PARAMETER DETERMINATION IN COMPOSTING – Part I

The use of overlaying interdependent sets of equations as a solution to the over parameterization problem

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Abstract

Over parameterization in composting is an issue for the more complex composting models. This work proposes using a simple microbial kinetics (first-order kinetics) with more attention to accurate determination of the kinetic parameters as a base on which to rest the remaining complexity of the 3 phase system which is composting.

With consideration of the theoretical basis on which parameters rest, it is shown to be possible to determine each microbial kinetic parameter with high precision by identification of a 'key' modelling parameter (transition time). This key parameter required fitting with least squares.

However, this level of precision is only possible for a data set that utilized a single electron acceptor/ substrate fraction combination. Consequently, separating a data set composed of several fractions into its contributing parts becomes a separate parameter determination problem requiring its own solution. A proportioning method is proposed to achieve this.

In this manner, fitting a model curve to a data curve by determination of the basic microbial kinetic parameters can be reduced to several computational levels requiring consideration of the interconnectivity between several sets of equations. High precision determination of microbial kinetic parameters is possible, but only within the part of the computational landscape set by the other parameters (aerobic proportion and fraction proportion). Iterative methods are needed to find the optimum solution for the complete system.

When applied to experimental data in its simplest form (no adjustment for aerobic proportion was assumed necessary due to the small particle size), the method generated a set of parameters that could describe two different sets of data with a very high r^2 (0.94 for one set and 0.99 for the other) for up to 114 days of composting.

However, further work may be needed to reliably determine the humification rate constant. Particularly with a reduced data set and the increased variability in the data arising in part from the reactor design used to get this experimental data.

An additional benefit of considering the theoretical basis is that the electron acceptor element of microbial kinetics can be accommodated. Diffusion laws are required to understand this distribution but, from the context of microbial kinetic parameter determination, this is best viewed as an overlay which places microbial kinetics into a space based framework. Interdependence between this

overlay (the physics of oxygen distribution) and the resulting experimentally observed composting rate, add a level of complexity to parameter determination which can be avoided by experimental design.

Indeed, the location of a possible anoxic contribution to the composting time course can be identified in the data used here. This occurred despite a small particle size being used to avoid such issues. If such a contribution were shown to be occurring then the r^2 could be expected to get beyond 0.99 for high quality data sets. This potential insight indicates the value inherent in basing parameter determination firmly in kinetic theory.

1. Introduction

The inherent complexity of composting means that a theoretical model that includes all of the known factors that impact on composting will suffer over parameterization problems. Attempts to solve this problem typically attempt to reduce the total number of parameters needing to be determined.

In order to retain microbial kinetics as the primary determinant of the composting time course consideration of the microbial significance of a rate constant is required. From this beginning, a mathematical and computational structure is formulated that enables high precision determination of the basic microbial kinetic parameters.

The total number of parameters is not reduced in this formulation; rather it is the number of parameters needing to be *visible* at each computation point which is reduced (in many cases to one). The remaining, computationally invisible, parameters are temporarily held constant until it is their turn to be computed. Iterative methods are ideal for finding the optimum solution for the system using this structure.

In this manner each parameter in each set of equations becomes identifiable, while the interdependence between a particular parameter and the other sets of equations becomes a separate computing problem; but one which avoids the over parameterization problem. In a sense, the analysis becomes multilayered and this structure is used as a computation aid.

The method is used to determine microbial kinetic parameters for two sets of experimental data. These parameters were able to describe the data set with a very high r^2.

Identification of interdependent sets of equations, segmentation of the data set, and a mathematical structure supportive of iterative methods enables each microbial kinetic parameter to be determined with high precision. This forms a very sound base on which to rest compost science.

2. Literature review

The essence of all microbial kinetic models is that they are describing a microbial ecosystem's interaction with its food supply and environment. In the language of kinetic models the food supply is called substrate, the concentration of the substrate is the modelling equivalent of the quantity of food, while the rate constant models the consumption rate of this substrate. Macro-scale models

such as those reviewed in Mason(2006) need a high quality set of microbial kinetic parameters as a base on which to sit.

2.1. Rate constant

The experimentally determined rate constant embodies the biomass's utilization rate of the substrate and includes: cellular machinery, nutrient transfer across the cell wall, exo-enzyme production etc, as well as the stoichiometry of the substrate/electron acceptor combination.

With stoichiometric analysis the energy as well as molecular weights must balance in a chemical equation (Battley, 1987). That is, if the substrate and electron acceptor on one side and biomass and breakdown products on the other side of the chemical equation balance, then the free energy states of all components of the equation will also balance – with any energy not stored in the compounds being released as heat (Battley, 1987). There is evidence that the yield of biomass is proportional to the free energy state of the substrate (Payne, 1970; Servizi & Bogan, 1963), and it would seem reasonable to assume a correlation between microbial yield and the rate constant, but this author has not yet found any evidence to support this. Rate constants are essentially phenomenological; with experimentation being the only means of determination.

There can be as many different forms of rate constant as there are components to a stoichiometric analysis. The rate constant units are most convenient if the units are the same as the measurement of composting rate and; because of the stoichiometric relationship, the rate of change of any of the components is equally valid as a measure of the whole. In addition, as sensors (Richard, 1997; Sadaka, Richard, Loecke, & Liebman, 2006; VanderGheynst, VanderGheynst, & Walker, 1997) and data processing equipment evolves (Richard, 1997), so too have the measures of composting rate evolved. Volatile solids being the earliest, and perhaps most common form (Wiley & Pearce, 1957), but CO_2 based ((Hadas & Portnoy, 1997; Richard & Walker, 2006; Sadaka et al., 2006; Schulze, 1960; Suler & Finstein, 1977; Tremier, Guardia, Massiani, Paul, & Martel, 2005; Vikman, Karjomaa, Kapanen, Wallenius, & Itavaara, 2002), oxygen based (Hamelers, 2001; Schulze, 1960; Sole-Mauri, Illa, Magri, Prenafeta-Boldu, & Flotats, 2007) with COD (Haug, 1993; Huang, Wang, & Jih, 2000) being a version of oxygen based, and more recently thermodynamic (Chapman, 2008) rate constants are becoming more common. Indirect measurements of rates include ATP (Tiquia, Wan, & Tam, 2002; Tseng, Chalmers, & Tuovinen, 1996; Vikman et al., 2002) – although this is used more for estimating biomass, enzyme activity (Garcia et al., 1993), and radioactive carbon (Van Veen, Ladd, & Amato, 1985). While other terms and measures which are not strictly rate constants, such as a compound's half-life (Gilmour, Broadbent, & Beck, 1977; Jury, Russo, Streile, & El Abd, 1990) and BOD_5, (Parker & Rhoades, 2003) can be useful as indicators of kinetics. Any rate constant form can be related to all other forms by stoichiometry (e.g. VS, CO_2, oxygen, energy released, are all comparable via stoichiometric analysis). Thus the amount of energy lost as heat can be determined from the amount of substrate or oxygen consumed, or CO_2 released, if the relevant chemical equation is known.

