The LDAT waste degradation algorithm

Summary: The chemical degradation stoichiometric equations represent the pathways along which the chemical degradation reactions take place. These equations link together the chemical compounds found in a landfill as the result of waste decomposition. This means we need to be able to convert the description of the waste in terms of the more familiar characteristics, Food; Green waste; Textiles; Paper and Cardboard; to a description in terms of chemical compounds, Protein; Fat; Carbohydrate; and Glucose.

The stoichiometric equations can be used to estimate the quantities of leachate and gas consumed or produced as the waste degradation reactions proceed. The equations are also used to describe the interaction between the dissolved waste compounds and the bacteria that are present. The bacteria only consume some of the waste that they break down. In fact they break down about 10 times the amount they consume. This phenomenon is known as a catalytic process which enhances the degradation reaction rates considerably, and determines the rate at which the products of waste degradation are produced.

Introduction

A set of chemical stoichiometric equations are defined in LDAT as waste degradation pathways. They are used to estimate the rate of change in mass and volume of the degradable substrate compounds in the waste (and their product compounds), and in addition take into account the impact of the activity of bacteria populations. Whilst these changes do not cause any overall change in mass, they do have the effect of changing the volumetric concentrations of the various chemical compounds in the waste. These volume changes contribute to the evaluation of the source term G_n^P in the LDAT constitutive equation, see Annex: The LDAT constitutive equation, which appended to this document for further information.

The parameter values required to configure the chemical degradation pathways may be edited using the LDAT editor. The initial parameters that are shown in the editor are the default values for LDAT. These values are given in the spreadsheet - LDAT default chemical pathways – configuration settings.xlsx, which may be downloaded from the Pathway Data editor information slot in www.ldatmodel.com.

There are 10 pathway configuration values and four groups of stoichiometric equation coefficient values that need to be set. When changes are made to the stoichiometric equation coefficient values, care should be taken to ensure that the values chosen result in a mass balance between reactants and products. Advice on how this can be checked is demonstrated in the spreadsheet containing the list of chemical stoichiometric equations - LDAT default chemical pathways – stoichiometric equations.xlsx which may also be downloaded from the Pathway Data editor information slot in www.ldatmodel.com.

Illustration of the organisation of the LDAT degradation algorithm

The organisation of degradation pathways within the degradation algorithm in LDAT, follows the arrangement used by (Bryers 1984) and (Reichel, Haarstrick et al. 2005).

To illustrate this matrix style format, which computes 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 the example approximates to the anaerobic degradation pathway of the glucose compound, $C_6H_{12}O_6$. The glucose is assumed to break down into acetic acid, $C_2H_4O_2$, methane, CH_4, and carbon dioxide, CO_2, as shown in equation (1).

$$C_6H_{12}O_6 = 2C_2H_4O_2 + CH_4 + CO_2 \qquad (1)$$

This is a stoichiometric equation, where each term has the units of moles/litre. The compounds are dissolved in water and each term represents the concentration of each compound. Thus, when a mole of glucose degrades along this pathway, it produces two moles of acetic acid and one mole each of methane and carbon dioxide.

There is a conservation of mass in the reaction. Bearing in mind that the molecular weight of carbon is 12 g/mole, hydrogen is 1 g/mole and oxygen is 16 g/mole, we can see that the molecular weight of glucose is 6 x 12 + 12 x 1 + 6 x 16 = 180 g/mole, or 0.180 kg/mole. Similarly, the molecular weight of acetic acid, $C_2H_4O_2$, is 0.060 kg/mole; for methane, CH_4, it is 0.016 kg/mole and for carbon dioxide, CO_2, it is 0.044 kg/mole.

Using these compound molecular weights, and substituting them into equation (1), demonstrates how the equation can be used to express conservation of mass as follows.

0.180 = 2 x 0.060 + 0.016 + 0.044

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.

Mass balances such as this one may be used in conjunction with estimates of the rate at which the substrate reaction is taking place to estimate the consequential rates of production of the product compounds. In the case of equation (1), if the rate of substrate 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 rate of change of the compounds on the left hand side of a stoichiometric equation will be negative, whereas on the right hand side they will be positive. The total change in mass of the constituent compounds in the equation will always be zero (in this case: -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 in the next section 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,

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

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

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

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

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

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 in the form of a product matrix thus.

$$\frac{\partial}{\partial t}\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{bmatrix} = \begin{bmatrix} -1 & -1 & 1.33 \\ 0.67 & 0 & 0 \\ 0.09 & 0 & 0 \\ 0.24 & 0 & 0 \\ 0 & -0.12 & 0.16 \\ 0 & 0.75 & -1 \\ 0 & 0.01 & -0.01 \\ 0 & 0.36 & -0.48 \end{bmatrix} \begin{bmatrix} r_1^P \\ r_1^G \\ r_1^D \end{bmatrix} = \begin{bmatrix} p_{11} & g_{11} & d_{11} \\ p_{12} & g_{12} & d_{12} \\ p_{13} & g_{13} & d_{13} \\ p_{14} & g_{14} & d_{14} \\ p_{15} & g_{15} & d_{15} \\ p_{16} & g_{16} & d_{16} \\ p_{17} & g_{17} & d_{17} \\ p_{18} & g_{18} & d_{18} \end{bmatrix} \begin{bmatrix} r_1^P \\ r_1^G \\ r_1^D \end{bmatrix} \quad (3)$$

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 normalize the other coefficients in the pathway to produce the elements of the matrix in equation (3).

