# Development of the LDAT degradation algorithm

Degradation pathways

The organisation of the degradation algorithm in LDAT follows the arrangement used by Bryers (1984) and Reichel et al (2005). To illustrate this matrix style format to compute the changes due to degradation of the mass of the constituents of an element of waste, a simple waste in the form of Glucose degrading along a single chemical pathway will be used as an example.

The stoichiometric equation used in LDAT for the anaerobic degradation pathway of Glucose is,

$$C_6H_{12}O_6 = 2C_2H_4O_2 + CH_4 + CO_2$$
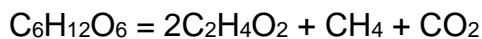
This expresses a mass balance relationship which implies that when 1 kg of glucose waste degrades 0.67 kg of acetic acid, 0.09 kg of methane and 0.24 kg of carbon dioxide are produced. If the rate of reaction is r_1^P per day, and the compounds are replaced by the symbols S_i,

$$\frac{\partial S_1}{\partial t} = -r_1^P$$

$$\frac{\partial S_2}{\partial t} = 0.67 r_1^P$$

$$\frac{\partial S_3}{\partial t} = 0.09 r_1^P$$

$$\frac{\partial S_4}{\partial t} = 0.24 r_1^P$$

$S_1 = C_6H_{12}O_6$, $S_2 = C_2H_4O_2$, $S_3 = CH_4$, $S_4 = CO_2$. r_1^P is the rate of degradation of the pathway substrate ($i = 1$, in this case) along the primary pathway, P for pathway 1.

Note that the total change in mass will always be zero (-1 + 0.67 +0.09 + 0.24) so that the mass balance will be preserved.

In LDAT, the reaction rate r_1^P is calculated by a Monod microbiological type function which is related to the rate of growth of the bacteria responsible for the degradation of a substrate in question, which in this example is Glucose. The calculation of r_1^P is discussed below.

The growth in bacteria arises from the consumption of the substrate and in the case of Glucose, the chemical reaction that takes place is represented in LDAT by,

$$C_6H_{12}O_6 + 1.2\ NH_4^+ = 1.2C_5H_7NO_2 + 1.2H^+ + 3.6H_2O$$
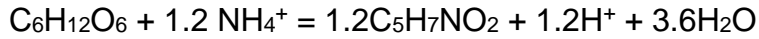
If the rate of this reaction is r_1^G, the process outlined above produces for this bacteria growth pathway,

$$\frac{\partial S_1}{\partial t} = -r_1^G$$
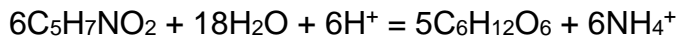
$$\frac{\partial S_5}{\partial t} = -0.12 r_1^G$$

$$\frac{\partial S_6}{\partial t} = 0.75 r_1^G$$

$$\frac{\partial S_7}{\partial t} = 0.01 r_1^G$$

$$\frac{\partial S_8}{\partial t} = 0.36 r_1^G$$

$S_5 = NH_4^+$, $S_6 = C_5H_7NO_2$, $S_7 = H^+$, $S_8 = H_2O$. r_1^G is the rate of degradation along the bacteria growth pathway, G, for pathway 1.

LDAT assumes that the population of the bacteria $C_5H_7NO_2$ will die back at a rate, say r_1^D, and produce Glucose and Ammonium in accordance with the following reaction.

$$6C_5H_7NO_2 + 18H_2O + 6H^+ = 5C_6H_{12}O_6 + 6NH_4^+$$

Consequently,

$$\frac{\partial S_6}{\partial t} = -r_1^D$$

$$\frac{\partial S_8}{\partial t} = -0.48 r_1^D$$

$$\frac{\partial S_7}{\partial t} = -0.01 r_1^D$$

$$\frac{\partial S_1}{\partial t} = 1.33 r_1^D$$

$$\frac{\partial S_5}{\partial t} = 0.16 r_1^D$$

Where a compound appears in more than one pathway the rates of change of the compound in each pathway are added to give the total rate of change for that compound.