Sampling frequency is another consideration in rate constant determination. Traditionally in composting, volatile solids was the basis of rate measurement and as this requires destruction of the sample, measurements were typically several days apart (Wiley & Pearce, 1957). However, any measurement which limits sample frequency to daily time frames has limited application as it cannot measure the instantaneous rate of composting. Chapman (2008) argued that a rate constant which degrades most of its fraction in a day, such as would occur with the reported rate constant values

noted in Van Veen et al.,(1985), would require a sampling frequency of around 30 minutes for such a fraction to be identified (based on Hamelers (2001), 40 data points being needed for identifiability).

The availability of suitable sensors and experimental techniques (discussed above), means composting rates can now be measured at the higher frequencies necessary to adequately separate any signal from these high rate constants, from its slower neighbours.

2.2. Rate constant base

Rate constants are determined as rate * quantity^{-1}; which in its most common form reduces to day^{-1}. However, there is no widely acknowledged base on which to rest the quantity. The base on which a rate constant is determined not only directly influences the magnitude of the constant, but it also limits the range of the application of the constant to similar materials. The word similar in the previous sentence contains far greater implications for composting than the term seems to imply, as it must be viewed from a microbial perspective (a rate constant is the model expression which contains the full range of factors of a biomass's interaction with its substrate – of which the free energy available from the substrate, discussed above, is but one of these factors). Similar from a microbial perspective therefore, would imply carbon accessibility with all the chemistry and physical structure (as argued to explain the difficulty in degrading lignocellulosics (Fan, Young-Hyun Lee, & Garpuray, 1982)) implications that impact on accessibility. But it also involves questions of the scale of analysis if a particle ceases to become uniform as composting proceeds (Chapman, 2008).

Without rate constants having any particular affiliation, the total sample has tended to become the base for rate constant determination. This suffices as a base if one is always using the same material, in particular considering that slower rate constants express later in the composting time course, so the two 'periods' can be treated as separate. A better fit, with wider application, can be achieved by acknowledging that a part of the substrate is at best poorly degradable and this can be deducted from the total (modelled using a zero contribution entity such as 'non-degradable VS' (Haug, 1993), 'equilibrium mass' ((Keener, Marugg, Hansen, & Hoitink, 1993), or lignin content (Eklind & Kirchmann, 2000)).

With identification of several fractions in composting (Haug, 1993; Kachaka, Vanlauwe, & Merckx, 1993; Kim, Kim, & Lee, 2000; Liwarska-Bizukojc, Bizukojc, & Ledakowicz, 2001; Tremier et al., 2005), considerations of the base on which the rate constant rests becomes even more important. However, there does not seem to have been adequate scrutiny of this issue. In many cases, it is difficult to understand what the base of many of the published values is, largely due to the increasing use of data fitting algorithms (Hadas & Portnoy, 1997).

2.3. Substrate concentration

Differences arise between kinetic models in how they include the effect of substrate concentration, a wide range of formulations have been tried (Andrén & Paustian, 1987; Kulcu & Yaldiz, 2004; Saviozzi, R. Levi-Minzi, & Riffaldi., 1993), but two are of main concern here:

- First-order - The rate is directly proportional to concentration (Bari & Koenig, 2000; Ipek, Arslan, Obek, Karatas, & Erulas, 2005; Lemus, Lau, Branion, & Lo, 2004).
- Monod kinetics - Where the effect on the rate ranges from a negligible effect at high concentrations (zero –order) to directly proportional at low substrate concentrations (first-

order) (Hamelers, 1993; Huang et al., 2000; Liang, Leonard, Feddes, & McGill, 2004; Stombaugh & Nokes, 1996).

Mason (2006) considered the Monod type kinetics to be *less* successful at modelling composting.

2.4. Model formulation

Often environmental considerations are included in the microbial kinetic models, such as:

- Toxicity effects (Haag, Wouwer, & Remy, 2005; Vavilin & Lokshina, 1996).
- Moisture effect (Hamelers & Richard, 2001; Richard, Hamelers, Veeken, & Silva, 2002; Stombaugh & Nokes, 1996).

However, it is understood that if the model becomes too complex then over parameterization problems arise. Hamelers (2004) chose a mathematical path to solve the over parameterization problem. Here several parameters were 'lumped' into one, thereby reducing the total number. However, some compromises were necessary to achieve this.

It is possible to get a 'best fit' using computer algorithms and statistical techniques (VanderGheynst, Gossett, & Walker, 1997). However, without the base of these parameters being firmly grounded, the applicability of the parameters to other experiments is likely to be limited. In the absence of well grounded parameters, all parameters tend to become phenomenological and it may be a consequence of this that may explain a part of Schloss & Walker's (2000) observation on the statistical power of composting experiments. In a subsequent paper, Schloss & Walker, (2001) noted "*...the great need for improved process reproducibility in the field of composting at both the research and application levels.*".

The possibility that a simple model, correctly applied, may be sufficient to explain much of the composting time course has only recently been proposed (Chapman, 2008), although similar arguments have arisen in the biofilm literature (Pérez, Picioreanu, & Loosdrecht, 2005).This raises the possibility that existing composting models are too complex, and that sufficient understanding is possible by using a simpler basic model and allowing the complexity to arise as necessary. In the case of Chapman (2008), diffusion laws were used within the framework of finite volume methods to explain the oxygen distribution in a composting particle.

Using a finite volume method, Chapman (2008) was able to identify 'micro-environments' (these being onion ring type volumes of compost) in a composting particle. What is relevant for microbial kinetic parameter determination is that with this formulation an experiment could be designed in which there was only one micro-environment (i.e. the particle is fully aerobic and there is only one electron acceptor in the observed composting time course). In this manner much of the complexity arising from composting being a 3 phase system can be experimentally controlled to enhance parameter determination. Consequently, he chose to determine the basic microbial kinetic parameters by using a small particle size. The effect of different electron acceptors (which also includes those which may have a contribution so low as to be effectively zero) on the composting time course was eliminated. These parameters were then used to successfully explain the time course of larger sized particles.

One criticism of Chapman's thesis was that he had manually fitted his parameters to the data. His intuition that there is more to parameter determination than could be accommodated by a 'parameter fitting algorithm', and that these elements needed to be thoroughly explored, is the essence of this paper.

3. Method

It is proposed to separate the parameter determination problem into different sets of interdependent equations. The use of groups of equations in different sets means each set of equations will contain parameters which can be determined with as much precision as possible while temporarily holding the output of the other sets constant. As there is a high degree of interdependence between the sets, using the output of one set as an input to the other sets is an ideal structure for use of iterative procedures to move towards the optimum solution for the system as a whole.

It is further suggested that these sets begin with microbial kinetics so that the computational needs of microbial kinetics shapes the equations of the other sets. Three sets would seem to cover most requirements: microbial set, electron acceptor set, and an environmental set, thus:

- Microbial kinetics is specific to each electron acceptor/substrate combination.
- The dominant electron acceptor in composting, oxygen, requires diffusion laws to understand its distribution. Other electron acceptors are inhibited by oxygen so occur in different places in a composting particle.
- Some environmental effects (such as pH) are site specific, and/or influenced by the microbial kinetic. Others, such as temperature exert their influence through parameters in other sets. The influence of these environmental parameters on already existing parameters needs to be accounted for before a separate parameter is formed. e.g. temperature affects:
    - The solubility of oxygen in water, the diffusion coefficient and aerobic proportion in the electron acceptor set,
    - The rate constant in the microbial set.

