Parameter estimation for modelling clogging of granular medium permeated with leachate

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Abstract: A numerical model called BioClog is used to backcalculate biological activity rate constants using measured values of water quality and clog chemical characteristics from well-controlled laboratory column experiments that contained a granular-sized material permeated with synthetic and real leachates. BioClog is a multispecies, reactive chemical transport model capable of predicting clogging of a porous media caused by the accumulation of biofilms, chemical precipitates, and entrained particles. Monod kinetic constants for acetate- and butyrate-degrading bacteria were obtained through inverse modelling of granular-sized material permeated with synthetic leachate. The model predicted the changes in concentrations of volatile fatty acids and dissolved calcium and it predicted the changes in clog composition from a juvenile clog containing biofilm to a mature clog containing biofilm with mineral matter. The kinetic constants were then applied to predict spatial and temporal water quality and clog composition for a granular-sized material permeated with real leachate. The kinetic constants deduced through inverse modelling of the synthetic leachate column experiments provided reasonable predictions of the behaviour of the columns permeated with real leachate.

Key words: clogging, landfills, leachate collection systems, biofilms, mineral precipitation.

Introduction

A leachate collection system (LCS) is a drainage layer, typically comprised of a granular material with embedded perforated collection pipes, that is constructed at the base of modern solid waste landfills. The LCS is designed to control the hydraulic head acting on the base of the landfill, thereby minimizing the advective migration of contaminants through the landfill liner and to any underlying aquifers. Field studies (Brune et al. 1991; Fleming et al. 1999) have demonstrated that failure of the LCS can occur because of an accumulation of inorganic and organic material within the void spaces of the drainage material or in the pipes; this failure is known as clogging. Clogging reduces the hydraulic conductivity of the drainage layer and hence its ability to effectively transmit leachate to the collection pipe. Chemical analyses of clog solids from field studies showed that calcium (Ca$^{2+}$) and carbonate (CO$_3^{2-}$) comprised more than 50% of the dry mass (Brune et al. 1991, Fleming et al. 1999). Additionally, the clog material contained significant amounts of bacterial slimes along with precipitated material and particulates (silt and sand) that become attached to the biofilm. Brune et al. (1991) suggested that the formation of clog material was caused by the microbial activity within the collection system.

Cooke et al. (1999, 2005) presented the theoretical basis for modelling biologically induced clogging in a saturated porous medium permeated with leachate (one-dimensional (1D) flow). The ability of this model (called BioClog) to simulate the measured changes in (i) chemical oxygen demand (COD) and Ca$^{2+}$ concentrations within synthetic leachate...
after passing through gravel-sized material of thickness 66 cm, and (ii) decrease in medium porosity with time, was demonstrated by Cooke et al. (2001). The bulk removal of organic acids (measured as COD) was modelled by selecting Monod kinetic constants for biomass growth and substrate utilization from literature-reported values. The ability of the model to simulate the spatial removal of individual organic acids (e.g., acetate, butyrate, and propionate), which comprised the total COD, was not verified. VanGulck and Rowe (2004a, 2004b) experimentally observed that as real leachate (which contains suspended biomass and inorganic solids) passes through a porous media suspended particles attach to and colonize the media surface. The particles then influence the rate of volatile fatty acid (VFA) fermentation, precipitation of minerals, and reduction in medium porosity. However, suspended solids were not modelled by Cooke et al. (2001) because the synthetic leachate did not contain significant amounts of suspended solids. Thus, when modelling clog accumulation with real leachate, input parameters that are used to characterize the straining and filtration of suspended particles onto granular sized material surfaces are required but are currently unknown.

The objective of this paper is to provide a rational basis for the selection of model input parameters that may be used to model clogging in granular-sized materials permeated with leachate. Particular emphasis is placed on the identification of (i) the Monod kinetic constants required for predicting VFA fermentation and biomass growth, and (ii) the suspended solid properties needed for modelling the fate and transport of these particles as leachate permeates a gravel-sized medium. The selection of these parameters was based on the ability of the numerical clogging model to simulate changes in acetate, propionate, butyrate, and Ca\(^{2+}\) concentrations with time as leachate permeated through a gravel-sized medium for two different series of laboratory column experiments; one series using synthetic leachate (VS series, reported in VanGulck and Rowe 2004a) and the other series using leachate from the Keele Valley landfill, denoted herein as KVL leachate (VK series, reported in VanGulck and Rowe 2004b). The laboratory column experiments provide idealized conditions of fluid flow (1D flow) and relatively controlled mass loading of organics, inorganics, and suspended solids compared to a LCS, thus providing suitable conditions to complete inverse modelling to characterize model input parameters. The deduced input parameters can then be applied to more complex design conditions. The VS series column data were used to establish the model parameters that were then used to predict the behaviour in the VK columns.

