect any variation which may exist.

Consider the effect on the calculated rate constant by using $E(t_2)$ with a variable $\alpha_{released}$. An increase in $\alpha_{released}$ in Equation 6 will result in an increase in $E(t_2)$ with a corresponding decrease in the rate constant calculated using Equation 5 – see Figure 2 for the effect of this.

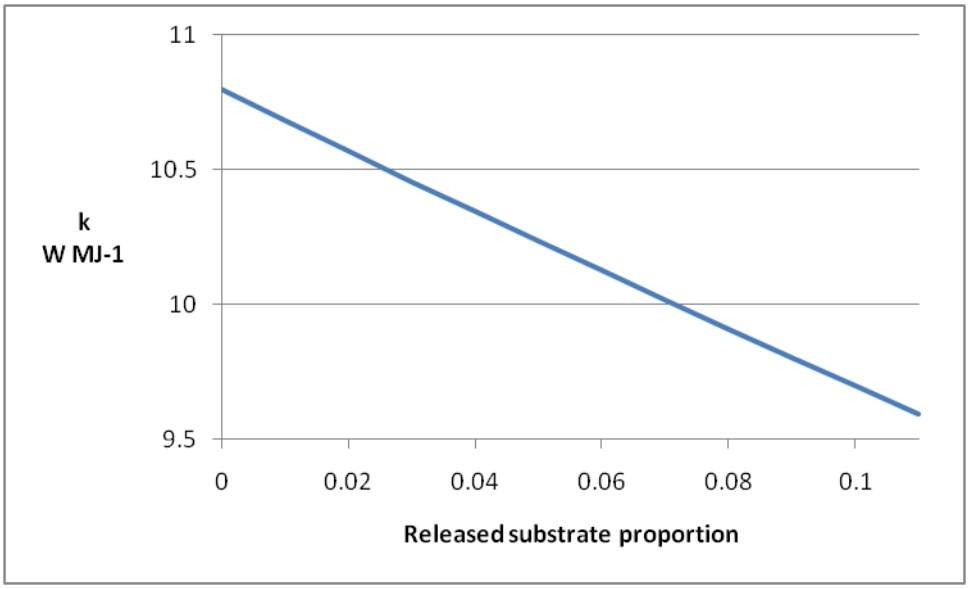

Figure 2 – The theoretical effect of changing $\alpha_{released}$ (or $\alpha_{diffused}$) on the calculated rate constant. Note that diffused substrate is entered as zero for this calculation as no change is expected in its proportion. The released substrate proportion begins at zero. Released substrate is assumed to be incorporated into the rate constant determination, and we will be detecting a change from this datum.

In Figure 2 that part of released substrate which occurs in the time period over which the rate constant is determined is assumed to be incorporated into the rate constant, hence the graph begins at zero and the x axis is the change from this datum. It is the change from this datum that could be detected in experimental data.

3 Results

If solubilised and diffused substrate contributions are constant then the rate constant determined at each point (using Equation 5 with the slope determined by linear regression - as detailed in Part I),

should show little variation in its value. Figure 3 however shows variation in its calculated value, rising to a peak and then falling[1].