For example in the case of water, S_8, in total,

$$\frac{\partial S_8}{\partial t} = 0.36 r_1^G - 0.48 r_1^D$$

These formulae can be presented as a matrix thus.

$$\frac{\partial}{\partial t}\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{bmatrix} = \begin{bmatrix} -1 & -1 & 1.33 \\ 0.67 & 0 & 0 \\ 0.09 & 0 & 0 \\ 0.24 & 0 & 0 \\ 0 & -0.12 & 0.16 \\ 0 & 0.75 & -1 \\ 0 & 0.01 & -0.01 \\ 0 & 0.36 & -0.48 \end{bmatrix} \begin{bmatrix} r_1^P \\ r_1^G \\ r_1^D \end{bmatrix} = \begin{bmatrix} p_{11} & g_{11} & d_{11} \\ p_{12} & g_{12} & d_{12} \\ p_{13} & g_{13} & d_{13} \\ p_{14} & g_{14} & d_{14} \\ p_{15} & g_{15} & d_{15} \\ p_{16} & g_{16} & d_{16} \\ p_{17} & g_{17} & d_{17} \\ p_{18} & g_{18} & d_{18} \end{bmatrix} \begin{bmatrix} r_1^P \\ r_1^G \\ r_1^D \end{bmatrix} \qquad (B1)$$

Each primary degradation pathway p_n thus has two microbiological pathways associated with it, g_n, d_n, and three rates of reaction associated with each pathway r_n^P, r_n^G, and r_n^D. Each pathway has a substrate, and the stoichiometric coefficient and molecular weight of the substrate is used to normalized the other coefficients in the pathway to produced the elements of the matrix in equation (B1).

This example has been developed for one degradation pathway. For P pathways in a system that has N constituents it is best to present the right hand side of equation (B1) as the sum of three matrices,

$$\frac{\partial}{\partial t}\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{bmatrix} = [P] + [G] + [D]$$

where,

$$[P] = \begin{bmatrix} p_{11} & \cdots & p_{n1} & \cdots & p_{P1} \\ \vdots & - & \vdots & - & \vdots \\ p_{1i} & \cdots & p_{ni} & \cdots & p_{Pi} \\ \vdots & - & \vdots & - & \vdots \\ p_{1N} & \cdots & p_{nN} & \cdots & p_{PN} \end{bmatrix} \begin{bmatrix} r_1^P \\ \vdots \\ r_n^P \\ \vdots \\ r_P^P \end{bmatrix}$$

$$[G] = \begin{bmatrix} g_{11} & \cdots & g_{n1} & \cdots & g_{P1} \\ \vdots & - & \vdots & - & \vdots \\ g_{1i} & \cdots & g_{ni} & \cdots & g_{Pi} \\ \vdots & - & \vdots & - & \vdots \\ g_{1N} & \cdots & g_{nN} & \cdots & g_{PN} \end{bmatrix} \begin{bmatrix} r_1^G \\ \vdots \\ r_n^G \\ \vdots \\ r_P^G \end{bmatrix}$$

$$[D] = \begin{bmatrix} d_{11} & \cdots & d_{n1} & \cdots & d_{P1} \\ \vdots & - & \vdots & - & \vdots \\ d_{1i} & \cdots & d_{ni} & \cdots & d_{Pi} \\ \vdots & - & \vdots & - & \vdots \\ d_{1N} & \cdots & d_{nN} & \cdots & d_{PN} \end{bmatrix} \begin{bmatrix} r_1^D \\ \vdots \\ r_n^D \\ \vdots \\ r_P^D \end{bmatrix}$$

The molecular weight of each of the compound terms in the stoichiometric equations given above is given by,

$$M_i^{P_n} = \sum_r A_i^{P_n} E_r^i M_r$$

i refers to the compound term, and p_n to the pathway. $A_i^{P_n}$ is the coefficient multiplying the compound i in pathway p_n. E_r^i is the number of elements of type E_r in compound i. M_r is the molecular weight of element r.

If $i_S^{p_n}$ is the substrate compound in pathway p_n then the terms such as p_{ni}, g_{ni} and d_{ni} in the matrices set out above are of the form,

$$p_{ni} = \frac{M_i^{p_n}}{M_{i_S^{p_n}}^{p_n}}$$

The compounds and pathways proposed for LDAT are given in Tables B1 and B2.