The boundaries of these sets of equations often seem to emerge naturally as a result of the analysis. For example, understanding electron acceptor distribution using diffusion laws to determine oxygen penetration distance requires only a single parameter from the microbial kinetics set – volumetric oxygen uptake rate (VOR). The entire set of microbial kinetic equations result in this one parameter which then becomes one of several parameters in the electron acceptor set.

Some reformulation of compost theory is therefore necessary so the optimum location of these boundaries is found.

3.1. Calorimetry

A thermodynamic approach to studying composting is used here. A calorimeter was used to obtain the experimental data and it was found more convenient to write the kinetics in a thermodynamic form so the heat production data could be used directly in the analysis. The relationship between a calorimetric rate constant and other forms (such as VS, CO_2 evolution etc) can be established by considering the stoichiometry of the substrate.

3.2.DERIVATION

As a microbial process, the observed composting time course will be a sum of all the microbes that make up the biomass which is present.

Equation 1

$$Q(t) = \sum Q_{microbe}\ (t)$$

While this could reduce to an individual microbe, computing power limits, and the inherent variability in any microbial eco-system, suggest a sufficient lower level of analysis would be groups of micro-organisms using the same electron acceptor with the same substrate concentration in similar environmental conditions. These analysis units were called micro-environments in Chapman (2008).

Thus each group of microbes would have a similar range of kinetic and environmental conditions. That is, micro-environment (m) would have conditions:

Equation 2

$$Q_m(t) = f(electron\ acceptor, substrate, environment)$$

These conditions would differ from those of micro-environment (m ± 1) and they would also differ from micro-environment (m) at time (t ± ti). Diffusion laws distinguish between micro-environment (m) and micro-environment (m ± 1), while microbial kinetics account for the changes in each micro-environment over time (primarily by changes in substrate concentration).

Oxygen as an electron acceptor was the basis of Chapman's (2008) thesis and for a full understanding it was found necessary to include particle size, as diffusion laws require consideration of concentrations over distance (space). Thus determination of the electron acceptor in Equation 2 requires a set of equations which 'overlay' the microbial kinetic set of equations and puts microbial kinetics into a space based framework, Equation 3. The two sets of equations are interdependent (hence substrate and environment occur in each equation), but can be computed separately.

Equation 3

$$electron\ acceptor = f(diffusion\ laws, particle\ size, substrate, environment)$$

An example of the effect of Equation 2 and Equation 3 on parameter determination can be seen if one considers a particle with a significant anaerobic/anoxic core[1]. In this case, two (or more) electron acceptors could be present and the effect on parameter determination arises from:

- The possibility that the observed composting time course is a net result of two different electron acceptor based rate constants, and any interactions between them. If the parameter determination algorithm allows for determination of only one rate constant, then

[1] Micro-environments are formed only where oxygen is present, therefore anoxic and anaerobic electron acceptors would occur outside micro-environment space, but would have a volume proportion related to micro-environment space i.e anoxic/anerobic volume proportion = 1-Φ.

the parameters determined will be somewhere between the two (depending on the relative contribution of each), but represent neither adequately.

- Even if the contribution from the anaerobic/anoxic rate constant is negligibly small or zero, but their volume proportion is significant, a distortion still remains. This distortion arises from the parameter determination being based on a unit quantity of compost (whether mass based as in VS, or volume based - as in this determination). If the proportion of the particle contributing to the observed composting rate (Φ_k) is less than 1, then the unit quantity of compost that is used for parameter determination must be correspondingly reduced (Equation 4). It is only if the electron acceptor is distributed throughout the particle i.e. Φ_k =1, that this effect can be ignored. This is even more critical for the fast fraction where Φ_k changes markedly over the period used for parameter determination.[2]

Equation 4

$$Q_k = \frac{W_{reactor}}{V_{reactor} \times \Phi_k} \qquad \text{W cm}^{-3}$$

- The starting substrate concentration E(0) will also be affected if $\Phi_k < 1$ as Q_k is a determinant of E(0).

Environmental effects will need to be treated on a case by case basis. Some, such as temperature, would affect all micro-environments similarly; others such as pH may be micro-environment based.

It would seem reasonable to assume that determination of microbial kinetic parameters specific to an electron acceptor/substrate combination would have wide application. A wider application than if parameter determination were to be done on a compost sample containing a range of substrates and electron acceptors. In the latter case the parameters would apply only to similar mixtures (primarily similar substrate proportions) with comparable particle sizes.

There are two ways of accounting for the effects of different electron acceptors in microbial kinetic parameter determination:

- Experimental design, where a particle size is used such that Φ_k is at, or very close to 1.
- Adjust for Φ_k in the parameter determination algorithm.

If Φ_k is used in the parameter determination algorithm then an iterative procedure must be used as Φ_k is itself determined by the rate constant (specifically the volumetric oxygen uptake rate). A set of equations for determining Φ_k are described in Chapman (2008).

The set of equations used for determining microbial kinetic parameters, described below, apply to a single electron acceptor, although this does not have to be oxygen. For example, if a data set contains anoxic degradation, and the proportion of a compost sample using this electron acceptor were determined using Equation 4, then the same subroutines could be used in parameter determination – oxygen uses k_{aer} and Φ_{aer} , while the anoxic electron acceptor uses k_{anoxic} and 1- Φ_{aer} . The net composting rate is $Q_{aerobic}(t) + Q_{anoxic}(t)$. The equations and procedures work equally well with

[2] Note that if the default position is that of not adjusting for aerobic proportion, then Φ_k =1 is implicitly assumed and this distortion becomes unwittingly structural.

either electron acceptor, although the computation load is much higher as Φ_{aer} must be calculated for each time interval and each iteration of k.

However, the simplicity of using a smaller particle size for determining microbial kinetic parameters, would likely appeal to most compost researchers.

Similarly, simplicity would require that parameter determination be done with only a single degradable substrate. The bulking material should preferably be inert, so all the observed effect can be attributed to the substrate and its parameters.

In thermodynamic form, the first-order kinetic equation is written as:

Equation 5

$$Q(t) = k \times E(t) \times NB(t) \qquad \text{W cm}^{-3}$$

Where:

k = Rate constant W MJ^{-1} ≡ day^{-1} * 10^6 / 86400 = day^{-1} * 11.57

E(t) = Substrate concentration MJ cm^{-3}

NB(t) - Normalised Biomass(t) is normalized to equal 1 when biomass ceases to limit the composting rate. It is described by two equations: an exponent function and a (1-exponent) function with a transition time (t_{trans}) being the time in the composting time course up to which the exponent function is used and beyond which the (1-exponent) function is used.

The normalised biomass (NB(t)) parameter is one that accounts for the growth phase (otherwise known as the biomass limiting stage or lag phase) in microbial kinetics. A formulation that microbiologists developed is widely used in composting and is based on the quantity of biomass (X) and the yield Y_m (gms biomass / gm substrate consumed). However, biomass is difficult to measure, and considering that most of composting occurs in the decline phase where biomass is not limiting, a normalised formulation (NB) was developed and is used here – see Chapman (2008) for the original derivation from the microbiologist's formulation.