**Column experiments**

A thorough description of the setup, operation, and results of the column experiments used in this study are presented in VanGulck and Rowe (2004a, 2004b). Only specific information from these experiments with respect to the required model input parameters are provided in the following.

Two series of experiments were performed with four columns in each series (eight columns in total). Each column in each series was, for all practical purposes, nominally identi-
mass capable of fermenting VFAs that are attached to the porous medium surface (this mass comprises part of the volatile film; also called the active biofilm); and suspended substrate degraders represent biomass capable of fermenting VFAs that are suspended in the leachate (this mass comprises part of the VSS).

The fate and transport of nine species are tracked in the model; these are the concentrations of (i) propionate, (ii) acetate, (iii) butyrate, (iv) suspended propionate degraders, (v) suspended acetate degraders, (vi) suspended butyrate degraders, (vii) suspended nonactive biomass, (viii) calcium, and (ix) suspended inorganic solids (also called fixed suspended solids (FSS)). The sum of the suspended propionate, acetate, butyrate degraders, and the suspended nonactive biomass comprise the leachate VSS. Consideration is given to the advective and dispersive movement of each species, in addition to the specified source and sinks fluxes described subsequently. The initial, clean medium porosity was specified for each element. The dispersion coefficients are computed from the dispersivity value and fluid velocity. A dispersivity value of 1 cm, used for all species and elements, was considered a reasonable value for laboratory scale transport based on Sun (1996), MacKay et al. (1996), and Grolimund et al. (1998). The measured influent flow rate was used to compute the velocities for each element. The concentration of each species is specified at the first node (corresponding to the screen–bead interface). A nonprescribed dispersive flux (open or free) was used as the outlet boundary condition. A finite difference approximation was used for the time derivative (central difference method) with a constant time step of 0.04 d. The element length and time step was selected as the optimal based on additional analyses with more refined meshes. The results showed that additional refinement of the discretization had an insignificant effect on the predicted VFA and Ca$^{2+}$ concentrations or volatile and inert film thickness.

**Substrate utilization**

Each element in the column is treated as a mixed fixed-film reactor. Methanogenesis of acetate and acetogenesis of propionate and butyrate can occur within the biomass attached to the porous medium surface (i.e., substrate degrader films) and also by suspended biomass in the leachate (i.e., suspended substrate degraders). Substrate is utilized within the substrate degrader films according to Monod kinetics and calculated using the method by Rittmann and McCarty (1981), which considers molecular diffusion within the substrate degrader film and mass transport resistance by a stagnant external liquid diffusion layer. Substrate utilization by suspended substrate degraders follows Monod rate limitations. The Monod kinetic constants, specifically the half-velocity coefficient, $K_s$ [M L$^{-3}$]; maximum specific substrate utilization rate, $\dot{q}$ [M M$^{-1}$ T$^{-1}$]; yield coefficient, $Y$ [M M$^{-1}$]; and decay coefficient, $b$ [T$^{-1}$] are required input parameters to assess the amount of microbial activity occurring within the column.

**Calcium removal**

Removal of calcium from the leachate is assumed to occur due to calcium precipitation and is calculated through a carbonic acid yield coefficient (VanGulck et al. 2003), which is a function of the fermentation of acetate, propionate, and butyrate by the substrate degrader films and suspended substrate degraders, and the availability of the precipitating cation (i.e., calcium). This yield coefficient links the degradation of organic acids and production of carbonic acid (H$_2$CO$_3$) to the precipitation of carbonate bound cations.
The carbonic acid yield coefficient of 0.170 and 0.116 mg cations as Ca$^{2+}$ removed per mg H$_2$CO$_3$ produced were deduced for the VS and VK series, respectively.

**Attachment rate of suspended solids**

The model calculates the attachment of suspended solids (suspended substrate degraders, nonactive suspended biomass, and FSS) from the leachate onto the medium surface of the porous medium through a first-order attachment rate coefficient (Tien 1989; Hornberger et al. 1992; Clement et al. 1997). An attachment rate coefficient is calculated for each suspended species using a clean bed filtration model developed by Rajagopalan and Tien (1976). The filtration model accounts for the processes of diffusion, interception, sedimentation, hydrodynamic retardation, and London – van der Waals attraction.