Reaction rates

The Monod form of growth rate for a population of bacteria is,

$$\frac{\partial C_B}{\partial t} = \mu_B \frac{C_S}{C_S + K^S} C_B \qquad \text{(growth rate)} \qquad \text{(B2)}$$

And the death rate is,

$$\frac{\partial C_B}{\partial t} = -k^D C_B \qquad \text{(death rate)} \qquad \text{(B3)}$$

μ_B is the effective growth rate after modification for any inhibition and bioavailability effects. C_B and C_S are the carbon mass concentrations in kg/m³ of the bacteria population and the substrate relevant to that population. K^S is a parameter known as the half saturation constant also in kg/m³. k^D is the death rate coefficient.

Multiplying through, in equation (B2), by the appropriate ratios of total carbon to mass, f_C^B and f_C^S, the volume of leachate V^L, and a bioavailability factor b, expresses the Monod equation in terms of mass. Thus,

$$\frac{\partial\left(C_B V^L / f_C^B\right)}{\partial t} = \mu_B \frac{b C_S V^L / f_C^S}{b C_S V^L / f_C^S + K^S V^L / f_C^S} \left(C_B V^L / f_C^B\right)$$

Or since, in the example above, the value of the suffix denoting the bacteria compound associated with this pathway is $i_B = 6$, and the value of the suffix denoting the substrate compound associated with this pathway is $i_S = 1$

$$\frac{\partial S_6}{\partial t} = \mu_6 \frac{S_1}{S_1 + K^S V^L / f_C^1 b} S_6$$

Furthermore,

$$\frac{\partial S_6}{\partial t} = 0.75 r_1^G = g_{16} r_1^G$$

and therefore,

$$r_1^G = \frac{1}{0.75} \frac{\partial S_6}{\partial t} = \frac{1}{g_{16}} \mu_6 \frac{S_1}{S_1 + K_1^S V^L / f_C^1 b} S_6$$

By definition the catalytic factor, or yield coefficient, Y_B is the mass of carbon biomass formed per mass of carbon substrate utilized. That is,

$$Y_B = \frac{f_C^B \dfrac{\partial S_6}{\partial t}}{f_C^S \dfrac{\partial S_1}{\partial t}} = \frac{f_C^B g_{16} r_1^G}{f_C^S \left(r_1^G + r_1^P \right)}$$

Thus,

$$r_1^P = r_1^G \left(\frac{1}{Y_6} g_{16} \frac{f_C^1}{f_C^6} - 1 \right)$$

Also,

$$r_1^D = k_6^D S_6$$

For a more general pathway p_n,

$$r_n^G = \frac{1}{g_{SS\,BB}} \mu_{BB} \frac{S_{SS}}{S_{SS} + K_{SS}^S V^L / f_C^S b} S_{BB}$$

ss refers to the substrate compound in pathway p_n, and S_{BB}, μ_{BB} and K_{BB}^S are the bacteria compound ($i = BB$) and Monod parameters related to pathway p_n.

Furthermore,

$$r_n^P = r_n^G \left(\frac{1}{Y_{BB}} g_{SS\,BB} \frac{f_C^{SS}}{f_C^{BB}} - 1 \right)$$

and,

$$r_n^D = k_{BB}^D S_{BB}$$

Restatement of the degradation algorithm development in terms of volumetric compound concentrations z_i^P

We have a set of primary pathways, p_n, and the associated bacteria growth and death pathways, g_n and d_n. In addition, for each group of three pathways, the index of the substrate compound and the index of the bacteria compound are referred to as SS and BB respectively. μ_{BB} and K_{BB}^S are the Monod parameters related to the pathway group.

The stoichiometric equations defining the pathways are

$$\sum_i A_i^{p_n} c_i = 0 \; ; \; \sum_i A_i^{g_n} c_i = 0 \; ; \; \sum_i A_i^{d_n} c_i = 0 \,.$$

$A_i^{p_n}$ is the coefficient multiplying the compound c_i in pathway p_n, etc. The compounds c_i are defined as chemical formula such as $C_6H_{12}O_6$ for glucose and have the units of mass.