Using a parameter that normalizes to 1 when microbes do not limit composting has advantages in rate constant determination (where the effect of biomass growth on the modelled time course, runs counter to the effect of the rate constant). It also avoids the need to determine actual microbial biomass.

For the exponent function:

Equation 6

$$NB(t) = NB(0) \times \exp(C_{exp} \times t) \qquad t \le t_{trans}$$

For the (1-exponent) function[3]

Equation 7

$$NB(t) = 1 - Exp(C_{1-exp} \times (t - t_{delay})) \qquad t > t_{trans}$$

Where t_{delay} is the time when the function crosses the x axis (i.e if the one-exponent function were the only function involved then, $NB(t_{delay}) = 0$). This formulation enables the time of the modelled Q_{max} to equate the data Q_{max}, and for the transition from exponent to (1-exponent) to occur seamlessly at t_{trans}.

Combining the two functions creates an S shaped curve that fits very well with the observed composting time course.

3.2.1. Exponent Constant

The exponent constant C_{exp} can be determined from knowing NB at two points: t_{trans} and t = zero. Using a partial derivative of the sum of squares, NB(0) can be determined by:

Equation 8

$$\frac{\partial s}{\partial NB\,(0)} = 2\sum_t \{k \times E(t) \times \exp(C_{exp} \times t) \times (Q(t)_{model} - Q(t)_{data})\} \qquad t \le t_{trans}$$

Equation 8 = 0 (minimum sum of squares), at the optimum value of NB(0). Either side of the best fit value, it returns either a positive or negative slope, a useful feature for the iterative methods needed here due to the interdependence of the parameters.

Knowing NB(0) from Equation 8, and $NB(t_{trans})$ from Equation 14, C_{exp} can be determined with Equation 9:

Equation 9

$$C_{exp} = \frac{\ln\left(\frac{NB\,(t_{trans})}{NB\,(0)}\right)}{t_{trans}} \qquad day^{-1}$$

3.2.2. Peak composting rate

With this model formulation, the peak composting rate occurs where the increase in NB is matched by the decrease in E. It is where the slope of the composting time course = 0, that is:

Equation 10

$$Q(t_{max})' = 0 = k \times [E(t_{max})' \times NB(t_{max}) + E(t_{max}) \times NB(t_{max})']$$

Where:

$$E(t_{max})' = E(t_{max}) \times -k \times 0.0864 \times NB(t_{max})$$

$$NB(t_{max})' = -C_{1-exp} \times \exp(C_{1-exp} \times (t_{max} - t_{delay}))$$

And $E(t_{max})$ is related to the experimental data by:

[3] Note that this formulation differs from that proposed in Chapman (2008). The (1-exp) format used here was suggested as a better formulation by Dr. K. Morison at the thesis oral.

Equation 11

$$E(t_{max}) = \frac{Q(t_{max})}{k \times NB(t_{max})} \qquad \text{MJ cm}^{-3}$$

$NB(t_{max})$ can be determined, for any combination of k and $C_{1\text{-}exp}$, by rearranging Equation 10. If ΔT denotes $t_{max} - t_{delay}$ then:

Equation 12

$$NB(t_{max}) = \sqrt{\left[\frac{C_{1-exp} \times Exp\left(C_{1-exp} \times \Delta T\right)}{(-k \times 0.0864)}\right]}$$

3.2.3. One-exponent constant

To determine the $C_{1\text{-}exp}$ constant, consider that it must satisfy two identifiable points on the composting time course - t_{max} and t_{trans}. To achieve this, rearrange Equation 7 so both points are in the same equation. From which $C_{1\text{-}exp}$ must satisfy:

Equation 13

$$\frac{\ln(1-NB(t_{max}))}{(t_{max} - t_{delay})} = C_{1-exp} = \frac{\ln(1-NB(t_{trans}))}{(t_{trans} - t_{delay})} \qquad \text{day}^{-1}$$

Where: $NB(t_{max})$ is determined by Equation 12.

$NB(t_{trans})$ is related to the data set by Equation 14.

t_delay is determined by Equation 15.

Equation 14

$$NB(t_{trans}) = \frac{Q(t_{trans})_{Data}}{k \times E(t_{trans})}$$

Equation 15

$$t_{delay} = t_{trans} - \frac{\ln(1-NB_{trans})}{C_{1-exp}} \qquad \text{day}$$

Where: E(t) as used in Equation 14, in finite element form with a time interval of ti, is determined, from:

Equation 16

$$E(t) = E(t - ti) \times \exp(-k \times \gamma \times ti \times NB(t)) \qquad \text{W cm}^{-3}$$

Where:

- $t \geq ti$
- γ converts the thermodynamic rate constant into the same time frame as ti (the author uses days as the analysis time frame meaning that for a data set with a 30 minute interval between data points, ti = 30/1440 = 0.02083 and γ = 0.0864).

- E(0) is the starting substrate concentration which occurs at t(0)[4].

If NB(t_{trans}) is determined first by Equation 14, and t_{delay} is determined by Equation 15, and these values are used in Equation 13, then $C_{1\text{-}exp}$ can be determined with reference to only:

- two parameters that need determination (k and t_{trans}) and
- two points on the data curve:
  - Q(t_{max}) – used to determine E(0) and E(t_{trans}),
  - Q(t_{trans}) – used in Equation 14.
- An iteration procedure, as $C_{1\text{-}exp}$ is required as an input in Equation 11.

3.2.4. Rate Constant – k

Beyond t_{max}, the reduction in E is greater than the increase in NB; t_{max} being the point where they are equal. As k dominates the change in E then it follows that the rate constant can be determined with minimal interference from the influence of $C_{1\text{-}exp}$ in the data segment beyond t_{max}.

From first-order kinetics, the rate constant can be determined from two points (t-ti & t+ti), thus:

Equation 17

$$k = \frac{\ln\left(\frac{E(t-ti)}{E(t+ti)}\right)}{2\times\gamma\times ti\times NB(t)} \qquad \text{W MJ}^{-1}$$

Where:

Equation 18

$$E(t) = \frac{Q(t)_{data}}{k\times NB(t)} \qquad \text{MJ cm}^{-3}$$

Substitute Equation 18 into Equation 17, cancel k and re-arrange:

Equation 19

$$k = \frac{\ln\left(\frac{Q(t-ti)}{Q(t+ti)}\times\frac{NB(t+ti)}{NB(t-ti)}\right)}{2\times\gamma\times ti\times NB(t)} \qquad \text{W MJ}^{-1}$$

If individual data points were to be used in Equation 19, then the time needed for Q to change sufficiently to reduce data variation (due to experimental error) to a minor proportion of the change in Q, constrains ti to periods in the order of one day (although the actual period is dependent on the rate constant – with shorter periods of time sufficient for higher rate constants).

Alternatively, use linear regression with a sample size large enough for the linear equation to adequately describe the data curve at time t, yet small enough to be able to ignore the fact that the composting time course is not linear, to determine a descriptor of the data time course at time t in the form of:

Equation 20

[4] The author determines E(0) by first determining E(t_{max}) using Equation 11 then using Equation 16 in reverse (i.e. E(t + ti) with a positive k) to adjust this concentration for the composting which has occurred between t(0) and t(max).

$$Q(t) = a \times t + b$$

Using Equation 20 to determine the two points needed in Equation 19, enables determination of k at each data point over the range of applicable data. The minimum magnitude of ti is set by the precision level of the computer, and is independent of the data variability; the effect of data variability is transferred to determination of the constants in Equation 20.