**Detachment and total bacterial loss rate**

The physical removal of attached substrate degraders and nonactive biomass from the medium surface into the leachate is calculated through a first-order loss rate coefficient using a slightly modified method by Rittmann (1982), which assumes detachment is controlled by fluid shear stress acting on the detachable films. Because fluid shear stress is a function of the level of clogging (i.e., porosity), a detachment rate coefficient is deduced for each substrate degrader species and nonactive biomass for each element and time step. Detachment of mineral films is assumed not to occur.

Biomass is also lost from the system through cell decay and maintenance and this is modelled using a first-order loss coefficient, $b_d$ [T$^{-1}$]. The biomass decay coefficient is assumed to be spatially and temporally constant.

**Suspended solids**

The concentration of each suspended substrate degrader for each node and time step is calculated with consideration given to (i) attachment of suspended substrate degraders from the leachate onto the medium surface, (ii) detachment of substrate film degraders from the medium surface into the leachate, (iii) suspended degrader growth, and (iv) suspended degrader decay.

The suspended nonactive biomass concentration for each node and time step is calculated considering (i) the attachment of suspended nonactive biomass from the leachate onto the medium surface, (ii) the detachment of nonactive attached film from the medium surface into the leachate, and (iii) the production of nonactive suspended biomass due to the decay of suspended substrate degraders.

Fixed suspended solids may be comprised of mineral precipitate and (or) soil particles (i.e., silt) that are suspended in the leachate (FSS are the difference between TSS and VSS). The calculation of the FSS concentration for each node and time step accounts for the attachment of this species from the leachate onto the medium surface.

**Volatile and mineral film thickness**

The substrate degrader film thickness for each element and time step is calculated from the sum of previous time step substrate degrader film thickness, the growth of the substrate degrader (i.e., biomass production), the attachment of suspended substrate degrader from the leachate onto the medium surface, and the decay and detachment of attached substrate degraders from the medium surface into the leachate. In deducing the substrate degrader film thickness, consideration is also given to the change in attached volatile film density for each element and time step (discussed later).

Upon decay of the substrate degrader films (a function of the cell decay rate, $b_d$), a fraction ($f_d$) of this biomass will degrade; thus, this mass is lost from the system. The remaining $(1 – f_d)$ nonbiodegradable organic solids (called nonactive biomass) contribute to the accumulation of the nonactive film layer.

The nonactive biomass film thickness for each element and time step is calculated from the sum of previous time step nonactive biomass film thickness, the production of nonactive biomass from the decay of substrate degrader films, the attachment of the suspended nonactive biomass from the leachate onto the medium surface, and the detachment of the nonactive biomass film from the medium surface into the leachate. The nonactive biomass film thickness calculation also accounts for the change in attached volatile film density for each element and time step (discussed later).

The inert film thickness for each time step is calculated from the sum of previous time step inert film thickness, attachment of FSS, precipitation of calcium carbonate solids (CaCO$_3(s)$), and precipitation of non-CaCO$_3(s)$ material. Since CaCO$_3(s)$ is the most abundant clog constituent (Brune et al. 1991; Armstrong 1998; Fleming et al. 1999; Rowe et al. 2000a, 2000b, 2002; VanGulck and Rowe 2004a, 2004b), the model uses the accumulation of CaCO$_3(s)$ as a surrogate to the accumulation of non-CaCO$_3(s)$ mass by considering the calcium removed and an estimation of the fraction of clog material that is CaCO$_3(s)$ ($f_{CaCO_3}$).

**Model parameters**

**Influent leachate composition**

Synthetic leachate composition was selected to resemble the chemical composition of KVL leachate (based on leachate collected between June and August 1993), but provides a relatively constant influent source concentration of nutrients to the columns (Rowe et al. 2002). It consists of three VFAs (acetate, propionate, and butyrate) with various salts and trace metals. In contrast to real KVL leachate, which varies daily and has a relatively high suspended solids loading and biological activity, synthetic leachate contains only a negligible amount of suspended solids and bacteria.