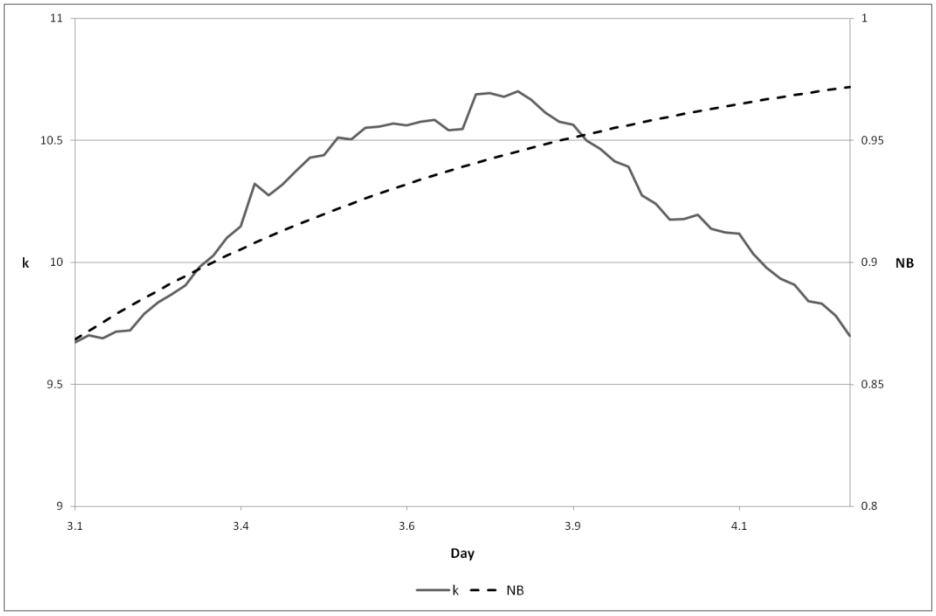

Figure 3 – The fast fraction rate constant determination for Trial 4 data (0.8 cm dog sausage) between t_{max} + 15 hours and Q/Q_{max} = 0.2. Source data from: Chapman (2008).

Up to the peak of the graph, precise rate constant determination is potentially compromised by an incorrect determination of the one-exponent constant used in determination of NB. The effect of the NB runs counter to the effect of the rate constant, and the two are interdependent making separation of the experimental signals more difficult. However, the impact of incorrect determination lessens as NB approaches 1, meaning that the value of k is likely to be more precise (less influenced by the NB value) as one moves to the right in Figure 3. If this were the only influence on determination of k then the graph should plateau when NB approaches 1 (or at the very least the rising trend should have continued). The influence of NB therefore is not a reason for the observed decline in k. Some other impact on determining the value of k must be involved.

It is suggested that this could be an effect of a change in the magnitude of the contribution from either solubilised or diffused substrate. In theory this effect is possible, and the experimental signal is consistent with an increase in either of these contributions (discussed above). In this case a change in the proportion in the order of 0.1 is a possible explanation for the decrease in the value of k from its peak.

Further possible reasons for this change are discussed below.

4 Discussion

The experimental evidence gave two apparently conflicting signals for this single set of data:

[1] Note the slow fraction k of the same trial showed a steady decline in the value of k over its equivalent period. The actual shape of each fraction's rate constant curve may be specific to each set of data. This example should not be considered to apply generally.

- A very high r^2 indicating a good fit for the model.
- Evidence from the rate constant determination suggesting further consideration is required.

It is possible that a full explanation lies in the "1-exponent" formulation for the NB developed in Chapman (2009a). This however, is not the subject of this paper. More high quality data would be needed to resolve this question.

Of the issues being discussed in this paper, there are five possible explanations for this decline in the rate constant (assuming the NB determination or refinement –as discussed above is unlikely to explain the *decline* in the rate constant):

- Variation in $\alpha_{released}$. Possible sources could include compounds from anoxic or anaerobic degradation or death of biomass.
- Variation in $\alpha_{diffused}$.
- Incorrect determination of the slow rate constant.
- The proportioning method described in Part I is not including the solubilised component in the fraction's composting time course.
- Experimental artefact, such as reactor calibration errors.

For example, variability in $\alpha_{released}$ could arise from the breakdown products of anoxic degradation (nitrous oxide etc), or anaerobic degradation (volatile organic acids, methane etc) which are subsequently oxidised in the aerobic zone and detected. The time course of anoxic, and anaerobic, degradation kinetics are likely to differ from aerobic kinetics (at the very least they occur in different parts of the particle) and could change the $\alpha_{released}$ proportion over time – discussed further below.

Dead biomass is known to be highly degradable and the death rate could be expected to increase as the declining quantity of substrate leads to starvation of the resident biomass. A steady death rate could be expected to be incorporated into the slow fraction rate constant determination (as there is little difference between the kinetics of biomass and soluble compound degradation this would be incorporated into $\alpha_{released}$) but if the death rate changed this could appear as unallocated $\alpha_{released}$ in the fast fraction.