The variability inherent in the number of determinations that result from determination of k at each data point, means a choice criteria is needed to determine a single k for use in subsequent calculations.

- This author chose to average the k's over the period of interest, assuming in doing so that successive iterations would draw the $C_{1\text{-}exp}$ constant to its true value and hence the variation in k determined at each time interval would also reduce to its true value. For this analysis, the end point for determination of k was limited to Q(t) > 0.3 * Q(t_{max}) of the fraction. Using more of the data set appeared to reduce the fit. No attempt was made to determine the reason for this reduced fit – although an intriguing theoretical explanation is discussed in part II of this series.
- Inspection of a plot of k determined by Equation 19 over the period of interest, suggested that changes in the calculated value of k have the potential to yield useful diagnostic information. For example, there will exist a short period of time when k is least influenced by the $C_{1\text{-}exp}$ constant and minimally influenced by either the next fraction, or the limits of the experimental apparatus. If this location could be identified, then this would clearly be the best part of the data set to use for determining k. The author has seen plots where the peak of the curve seems to coincide with this point. However, one would need to know that such an effect occurred consistently before it could be used in determination of k. The influence of other electron acceptors may also be detectable in this plot, where 'bulges' in the centre of a slow k plot possibly indicate the influence of anoxic degradation.

3.2.5. T_transition

Transition time (t_{trans}) arises as a modelling parameter, rather than a microbial parameter. If a single function could be devised that described the time course of NB(t), then there would be no need for t_{trans}.

Unfortunately t_{trans} impacts the determination of all other parameters, either directly or indirectly. Directly as in $C_{1\text{-}exp}$ which uses the point in its determination, or indirectly via its data related parameter NB(t_{trans}). A second level of impact also arises in that if $C_{1\text{-}exp}$ changes, then NB(t_{max}) and E(0) would also change. Similarly, a minor impact on k could occur as $C_{1\text{-}exp}$ plays a role in NB determination which, while < 1 will impact on the determination of k.

Considering that for any t_{trans} all the microbial kinetic parameters can be determined from either:

- Partial derivative (NB(0)), or
- Reference to the data at fixed points (E(0), NB(t_{trans}), NB(t_{max}), $C_{1\text{-}exp}$), or
- Determined directly from the data (k), or
- Computed (C_{exp}, t_{delay}),

Then determination of the kinetic parameters can be 'fine tuned' by choosing a t_{trans} which has minimum least squares for the whole data set. The iteration procedure will need to recalculate the microbial kinetic parameters for each t_{trans}, before least squares are determined.

One could argue that the number of parameters to be determined by curve fitting procedures has been reduced to one (t_{trans}); a long way from an over parameterization 'problem'. In truth the total number of parameters has not been reduced, rather their interdependence is fully acknowledged and the 'key' parameter linking them all has been identified. Within the constraints of this key parameter, the others can be determined with a high degree of precision by data segmentation techniques and identification of their mathematical linkages. Transition time is a 'subtle controller' of the system; an acceptable solution could be found for a number of different values of t_{trans} (albeit within a limited range), but there is only one value which gives a least squares minimum.

It is necessary for t_{trans} to have a value at the beginning of the analysis as it determines which equation to use in calculations. This initial estimate was taken as the time when $Q(t_{trans}) = Q(t_{max}) *0.5$.

3.2.6. Calculation order

With k being determined relatively independently of the NB parameters, yet playing a part in determination of the NB parameters, suggests determination of k should be done before determination of the NB parameters. The suggested order of calculation is:

1. Proportion the data set into fractions,
2. Rate constant - k
3. Exponent parameters: NB(0), $NB(t_{trans})$, C_{exp}
4. One – exponent parameters: $C_{1\text{-}exp}$, t_{delay}
5. Least squares of the entire data set.
6. Change transition time: t_{trans}

This author iterates 15 times through 1→4 (with 2 → 4 repeated for each fraction), for each t_{trans} .

3.3.SEPARATING THE FRACTIONS

The preceding discussion applies to any substrate specific rate constant. It was argued above that different rate constants will apply for different electron acceptor/ substrate combinations. This section proposes a method to separate a composting data set into its component fractions[5], so the parameters specific to each fraction can be determined as above.

In this work it is assumed that in any composting time course, all fractions are expressing simultaneously. While specific molecules may undergo sequential degradation (i.e exo-enzymes break down the larger molecules into smaller components which can then cross the cell wall and be utilized for microbial growth), this would need to occur simultaneously with a large quantity of molecules for the effect to be observed experimentally. Clearly, this will not occur.

In an important sense, the concept of a rate limiting substrate has application. For example, if lots of dead biomass, or cell contents from cut or crushed plant material, is present then this material (which is easily degradable) will have a fast rate constant and have a significant effect on the

[5] A fraction in this sense is likely to be composed of a range of substrates with similar rates of degradation.

composting time course. As this easily degraded resource is depleted, the more refractory compounds will supply the main energy source for the biomass. That is, after the initial flush, the rate constant which is experimentally detected will reflect the rate at which usable carbon is able to be released from the less degradable substrates. For plant material, the main compounds that are less degradable are hemicellulose, cellulose and lignin. So while a different rate constant could be determined for each compound that exists, the presence of large quantities of compounds that have *similar* degradation characteristics (such as the cellulosics) would indicate that a limited number of substrate based rate constants may be sufficient for most compost modelling.

The experimental evidence used by this author indicates three fractions, with the third fraction being roughly equivalent to the non-degradable component of other researchers, but with a low rate constant. This author sees a mathematical continuum between the processes we call composting and the processes that soil scientists find in soil respiration. While the terms may change across the boundary (rate constant in composting, respiration rate in soil science), the models are sufficiently similar to easily fill this need. However, this continuum is effectively blocked by the compost researcher's tendency to use terms such as non degradable volatile solids and equilibrium mass. Converting these 'blocks' into a third fraction, provides for this continuum, although full continuity would require more fractions to account for the century model of soil organic matter.

The three fractions are called: fast, slow and humification. The fast and slow terms reflect current usage in composting research, while the humification term reflects, in part, some of the processes that may actually be occurring at this stage (formation of large complex molecules called humus). In part, that composting is generally viewed as turning organic matter into humus.

The issue for parameter determination is to separate the data into individual fraction based data sets from which determining the value of the necessary parameters is a comparatively simple process described above.

A proportioning method is proposed where the value of each data point is allocated to the three fractions based on the proportion of the modelled data.

All fractions begin with a known proportion of the substrate energy $E_S(0)$ and over the composting time course the proportion will change depending on the rate constant of the fraction.

The observed composting rate at any point in time is a sum of all three fractions.

Equation 21

$$Q_{total}\,(t) = Q_f(t) + Q_s(t) + Q_h(t) \qquad \text{W cm}^{-3}$$

However, Q in Equation 21 can apply to either the model output or the data set. The task is to model each fraction's composting time course so the *sum* of the three modelled time courses is the same as the experimental data. The correct parameters are when $Q(t)_{model} = Q(t)_{data}$ for all t's.