The synthetic leachate was initially inoculated with KVL leachate for the first 9 d of operation to seed the medium with typical real leachate microorganisms (full details are provided in VanGulck and Rowe 2004a). The KVL leachate used in the VK series had an average FSS and VSS concentration of 550 and 350 mg/L, respectively. The leachate was equilibrated to column operating temperatures prior to injection.

A reduction in suspended solids concentration in the leachate occurs as it travels from the measurement location (just prior to entering the column) to the screen – porous medium interface (Babcock 2005; McIsaac 2006). To account for this, the modelled FSS and VSS concentrations were reduced by a factor of 2 and 1.3 times less than the measured values, respectively, to account for settling of particles.
in the reservoir below the porous medium. The reduction factors were selected based on measured results by R. McIsaac (personal communication 2003) in a larger scale column experiment (compared to this study) with similar flow rate.

The average acetate, propionate, butyrate, and Ca\(^{2+}\) concentrations measured at port P1 (i.e., in the reservoir just below the porous media; see Fig. 1) were: 6540 mg COD/L, 7050 mg COD/L, 1700 mg COD/L, and 790 mg/L, respectively, for the VS series as shown in Fig. 2 (propionate concentrations not shown), and 3340 mg COD/L, 3940 mg COD/L, 1610 mg COD/L, and 460 mg/L, respectively, for the VK series as shown in Fig. 3 (propionate concentrations not shown). The influent leachate concentrations for the VS series were less variable with time than the VK series because it was synthetically produced in the laboratory. When the columns were cut open to assess clog material characteristics, slimes and encrusted material were observed within the reservoir below the screen–bead interface, suggesting that there will be a change in leachate concentrations from the measurement location of port P1 to the screen–bead interface. The leachate concentrations specified at the bead–screen interface were deduced from the values measured at port P1 (for details see VanGulck 2003).

Typically the measurements of influent leachate concentrations were completed 2–4 d (average about 3 d) after a new batch of leachate was supplied to the columns. With each new batch of leachate the influent leachate concentrations changed. In the model, to approximate the times when the influent leachate concentrations changed, the change in influent concentrations were assumed to occur 3 d before the measurement time (measurement times shown in Figs. 2 and 3).

Clog properties

Rowe et al. (2002) reported that in laboratory column studies where glass beads were permeated with synthetic and KVL leachate, COD removal (and also calcium) within the column occurred in three stages: a lag (<10% removal), a transition, and a steady-state phase (about 50% removal). Subsequent column studies (Rowe et al. 2002; VanGulck and Rowe 2004a, 2004b) used these different phases of COD removal to benchmark when to disassemble a column and assess the clog properties. Thus in the VS and VK experiments, a column was disassembled at the end of the lag phase, in the middle of the transition phase, at the end of the transition phase, and after steady-state COD removal was well established. A single column was disassembled at an elapsed time of 247, 295, 357, and 427 d for the VS series, and 57, 115, 157, and 245 d for the VK series.

The disassembly results indicate that the volatile film density increased as clogging intensified. The increase in volatile film density was largest near the influent end of the column where there was the greatest amount of clogging and therefore highest seepage velocity. This finding is consistent with Rittmann and McCarty (2001), who stated that mechanical stresses (i.e., fluid shear stress) on the biofilm tend to increase biofilm density and that high-stress anaerobic biofilms could reach densities up to as much as 200 mg volatile solids per cubic centimetre (VS/cm\(^3\)). An approximately linear relationship between volatile film density, \(X_{fa}\) [M L\(^{-3}\)] and fractional decrease in porosity, \((n_i - n)/n_i\) (Fig. 4) was implemented into the clogging model.

\[
[1] \quad X_{fa} = A \left( \frac{n_i - n}{n_i} \right) + B
\]

where \(n_i\) [-] is the initial clean medium porosity, \(n\) [-] is the clog affected porosity, and \(A\) and \(B\) are regression coefficients; \(A = 256\) and \(B = 46\) for the VS series, and \(A = 247\) and \(B = 72\) for the VK series.