The molecular weight of each of the compound terms in the stoichiometric equations is given by,

$$M_i^{p_n} = A_i^{p_n} \sum_r E_r^i M_r \; ; \; M_i^{g_n} = A_i^{g_n} \sum_r E_r^i M_r \; ; \; M_i^{d_n} = A_i^{d_n} \sum_r E_r^i M_r \,.$$

E_r^i is the number of elements of type E_r in compound i. M_r is the molecular weight of element r. (E_r is the array of elements C, H, O, N, S and so on.)

The weighting terms p_{ni}, g_{ni} and d_{ni} may then be defined as,

$$p_{ni} = \frac{M_i^{p_n}}{M_{SS}^{p_n}} \; ; \; g_{ni} = \frac{M_i^{g_n}}{M_{SS}^{g_n}} \; ; \; d_{ni} = \frac{M_i^{d_n}}{M_{BB}^{d_n}} \,.$$

Note that p_{ni}, g_{ni} are normalized with respect to the substrate compound mass, whereas d_{ni} are normalized with respect to the bacteria compound mass.

The compound masses present are then defined as S_i in an element of material with a total volume of V_E. Thus following the argument in the example above: (changing the notation for the rate r slightly)

$$\dot{S}_i = \sum_n \left(p_{ni} r_{p_n} + g_{ni} r_{g_n} + d_{ni} r_{d_n} \right)$$

We now define the concentration by volume of the fraction of the component i in phase P to be z_i^P. Note that all component fractions involved in the degradation process are in

the liquid phase, L, apart from the substrate and bacteria compounds, which are in the solid phase S. Also, if z^S, z^L, and z^G are the overall solid, liquid and gas phase concentrations in the volume V_E then,

$$z^S = \sum_i z_i^S, \quad z^L = \sum_i z_i^L, \quad z^G = \sum_i z_i^G, \text{ and } z^S + z^L + z^G = 1$$

$$\phi = z^L + z^G, \quad 1 - \phi = z^S$$

Now for the substrate and bacteria compounds S_{SS} or S_{BB},

$$S_{SS} = \rho_S z_{SS}^S V_E \text{ and } S_{BB} = \rho_S z_{BB}^S V_E \text{ where } \rho_S \text{ is the density of the solid phase.}$$

Thus the rate equations become,

$$r_{g_n} = \frac{1}{g_{SS\,BB}} \mu_{BB} \frac{\rho_S z_{SS}^S V_E}{\rho_S z_{SS}^S V_E + K_{SS}^S V^L / f_C^S b} z_{BB}^S \rho_S V_E = r_{g_n}' \rho_S V_E$$

$$r_{p_n} = r_{g_n} \left(\frac{1}{Y_{BB}} g_{SS\,BB} \frac{f_C^{SS}}{f_C^{BB}} - 1 \right) = r_{p_n}' \rho_S V_E$$

and,

$$r_{d_n} = k_{BB}^D z_{BB}^S \rho_S V_E = r_{d_n}' \rho_S V_E$$

Also, $\dot{S}_i = \rho_P z_i^P V_E$ where ρ_P is the liquid or solid density depending on the phase of z_i^P. So,

$$\dot{S}_i = \sum_n \left(p_{ni} r_{p_n} + g_{ni} r_{g_n} + d_{ni} r_{d_n} \right)$$

Becomes,

$$\dot{z}_i^P = \frac{\rho_S}{\rho_P} \sum_n \left(p_{ni} r_{p_n}' + g_{ni} r_{g_n}' + d_{ni} r_{d_n}' \right)$$

where,

$$r_{g_n}' = \frac{1}{g_{SS\,BB}} \mu_{BB} \frac{z_{SS}^S}{z_{SS}^S + K_{SS}^S z^L / \rho_S f_C^S b} z_{BB}^S$$

$$r'_{p_n} = r'_{g_n}\left(\frac{1}{Y_{BB}}\,g_{SS\,BB}\,\frac{f_C^{SS}}{f_C^{BB}} - 1\right)$$

and,

$$r'_{d_n} = k_{BB}^D z_{BB}^S$$

Note that as a result of the degradation changes, whilst mass is conserved and $\sum \dot{S}_i = 0$, there will generally be a volume change as the result of the solid phase degrading into the lower density liquid phase, i.e. $\sum \dot{z}_i^P \neq 0$. Further volume changes could subsequently take place as the result of equilibrium phase changes and compression of the solid matrix, all of which will induce consequential flows in the liquid and gas phases.