If the proportion of the time course that comes from any fraction (S) at time t is determined as:

Equation 22

$$\propto_S (t) = \frac{Q_S(t)}{Q_{total}\,(t)}$$

Then, if the model values are used to determine $Q_S(t)$ for each fraction (S) in Equation 22 and $Q_{total}(t)$ is the sum of the modelled fractions, then $\alpha_f(t) + \alpha_s(t) + \alpha_h(t) = 1$. These same proportions can then be used to allocate the experimental data to its respective fraction (Equation 23). That is, the output of the model ($\alpha_S(t)$) generates the input (a data set) for the next iteration; an ideal set up for iterative methods.

Equation 23

$$Q_S(t) = Q_{data}\,(t) \times \propto_S\,(t)$$

The solution has been found when the model parameters generate a data time course for each fraction (using Equation 22 and Equation 23), from which the same parameters are determined using the microbial kinetics set of equations above.

Allocating the data using Equation 23 is surprisingly robust of inaccuracies in the initial estimates of k. Successive iterations quickly draw to an optimum value. This is primarily because during a fraction's decline phase the composting time course is dominated by a single fraction, and this coincides with the data used to determine the fraction's rate constant. Thus, an error in a neighbouring fraction's rate constant has a proportionately small impact on the time course of the data segment used for a fraction's rate constant determination. The magnitude of the rate constant determined in the second (and subsequent) iterations changes little from this initial estimate. This precision is then passed on to the next fraction's growth phase as the data for this growth phase is strongly influenced by the decline phase of the previous fraction (this is dominated by the rate constant for which we have a very good estimate) – see Figure 1.

Because the general shape of a fraction's data curve, including the growth phase, emerges so readily from the data and the observation that the peak Q of the slower fractions is not always obvious in the data, it was found that the only parameters that needed to be input initially were the time of the fast fraction peak and NB(0). The parameters necessary for the slow fraction could then be either: detected (peak Q), or calculated (t_{trans} and NB parameters) by the computer algorithm without further input.

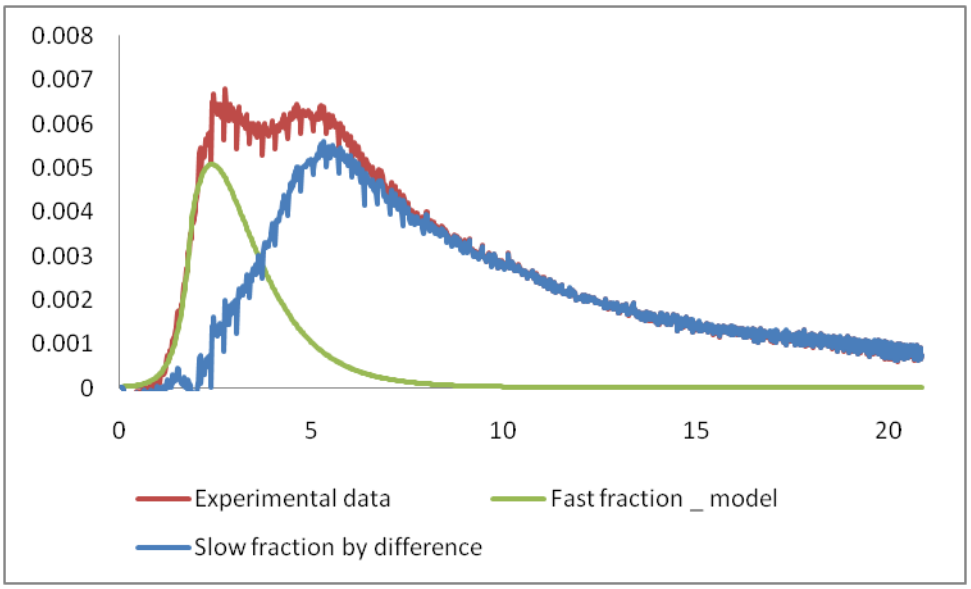

Figure 1 - The shape of the slow fraction's data time course determined by difference at the first iteration. The fast fraction's time course was determined from model parameters which were either: manually entered (t_{max} , NB(0)), computed from the data (t_{trans} , NB(t_{trans}), C_{exp} , $C_{1\text{-}exp}$, E(0)), or assumed (k = 10 W MJ^{-1}). The humification fraction contribution is undetermined and hence assumed to be 0. Axis are W cm^{-3} versus time (days), substrate is 0.8 cm dog sausage with old compost as a bulking material.

For the first iteration, fast fraction parameters entered are:

- t_{max} = observed data peak
- NB(0) = 0.001
- k_f = 10 W MJ^{-1}

Parameters computed for the fast fraction in the first iteration are:

- t_{trans} = time when $Q(t_{trans}) = Q(t_{max}) * 0.5$
- NB(t_{trans})
- C_{exp}
- $C_{1\text{-}exp}$ = same slope at t_{trans} as C_{exp} – see footnote[6]
- E(0)

Then the slow fraction's data can be determined by (see Figure 1):

- $Q_s(t) = Q_{data}(t) - Q_f(t)$

Parameter estimation for the slow fraction followed the first four points above, while k_s was input as 1 W MJ^{-1}.

However, determination of the humification fraction parameters was delayed until the second iteration, as negative values for $Q_{humification}$ could occur if the slow fraction rate constant estimate was

[6] For the derivative of the exponent phase and the 1-exponent phases to equate then C(1-exp) = - NB(t_trans) * C_{exp} / (1-NB(t_trans)). For subsequent iterations the two point method described in the equations above was used.

too low and Q_h was determined by difference as above. The proportioning method used in subsequent iterations did not have this characteristic, so the humification parameters could be determined without this potential error.

4. RESULTS

These sets of equations were applied to two different substrates (see Chapman (2008) for the original trial data).

- Dog sausage cut into 0.8 cm cubical particles.
- Pig faeces with a range of particle sizes (69% smaller than 0.74 cm)

The dog sausage trials (Figure 2) were carried out using particles with a diameter taken at 0.8 cm (the particles were formed from 1 cm cubical cut particles which were then 'chopped' into smaller sizes – this 'chopping' was done using a hearth shovel on the reactor sized sample (2.5 litres) after the bulking material was added, hence a range of sizes and shapes would exist in the sample, but all would be less than 1 cm). Trials were done at 16^{o}C. Bulking material was old compost.

The pig faeces trial (Figure 3) was run at 20^{o}C for 114 days and used old compost as a bulking material. A range of particle sizes arose due to the need for the faeces to be well mixed with the bulking material to achieve the compostable mixture. Note that the data immediately after the composting peak was adversely affected by ice in the exit air tube. This restricted the air flow to the compost and the consequence of this is apparent in the data up to day 2 – see Figure 3 .