During the steady-state phase (when calcium precipitation mainly occurred) the mineral film density, \(X_{fi}\) [M L\(^{-3}\)], value ranged from 2420 to 2750 mg nonvolatile solids per cubic centimetre (NVS/cm\(^3\)) for the VS series (VanGulck and Rowe 2004a) and from 2500 to 3030 mg NVS/cm\(^3\) for the VK series (VanGulck and Rowe 2004b). The difference in mineral density between the VS and VK series is likely due to differences in the fraction of CaCO\(_3\) (\(f_{CaCO_3}\)) in the non-volatile clog material. In the VS series, 94% of the non-volatile solids were CaCO\(_3\) and in the VK series this was 78% during the steady-state phase. The lower fraction of CaCO\(_3\) in the VK series is a result of differences in the chemical composition of synthetic and KVL leachates, more specifically, a larger concentration of non-Ca\(^{2+}\) cations was available to precipitate with carbonate in the KVL leachate (VanGulck et al. 2003). The fraction of CaCO\(_3\) in non-volatile clog solids measured during the steady-state COD removal phase (i.e., when there was about 50% removal of COD within the column) and a mineral film density of 2750 mg NVS/cm\(^3\) were used as inputs for the model.

Suspended solids

The suspended solids attachment calculations in the model require an estimate of the size and density of the suspended particles. The model assumes that the suspended solids are comprised of VSS and FSS, with each represented as having an effective size and density.

It may be expected in wastewaters that a portion of the VSS consists of inert biomass (i.e., nonactive or nonsubstrate consuming biomass, Rittmann and McCarty 2001). The percentage of active biomass is unknown for leachate. Thus, it was assumed that 70% of the VSS in the KVL leachate consisted of active biomass capable of substrate utilization for all times. It was also assumed that the 70% suspended active biomass contained an equal distribution of acetate to butyrate to propionate suspended degrader types (i.e., 33.3% of the active VSS is comprised of acetate, butyrate, and propionate degraders).

The VSS was assigned a diameter of a typical bacterium of 1 \(\mu\)m (Metcalfe and Eddie Inc. 1991). Suspended biomass may exist in clusters or flocs (Liu et al. 2003) and therefore may not have a single size. Brune et al. (1991) suggested that suspended bacteria provide nucelation sites for mineral precipitation and therefore may not have constant density. Given the uncertainty associated with predicting the attachment rate of VSS onto the surface of the beads, the density of the VSS used in modelling the VK series was varied (thereby influencing the calculated attachment rate) while keeping the diameter of the VSS constant to best capture the volatile film thickness. Based on this sensitivity study, a
VSS density of 1030 mg/cm\(^3\) was selected to reasonably predict the VK series volatile film thickness (described later).

An effective FSS diameter size of 0.0002 cm was based on a particle size distribution range of 0.0002–0.0075 cm for suspended solids in landfill leachate reported by Koerner and Koerner (1992). Based on a model sensitivity study (VanGulck 2003) where the density of the FSS was varied and the diameter of the FSS was held constant, a value of 1065 mg/cm\(^3\) was selected to predict a FSS removal of about 60%–90% within the column.

Biomass and biofilm properties

In this study it is assumed that biofilm detachment is solely due to shearing. The fraction of biomass degradable by decay was taken to be 0.8 based on Rittmann and Snoeyink (1984). The transport of substrates to the surface of the biofilm requires the free solution, \(D_o\) [L\(^2\) T\(^{-1}\)], and biofilm, \(D_f\) [L\(^2\) T\(^{-1}\)], diffusion coefficient to be specified. Based on the work of Yu and Pinder (1994), the \(D_o\) values applied for acetate, propionate, and butyrate were 1.50, 1.27, and 1.10 cm\(^2\)/d, respectively; and the \(D_f\) values applied for acetate, propionate, and butyrate were 0.47, 0.52, and 0.31, respectively. The external diffusion layer thickness is deduced through a correlation by Skelland (1974) and is a function of the fluid properties, porous medium size, and fluid velocity, and therefore is calculated for each time step and element.

Kinetic constants

The activity of acetate, propionate, and butyrate degraders is represented by the four Monod kinetic constants for each substrate degrader. There are various factors that contribute to the activity of microbial activity, including: temperature, pH, toxicity inhibition, bacterial culture properties, nutrient availability, and mass transfer resistance. As a result, the range of literature reported values for Monod kinetic constants for each acid of interest is large (see Table 1; data adapted from summaries reported in Pavlostathis and Giraldos-Gomez 1991; Vavilin and Lokshina 1996; Cooke et al. 2001). Additionally, the majority of measured kinetic constants for anaerobic decomposition of the three acids of interests have largely been determined for the treatment of wastewater at loading rates and temperatures not consistent with the experimental conditions described in this study. Thus, the kinetic constants for acetate and butyrate degradation and degrader growth and loss were obtained through inverse modelling to obtain the “best-fit” between the measured and predicted concentrations with time and position within the VS column experiments. The deduced kinetic constants from the VS series were then used in modelling the VK series.