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 (3) as the sum of three matrices,

$$\frac{\partial}{\partial t}\begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{bmatrix} = [P] + [G] + [D] \qquad (4)$$

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,

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

Note also that since p_{ni}, g_{ni} and d_{ni} are derived from stoichiometric equations the summation over the compound index i is zero. That is the sum of the column elements in the matrices $[P], [G]$ and $[D]$ are all zero, meaning that $\sum_i \frac{\partial S_i}{\partial t} = 0$, and mass is conserved.

Details of the compounds and pathways used in the LDAT degradation algorithm are given in the spreadsheet files:

LDAT default chemical pathways – configuration settings.xlsx
LDAT default chemical pathways – stoichiometric equations.xlsx

Links to download these files are available in the Pathway Data editor information slot in www.ldatmodel.com.

As indicated in the introduction, these waste degradation pathways may be used to estimate the rate of change in mass and volume of the degradable substrate compounds in the waste (and their product compounds), and in addition take into account the impact of the activity of bacteria populations. Mass balance relationships are derived from stoichiometric equations such as equation (1), and then these are organized into a degradation algorithm that takes the form of the sum of three product matrices, equation (4). These rates of change of compound mass do not cause any overall change in the total mass of compounds. However, they do have the effect of changing the volumetric concentrations of the various chemical compounds in the waste. These volume changes contribute to the evaluation of the source term G_n^P in the LDAT constitutive equation, see Annex: The LDAT constitutive equation.

Calculation of the reaction rates r_n^P, r_n^G, and r_n^D

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

$$\frac{\partial C_B}{\partial t} = \mu_B \frac{C_S}{C_S + K^S} C_B \qquad \text{(growth rate)} \qquad (5)$$

And the death rate is,

$$\frac{\partial C_B}{\partial t} = -k^D C_B \qquad \text{(death rate)} \qquad (6)$$

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/m^{3}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/m^3. k^D is the death rate coefficient.

Multiplying through, in equation (5), 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,

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

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,

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

A general statement of the LDAT degradation algorithm and associated reaction rates

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 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,

$z^S = \sum_i z_i^S$, $z^L = \sum_i z_i^L$, $z^G = \sum_i z_i^G$, and $z^S + z^L + z^G = 1$

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

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

$S_{SS} = \rho_L z_{SS}^S V_E$ and $S_{BB} = \rho_S z_{BB}^S V_E$ where ρ_L is the density of the liquid phase, and ρ_S is the density of the solid phase.

Thus the rate equations become,

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

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

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,

$$r'_{g_n} = \frac{1}{g_{SSBB}} \mu_{BB} \frac{z_{SS}^S}{z_{SS}^S + K_{SS}^S z^L / \rho_L f_C^S b} z_{BB}^S$$

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

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 dissolution and equilibrium phase changes and compression of the solid matrix, all of which will induce consequential flows in the liquid and gas phases.

Annex: The LDAT constitutive equation

The landfill degradation and transport model LDAT (White, Robinson et al. 2004), (White, Nayagum et al. 2014) solves the landfill process constitutive equations using a finite difference algorithm within a framework of rectangular representative elementary volumes.

The waste is represented as the assembly of a number of component chemical compounds and species, each of which can exist in one or all of the three phases solid, liquid, and gas. The conservation of the mass m_n^P of the n^{th} component of the waste in phase P (solid, liquid or gas) in the context of a representative elementary volume, may be expressed by the following equation,

$$\frac{\partial\left(m_n^P\right)}{\partial t} = G_n^P - \sum_{ijk} \frac{\partial\left(m_n^P v_n^P\right)_i}{\partial x_i} \qquad \text{(A1)}$$

Where v_n^P is the flow velocity associated with component n in phase P.

The mass of a component m_n^P is the key parameter that LDAT calculates and tracks through time and space.

G_n^P is a source term which in the case of the LDAT algorithm accommodates changes in mass due to degradation, diffusion, settlement, heat generation and transfer, and changes due to chemical equilibrium and phase changes. The second term on the right hand side of equation (A1) accounts for settlement and movement of the solid phase, and gas and liquid mass transfers in the fluid phases. In LDAT the solid phase is decoupled from the fluid phase and becomes part of the fluid source term. The resulting two phase fluid system is then solved by a conventional multi-component multi-phase procedure.

References

Bryers, J. D. (1984). "Structured modelling of the anaerobic digestion of biomass particulates." Biotechnology and Bioengineering, Vol. XXVII, 638-649. John Wiley and Sons. 1985.
Reichel, T., A. Haarstrick and D. C. Hempel (2005). "Modeling long-term landfill emission - a segregated landfill model." Proc. Sardinia 2005, Tenth International Waste Management and Landfill Symposium, Cagliari, Italy, October 2005.

White, J. K., D. Nayagum and R. P. Beaven (2014). "A multi-component two-phase flow algorithm for use in landfill processes modelling." Waste Management **34**(9): 1644-1656.
White, J. K., J. P. Robinson and Q. Ren (2004). "Modelling the biochemical degradation of solid waste in landfills." Waste Management, Vol 23,3 March 2004.

LDAT default chemical pathways – configuration settings.xlsx
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