For the fast and slow fractions:

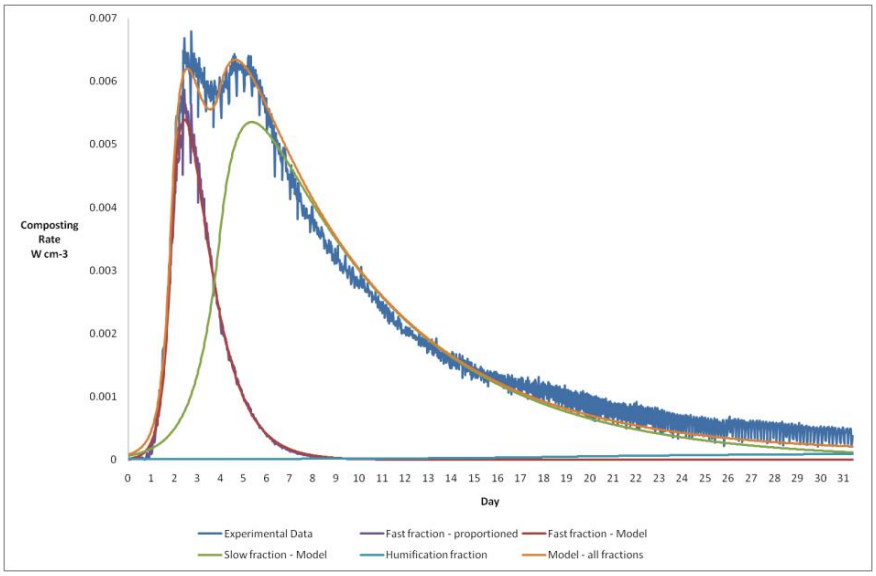

Figure 2 – 0.8 cm dog sausage with old compost as bulking material. Mixture composted at 16^{0}C

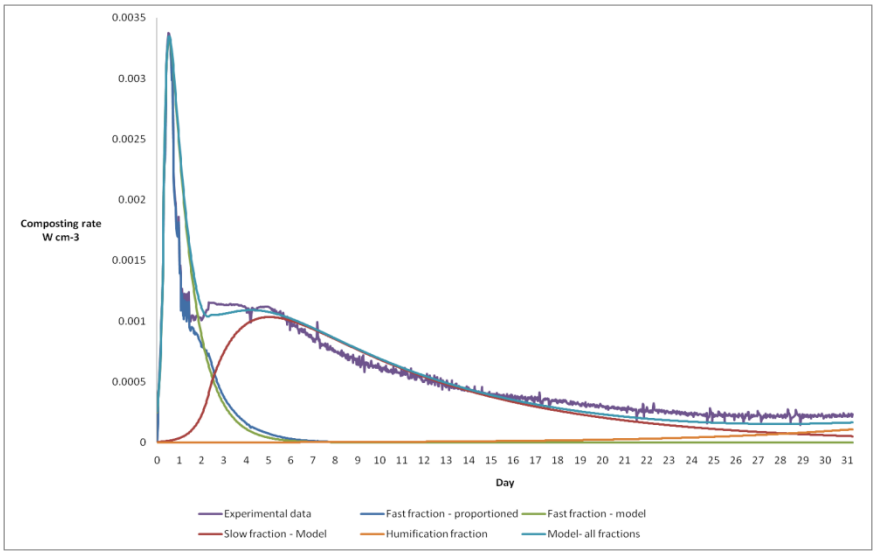

Figure 3 – Pig faeces with old compost as bulking material well mixed in resulting in a range of particle sizes. Compost temperature was 20^{0}C. Note that ice build up in the exit air tube restricted air flow and impacted on the data curve between composting peak and day 2.

A comparison of Figure 2 with Figure 3 suggests two different composting rate time courses for the two substrates. The pig faeces have a more pronounced peak which occurs earlier in the composting time course yet is only about half of the composting rate of the dog sausage. The parameters determined using the sets of equations described above can be seen in Table 1.

Table 1 – Parameters determined for the two substrates: pig faeces and dog sausage.

Parameter	Fraction	Pig faeces	Dog Sausage
Rate constant W MJ^{-1}	Fast	11.9	10.3
	Slow	1.4	1.77
	Humification	0.179	-[7]
Substrate concentration (E(0)) MJ cm^{-3}	Fast	0.000409	0.00113
	Slow	0.00109	0.004288
	Humification	0.00128	-[7]
Time of peak composting. Days	Fast	0.56	2.46
	Slow	5.1	5.38
	Humification	44.6	40.3
NB(0)	Fast	0.044	0.0011
	Slow	0.0039	0.0079
	Humification	0.0068	0.0059
r^2	All fractions	0.943	0.990

Of particular note in Table 1 is:

[7] Note insufficient data to determine rate constant and substrate concentration. The value had to be programmatically constrained to prevent values higher than the slow k being computed.

- The magnitude of the fast and slow rate constants are comparable between the two substrates. Note, that the pig faeces were run 4^{O}C hotter than the dog sausage so one would expect a higher rate constant.
- There is a difference in substrate concentration not explained by the rate constant difference; but most likely explained by the biological fact that it is primarily indigestible food which is excreted.
- The slow and humification peaks occur at similar times, while the fast peak occurs substantially earlier in the faeces trial (0.56 v 2.46 days).
- There is a big difference in fast fraction starting biomass (NB(0)) between the two substrates.

While firm conclusions should await experimental evidence based on a better trial setup (these two examples are part of two separate trials, and hence are not directly comparable. Neither was the trial dog sausage used to feed the pigs, which would be necessary if one were to compare the composting time course of the food with the faeces).

Despite these limitations on comparing the two sets of data, it seems that starting biomass would explain the earlier (and more pronounced) peak in the pig faeces trial, rather than either rate constant or substrate concentration. Such a conclusion would also be consistent with the history of the two substrates:

- Faeces had a rich intestinal microbial flora (albeit anaerobic) mixed throughout the material.
- Dog sausage is cooked and sealed in plastic; hence the old compost which was used as bulking material would be the primary source of the starting biomass which would need to grow from this low base on the particle surface.

Rate constant determination for the humification fraction in the dog sausage would require a longer experimental time to reduce the influence of the one-exponent constant. Hence while a good descriptor of the composting time course is possible (Figure 4) separating the contributions between the biomass growth (which run counter to the effect of the rate constant) from the effect of the rate constant is not possible with such a short data set. Indeed the upper value of k is constrained programmatically to 0.7 (if unconstrained, values higher than the slow rate constant were computed). Insufficient data to determine k will also affect determination of E(0) due to the dependence of E(0) on k.