The relative least square (RLS) residual between the model predicted and measured values of acetate and butyrate with column position and time were calculated for various combinations of acetate and butyrate kinetic constants, as follows:
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\[ \text{RLS} = \left[ \frac{1}{m} \sum_{i=1}^{m} \left( \frac{y_i - y_i^*}{y_i} \right)^2 \right]^{0.5} \]

where \( m \) is the number of data points; \( y_i \) is the measured concentration for species \( i \); \( y_i^* \) is the predicted concentration for species \( i \); and \( y_i - y_i^*/y_i \) is the residual. Saez and Rittmann (1992) stated that the RLS is a more appropriate least squares technique than the absolute least square calculation for biological systems where the measured concentrations can range over two orders of magnitude, as was the case in this study. The values of kinetic constants used in inverse modelling extended beyond the upper- and lower-bound literature reported range for reasons described previously. The inverse modelling procedure involved calculating the RLS by altering one kinetic constant successively over a predefined range, while holding the remaining seven kinetic constants each at a single value. The RLS was therefore deduced for every combination of kinetic constant values (more than 125,000 combinations were examined) and allowed for an assessment of the global minimum RLS. The minimum RLS that yielded a prediction of volatile and mineral film thicknesses that reasonably resembled the measured temporal and spatial thickness were selected as the “best-fit” kinetic constants and are provided in Table 1. The “best-fit” kinetic constants \( K_s, Y, \) and \( b \) for acetate are within the literature reported range. However, \( \dot{q} \) for acetate was below the literature reported lower bound range. Since there are only two reported cases that provided measured kinetic constants for butyrate degradation under anaerobic conditions, there is little basis for a comparison of the butyrate parameters with literature values.

Propionate was not measurably removed in the VS series, and only experienced minor removals in the VK series during the length of time the columns were in operation. As such, propionate kinetic constants could not be deduced through inverse modelling of propionate degradation. Additionally, since only minimal removal of propionate occurred in relation to acetate and butyrate, any production of bio-

Fig. 3. VK series measured and predicted acetate, butyrate, and calcium concentrations with time for column port P1–screen, port P3, port P5, and port P7, where the flow path length from the screen to P3, screen to P5, and screen to P7 is 12, 24, and 36 cm, respectively.

Fig. 4. Volatile film density relationship with fractional decrease in porosity.
mass from propionate degraders is likely minimal in comparison to acetate and butyrate degraders. However, if propionate suspended degraders attached to the surface of the porous medium from the passing leachate, this biomass would undergo detachment and decay. A fraction of the attached propionate degraders that undergo decay will contribute to the nonactive biomass thickness. The average literature-reported value for propionate degrader decay rate, 0.061 d⁻¹, was used in modelling the VS and VK series.

### Results and discussion

#### Measured and predicted leachate concentrations

The measured and predicted acetate, butyrate, and Ca²⁺ concentrations are shown in Figs. 2 and 3. Details regarding the removal of each acid and its relation to calcium precipitation and clog formation are given by VanGulck and Rowe (2004a, 2004b). The focus of this discussion will solely deal with the ability of the model to predict the measured concentrations.

The model predicted the spatial and temporal concentrations of acetate, butyrate, and Ca²⁺ for the VS series, closely matching the measured concentrations, in particular the lag time, or acclimation phase prior to significant removal of acetate (about 250 d), butyrate (about 300 d), and Ca²⁺ (about 250 d) concentrations, as shown in Fig. 2. The removal of butyrate was overpredicted from about day 250 until about day 350. The lag phase prior to significant organic acid removal represents a time when the acetate and butyrate films were too small (due to the short inoculation time when the columns operated with a mixture of synthetic and KVL leachate) to remove significant quantities of these acids. However, over time these films began to grow, allowing for greater removal of organic acids, which in turn caused these films to grow larger. Thus, the accumulation of active biomass (i.e., thicker substrate degrader films) and the related increased rate of substrate removal marks the end of the lag phase. Eventually the substrate degrader films develop to a point where detachment of the biomass from the medium surface into the passing leachate is significant enough, and the detention time of leachate within the column is reduced (due to the reduction in medium porosity) to slow the removal rate of the organic acid within the column.