Incorrect determination of the slow fraction's rate constant could leave a residue quantity of soluble compounds not accounted for in the slow fraction's rate constant determination, but visible in the experimental data of the fast fraction. In part I of this series the possible existence of a small anoxic contribution to the composting time course was raised and it was argued that, as it was not allowed for in the parameter determination algorithm, this could have affected the magnitude of the slow fraction rate constant. The model overestimate of the slow fraction composting rate (noted in part 1) became apparent at day 6 but could have been exerting an influence by day 3.8 when the decline in the value of the fast fraction rate constant began in Figure 3 above. The steady decline in the value of k indicates a constantly increasing $\alpha_{released}$ and this would be consistent with the growth phase of the anoxic period.

Alternatively, an explanation may arise from either a methodological source (the proportioning method) or errors in measurement arising, for example, from calibration errors in the experimental reactors. Measurement errors would become more significant at low composting rates so the net

effect will change over the composting time course and affect the slow and humification fractions more than the fast fraction.

Of these possible sources of variation in $\alpha_{released}$ or $\alpha_{diffused}$ as reflected in the variation in the value of k, this author would suggest that resolving the possible anoxic contribution that was identified in Part I should be done first. A possible anoxic contribution has both analytical space and experimental evidence to support its existence. Accommodating an anoxic contribution would impact on the value of the slow fraction rate constant and the effect of this on the plot in Figure 3 should be assessed before investigation of alternative explanations.

Whatever the source of this variation in the value of k that is determined, the effect of constraining the segment of the data set used for rate constant determination, transfers the impact of this variation in $\alpha_{released}$ or $\alpha_{diffused}$ to the latter part of the fraction's composting time course. Using only a part of the data set means that the rate constant would only be valid for the part of the time course used in the rate constant determination. Consequently, the part of the time course *not* used in rate constant determination (but used in the model prediction) may well have a low r^2 that arises from the first-order assumption failing due to a changing magnitude of $\alpha_{released}$. However, as this part of the fraction's time course coincides with the next fraction dominating the composting rate, this error becomes insignificant in terms of the modelled composting time course. That is, while the error may be significant for the fraction there is little impact on the model regression coefficient.

The modelling question needs to be whether this constraint (which retains high precision microbial kinetic parameter determination by treating all sources of substrate as one – a requirement identified in part I of this series) is preferable to the additional parameters that would be required if solubilisation and diffusion were modelled separately – with the possible loss of precision in determining the values of the kinetic parameters due to over-parameterisation?

5 CONCLUSION

A model which is inherently capable of describing all the physical characteristics of a composting time course (lag/growth phase, two (or more) composting rate peaks, rounded and sharp peaks etc) will be useful from a pragmatic perspective (in that with calibration it can adequately describe the composting time course). However the ability of the model to predict other situations is potentially limited by the assumptions inherent in the model formulation. If these assumptions (and their associated parameters) are based firmly in microbial kinetics and the laws of physics then the applicability of the model will be widened.

With composting being an inherently complex 3-phase system, the number of fundamental parameters that could be included is considerable. This complexity is further compounded by the interdependence between all the parameters. With insufficient data to be able to determine each parameter accurately the model in essence becomes phenomenological where the regression coefficient may be high, but the parameters lose their close association with their scientific roots. Over parameterization emerges as a problem not only in terms of determining the value of the parameter, but also the parameter's connection to its roots.

It is argued here that a simple kinetic incorporates considerable complexity in its parameter determination by forming 'combined' parameters. This suggests that for complex systems it is

sufficient for most pragmatic purposes to use a simple structure, so long as the model closely resembles the base dynamic. It is only if the specific question being asked by the researcher requires unbundling of these combined parameters that the task needs to be done.

It would seem that many parameters which currently compound the over parameterization problem in composting science can be ignored in most modelling applications. The possibility that using a model with a smaller number of precisely determined parameters may result in greater compost understanding is the question than seems to be answered in the affirmative by this work.

The theoretical basis for this conclusion is established here, as is a theoretical and computational method to test the validity of the theoretical conclusions. At the very least, these are tools which can be used for detecting aspects of the composting time course. These may have value in reducing some of the statistical variation that makes composting research so difficult.

6 Bibliography

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