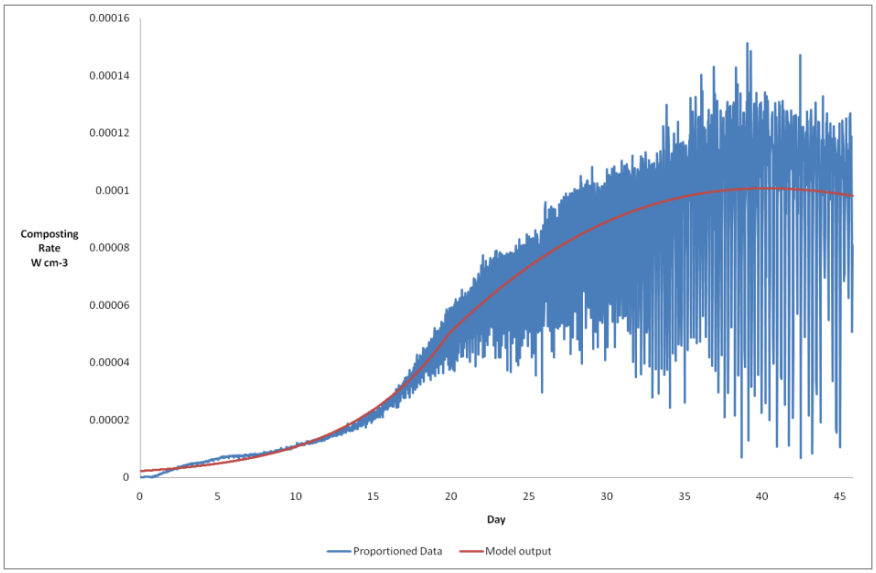

Figure 4 – The humification fraction of the dog sausage trial using a rate constant of 0.7 W MJ^{-1}. Note the increasing variability in the data arose primarily from the frequency of the aeration events exceeding the final storage frequency. The energy required to humidify the new air was detectable by the experimental apparatus as a drop in the composting rate (the composting rate would be unchanged but the energy goes into latent heat of evaporation rather than lost by conduction) – the lower points occur immediately after these events.

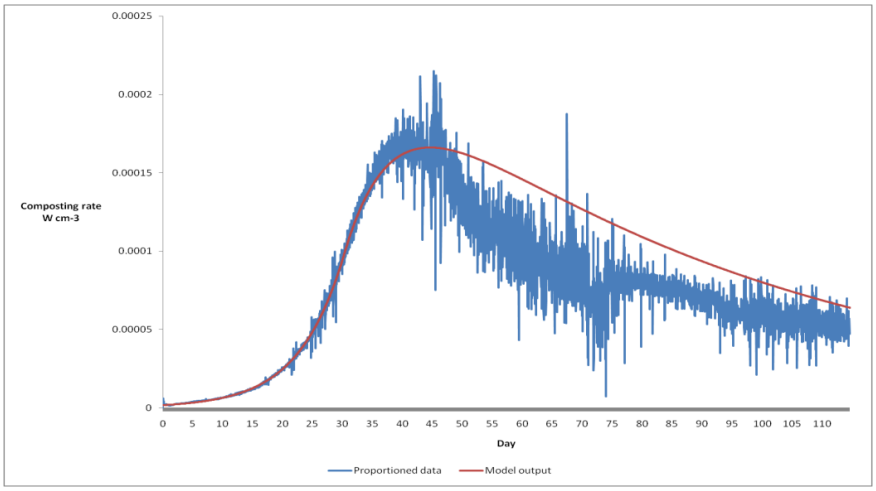

Figure 5 – The humification fraction for the pig faeces trial. Note the increasing variability in the data arose from the aeration events being detected by the experimental apparatus. Parameter values are noted in Table 1.

5. DISCUSSION

The intention of these two examples, is to show that using a parameter determination algorithm which is soundly based in microbial kinetics has the potential to give insights into composting which, due to being strongly rooted in scientific fundamentals, are applicable across a wide set of circumstances. In these examples, despite two different composting time courses (from two different substrates in two unrelated experiments), the microbial rate constants are similar. Most of

the difference between the two substrates seems to arise from substrate concentration and starting biomass.

With appropriate experimental rigour, combined with soundly based parameter determination as above, substantially more insights into the composting dynamic would seem to be possible.

For example, the slow fraction in both the examples above seems to overestimate the composting rate in the period immediately after the slow peak, while underestimating composting later in the fraction's time course. The parameter determination algorithm used in the above examples did not adjust for aerobic proportion as in Equation 4 consequently the slow fraction rate constant could be a combination of two different electron acceptor based rate constants (oxygen and nitrite[8]). The presence of such a contribution, even in the small particle size used above, would be consistent with the evidence from the larger particle sizes of the same trial. These larger particle sizes had a pronounced rewarming section in this part of the time course which peaked around day 10, although this was not proven to be anoxic degradation it was noted as one of the possibilities – see P. 106 Chapman (2008) for the original data. The existence of anoxic degradation could be detected by noting the presence of breakdown products in the exhaust gases (e.g. nitrous oxide).

Extending the parameter determination algorithm to accommodate an anoxic contribution is possible within the theoretical framework outlined above and, if proven to exist, would only further enhance the precision of the rate constant determination. A higher slow fraction rate constant would give a better fit immediately after the peak, while anoxic degradation in the non-aerobic parts of the particle could explain the underestimate later in the fraction's time course. The r^2 could rise even higher than the 0.99 computed for the dog sausage trial above if this possible contribution were allowed for in the parameter determination algorithm.

The magnitude of the fast fraction rate constant determined by this method is of the order identified by Van Veen et al., (1985) for biomass, but is substantially higher than values reported in the composting literature (12 W MJ^{-1} equates to 1.03 d^{-1}). It is suggested that this difference arises in part from the sampling frequency of the experimental data (this data is at a 30 minute frequency and therefore able to identify rate constants of this magnitude), and in part due to the base on which the rate constant sits (only 15% of the substrate was fast fraction in the faeces trial).

Indeed the *slow* fraction rate constants determined for these data sets are of the magnitude of those reported for the *fast* fraction in the composting literature (1.5 W MJ^{-1} equates to 0.12 d^{-1}). This suggests that in the current composting literature, the two fractions as identified in this study have been merged into one, most likely due to sampling frequency being unable to separate the signal from the fast fraction.

Basing parameter determination on firm theoretical footings would appear to have substantial benefits for compost understanding.

6. CONCLUSION

[8] Nitrite was listed as an ingredient on the label.

The over parameterization problem in composting was addressed by breaking the computational requirement into interdependent sets of equations. This structure had the following benefits arising from three areas:

- Determination of microbial kinetic parameters:
    - The crucial set of parameters, i.e. the microbial kinetic parameters, could be rigorously determined from the data, but only for a single fraction.
    - Proportioning the experimental data into fractions could be done by a separate calculation using these kinetic parameters.
    - Successive iterations refined the proportions.
- Mathematical linkages to other sets of equations, particularly:
    - The electron acceptor set – enables other electron acceptors to contribute to the composting time course and the magnitude of their contribution to be assessed.
    - Environmental set - enables environmental effects to be attributed to their most fundamental area of influence. For example, temperature affects the solubility of oxygen in water, and the diffusion coefficient, in addition to its effect on the microbial rate constant.
- Identification of preferred experimental setups – preferably choose a single degradable substrate and small particle size.

Formulating the problem into these sets of equations (in a sense arranging the complexity into layers), meant that each of the microbial kinetic parameters could be computed to high precision, but only within the constraint of the other layers being held temporarily constant. Sequential computation of each set of equations over several iterations could then be used to draw the 'system' to an optimum solution.

The resulting algorithm produced a model curve for each of two data sets with an r^2 better than 0.94 (0.99 for the higher quality data set).

Considerable insights into composting seem to be possible if parameter estimation is based on the firm theoretical footing described above. For example, it appeared that the primary differences between the composting time courses of the two substrates may be due to substrate concentration and starting biomass differences, and not microbial kinetic parameters.

Secondly, the suggestion that the experimental results may include anoxic degradation – even in these small particle sizes, and that there is mathematical space in the theory for such a contribution would suggest that the method has more potential than being just a 'best fit' exercise.

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