The model also reasonably predicted the spatial and temporal lag phase for acetate (between 15 and 50 d), butyrate (about 15 d), and Ca²⁺ (about 15–50 d) concentrations for the VK series, as shown in Fig. 3, using the kinetic constants deduced from the VS series. As there was a continuous supply of biomass into the VK columns, the length of the lag phase is not as readily apparent as it is in the VS series. Butyrate removal was overpredicted between about 50 and 70 d. Acetate removal was underpredicted after about 150 d, which coincides with times when the acetate concentrations were lower than earlier elapsed times. Given the dramatic changes in influent KVL leachate acetate, butyrate, and calcium concentrations with time, in addition to the fact that only 73% of the total COD in the influent leachate was represented by the three measured VFAs (acetate, butyrate, and propionate), the model reasonably predicted the temporal and spatial trends in the measured leachate acetate, butyrate, and Ca²⁺ concentrations. The existence of about 27% of the total COD that is not acetate, butyrate, and (or) propionate may include longer chain organic acids that could be fermented in the column and generate acetate, butyrate, or propionate as a by-product, and also generate biomass that is not accounted for in modelling the volatile film thickness. The experimental data showed that about 500–1000 mg COD/L of nonacetate–butyrate–propionate organics degraded within the column, with most of this removal occurring within the lower half (i.e., near the influent end) of the column.

It is well known that the fermentation of butyrate produces acetate (Parkin and Owen 1986; Bjerg et al. 1995). Consequently, during the first approximately 70 d, more acetate was produced within the column due to butyrate fermentation than was fermented. Thus the decrease in butyrate concentration led to an increase in acetate concentration. This is most evident for the VK series during the first 70 d, but was also observed in the VS series. The precipitation of Ca²⁺ during this period was relatively low because of the strong dependency of calcium precipitation on acetate fermentation and not butyrate fermentation.

In the VS series, the columns operated for a relatively short time to inoculate the medium with microorganisms. After the inoculation process, the amount of suspended substrate degraders was minimal. Thus, the removal of acetate and butyrate within the column was primarily due to the growth of acetate and butyrate degrader films, not suspended substrate degraders. In the VK series, the leachate contained suspended substrate degraders, and therefore acetate and butyrate removal could occur as a result of suspended substrate degraders and suspended film degraders. In addition to the short residency time (<3 h) for suspended degraders in the column, the suspended substrate degrader mass in the leachate is small in comparison to the substrate film degrader mass, suggesting that the substrate film degraders and not the suspended substrate degraders were largely responsible for the decrease in acetate and butyrate within the column. It is important to note that suspended substrate degraders may not have significantly contributed to the decrease in acetate and butyrate concentrations; however, the
attachment of suspended substrate degraders from the leachate onto the surface of the beads significantly contributed to the development of the substrate film degraders, and therefore, are the primary reason why acetate and butyrate fermentation occurred at an earlier time in the VK series than the VS series.

**Calculated and predicted volatile and inert film thickness**

The predicted volatile film thickness along with the measured values at four different elapsed times with position in the columns for the VS and VK series is presented in Figs. 5 and 6, respectively. The model captured the general trends in the measured volatile and mineral film thickness, such as (i) the quick accumulation of volatile solids during the lag phase of leachate treatment; (ii) the increase in mineral material (primarily due to mineral precipitation in the VS series, mineral precipitation, and to a lesser extent FSS accumulation in the VK series); and (iii) the change in total clog distribution along the column with time. For example, the VS- and VK-series-predicted mineral and volatile results at disassembly of the first column (247 d for the VS series and 57 d for the VK series) had a relatively large volatile film thickness compared to the small mineral film thickness. However, between disassembly of the first and last column (427 d for the VS series and 245 d for the VK series) the mineral film thickness increased significantly, and the volatile film also increased in thickness. Thus, at disassembly of the first column in both series, the volatile film was primarily responsible for the decrease in medium porosity, while at disassembly of the last column, both the mineral and volatile films contributed to the decrease in medium porosity (discussed later).

The volatile film thickness in the VS series was underpredicted along the length of the column at 247 d, underpredicted near the influent end of the column and overpredicted in the top half of the column at 295 d, underpredicted near the influent end of the column and overpredicted at higher column elevations at 357 d, and overpredicted in the lower half of the column and closely matched the measured film thickness in the top half of the column at 427 d. The deviation between the model predicted volatile film thickness may be attributed to (i) biomass being produced in the reservoir and transported into the porous medium where it may attach and grow on the surface of the beads (not accounted for in the model simulation); (ii) uncertainty in the measurements of volatile mass (there was only enough clog material for one measurement) used to deduce the measured volatile film thickness and the inability to separate water adhered to the clog–bead surface and water comprising the biofilm; and (iii) the assumptions regarding the properties of the suspended solids in the influent leachate and also the biomass detached from the surfaces of the beads. The predicted mineral film thickness closely matched the measured values at all elapsed times and position in the column with the exception of an overpredicted thickness at 427 d at the influent end of the column. Despite the deviations in the measured and predicted film thickness, the model did reasonably capture the trends of each film type along the length of the column at different stages of leachate treatment. This is the first time temporal predictions of film thickness have been compared to measured data.

The VK series volatile film thickness was underpredicted at 57 d, reasonably predicted at 115 d, overpredicted at 157 d in the top two-thirds of the column, and underpredicted near the top of the column at 245 d. The mineral film thickness reasonably matched the measured values at 57, 115, and 245 d; however, the 157 d predictions did not match the measured value well. In addition to the reasons previously described for the VS series, the deviations between the predicted and measured film thickness in the VK series also may be due to (i) the reduction factor used to account for removal of suspended solids below the column screen; (ii) the change in suspended solids concentration with time due to settling within the storage tank or manifold distribution system (in modelling the VK series it was assumed that the suspended solids concentration was constant between measurement times); and (iii) the assumption that for all times the distribution of suspended biomass types and percentage of active biomass within the VSS was constant.

**Calculated and predicted porosity**

The increase in volatile and inert films within the column caused a reduction in medium porosity. The measured porosity was deduced from the mass and bulk density measurements of the clog material at column disassembly (see VanGulck and Rowe 2004a, 2004b) using standard mass–volume relationships. The model predicted porosities along the length of the column closely resembled the measured values in the VS series (Fig. 7), in particular, the relatively uniform and small decrease in porosity at 247 and 295 d and the larger amount of clogging that occurred in the lower half of the column compared to the top half at 427 d. The VK series model predicted porosities closely resembled the measured values at 57 d; however, the 115, 157, and 245 d porosities experienced some larger deviations from the measured values but followed the trend that there was a greater degree of clogging in the lower half of the column compared to the top half (Fig. 8).

It is important to note that although the porosity of the medium is a useful parameter to assess the degree of clogging within the granular sized material, its value is deduced from the predicted volatile or mineral film thickness. Thus, it is possible to have the same predicted porosity, as shown in Figs. 7 and 8, with an incorrect distribution of clog type. This highlights the importance of being able to correctly model the development and distribution of volatile and mineral films (Figs. 5 and 6).

**Conclusions**

A numerical clogging model capable of simulating the spatial and temporal changes in acetate, butyrate, and calcium concentrations due to biological activity as it permeated through a gravel-sized medium, along with the reduction in porous medium void space due to the development of volatile and mineral films on the surfaces of the porous medium was used to model laboratory columns permeated with synthetic and Keele Valley landfill leachate. The increase in volatile and mineral films was due to biological activity (i.e., attached biofilms on the surfaces of the porous medium and suspended biomass in the leachate) fer-
menting volatile fatty acids, which provided conditions conducive for the precipitation of minerals (primarily calcium carbonate). Both the biological and chemical processes resulted in clogging of the porous medium, which in turn, affected the removal rates of volatile fatty acids and calcium from the leachate. Compared to measured values, the model was able to reasonably predict the spatial and temporal changes in leachate acetate, butyrate, and calcium concentrations in addition to the distribution of clog type (i.e., volatile or mineral films). Parameters deduced by inverse
modelling of the columns permeated with synthetic leachate provided reasonable predictions of the behaviour of the columns permeated with Keel Valley leachate, suggesting that these parameters may be useful for predicting clogging in other situations. Thus this study represents an important step towards being able to predict biological, chemical, and physical clogging within landfill LCSs because it provides guidance in the selection of model parameters, such as the kinetic constants needed for acetate and butyrate degrader growth and decay, as well as suspended solids size and density values that may be used by others to model clogging in granular sized materials. This is the first time model predicted individual volatile fatty acids and clog type-distribution were compared to measured values for synthetic and real leachate permeated porous medium.

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