A MATHEMATICAL MODEL FOR MANGANESE DIAGENESIS IN BIOTURBATED SEDIMENTS

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ABSTRACT. An analytical steady-state model for manganese diagenesis has been developed. The model incorporates diffusion analogous bioturbation and bioirrigation of sediment and first-order dissolution and precipitation of manganese. Application of the model to data sets from the Laurentian Trough environment of the Gulf of St. Lawrence gives values of 50,000 yr\(^{-1}\) for the precipitation rate constant and 250 yr\(^{-1}\) for the dissolution rate constant. The rate constant for precipitation is in agreement with laboratory measurements on sediments from the same region. The model was used to examine the reason for an order-of-magnitude range in the maximum concentration of dissolved manganese in the sediments along the axis of the Trough. The model calculations show that this large range can be explained by differences in the rate at which bioturbation transports dissolvable manganese downward across the redox boundary into the reducing zone of the sediment.

INTRODUCTION

Interest in the origin and growth of manganese nodules found on the sea floor and improvements in the chemical analysis of manganese in seawater have resulted in many studies of the geochemical cycling of manganese in marine sediments in recent years (Lynn and Bonatti, 1965; Elderfield, 1976; Froelich and others, 1979; Klinkhammer, 1980; Calvert and Price, 1972; Sundby, Silverberg, and Chesselet, 1981; Aller, 1980; Sundby and Silverberg, 1985; Pedersen, Vogel, and Southon, 1986). The distribution of solid and dissolved manganese in sediments is primarily a result of the redox sensitivity of this element. The stability boundary between the two valency states of manganese lies within the range of redox potentials found in most marine sediments, so that soluble divalent manganese is produced in reducing sediments, diffuses upward along a concentration gradient, and precipitates as the tetravalent form in oxidizing sediments (Glasby, 1984). However, other processes, such as adsorption of divalent Mn onto other particles, formation of authigenic Mn minerals, and the mixing activity of benthic organisms, may also significantly influence the distribution of Mn in sediments. Bacteria are capable of carrying out manganese oxidation and reduction under certain environmental conditions (Ehrlich, 1981), but little is

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currently known about the extent of their participation in these redox reactions in marine sediments (Ehrlich, 1982; Burdige and Kepkay, 1983; Edenborn, Paquin, and Chateauneuf, 1985).

Several mathematical models have been developed to describe the distribution of solid and dissolved manganese in sediments (Michard, 1971; Robbins and Callender, 1975; Holdren, Bricker, and Matisoff, and others, 1975: Boudreau and Scott, 1978: Burdige and Gieskes, 1983). Of these, the model of Burdige and Gieskes (1983) was the first attempt to account for changes in both porewater and solid-phase manganese profiles in marine sediments. Because this model was primarily intended for use in sediments in which manganese reduction/oxidation takes place below the zone of bioturbation, it does not include terms for the biological transport of manganese. It is therefore not applicable to modeling manganese diagenesis in many estuarine, coastal, and pelagic sediments in which bioturbation takes place across the redox boundary. For that reason we have modified the original model of Burdige and Gieskes (1983) to incorporate bioturbation and bioirrigation activity. In this paper, we describe the modified model and apply it to data from the Laurentian Trough of the Lower St. Lawrence estuary, an environment for which estimates of the large number of parameters required by the model are available.

THE MODEL

Following Burdige and Gieskes (1983) we have divided the sedimentary column into four distinct zones (fig. 1): the oxidized zone, the oxidizing zone, the reducing zone, and the reduced zone. Typical (theoretical) pore water and solid phase manganese profiles in each zone are presented in figure 1.

In the oxidized zone, pore water manganese is essentially zero. It is assumed that there is a constant, time-independent supply of solid manganese from the water column. Therefore, the concentration of solid manganese is constant with depth. In the oxidizing zone, upward diffusion of dissolved manganese from the reducing zone and consumption via oxidation (precipitation) cause both pore water and solid manganese concentrations to increase with depth. Below the redox boundary, solid manganese is quickly reduced (dissolved). Finally, to (mathematically) close the problem, it is assumed that the pore water concentrations must remain finite as the depth goes to infinity. The manganese chemistry in each zone is discussed in detail in Burdige and Gieskes (1983). The model is improved by adding bioturbation to the oxidizing zone and by dividing the reducing zone into two layers: a bioturbated upper layer and a lower layer without bioturbation.

Because the sedimentary environment in reality has a complex three-dimensional structure, the one-dimensional model is a great oversimplification and, in some ways, even a contradiction. For example, we have parameterized the enhanced upward transport of dissolved manganese, which is due to the activity of benthic organisms, as a
vertical (bio)diffusion process. Yet, such transport may to a large extent be taking place through horizontal diffusion from the reducing sediment into the oxygenated water of irrigated burrows (Aller, 1980). Boudreau (1984) has shown that this process is better described as non-local transport than as diffusion. However, since the data needed for a three-dimensional description of manganese diagenesis are usually not available, we have retained the diffusion formalism rather than incorporating a non-local transport term. Finally, because of lack of data on the time-variation of the manganese distribution and fluxes, we have chosen to assume steady-state diagenesis in spite of evidence that the distribution dissolved manganese near the sediment interface is not in steady state (Gobeil and others, 1987).

The effects of physical, biological, and chemical processes on the mass conservation of solid and pore water manganese are expressed by the steady state diagenetic equation (Berner, 1980):

\[
(D_s + D_t + D_B) \frac{\partial^2 P}{\partial z^2} (z) - w \frac{\partial P}{\partial z} (z) + R(z) = 0
\]  

(1)

\[
D_B \frac{\partial^2 S}{\partial z^2} (z) - w \frac{\partial S}{\partial z} (z) - \frac{\phi}{1-\phi} R(z) = 0
\]  

(2)
where $P(z)$ is the concentration of manganese in pore water, $S(z)$ the concentration of manganese in the solid phase, $w$ the constant sedimentation rate, $\phi$ the porosity, and $R(z)$ a source (or sink) term representing the chemical transfer of mass by either oxidation (precipitation) or reduction (dissolution). The depth coordinate, $z$, is positive downward. The effects of bioturbation, bioirrigation, and bulk sediment diffusion are parametrized by the constant (in each layer) coefficient $D_B$, $D_1$, and $D_S$, respectively.

Eqs (1) and (2) are obtained from the general diagenetic equations (Berner, 1980, eqs 3.73 and 3.74) with the help of the following assumptions.

1. The diagenetic processes are time-independent (steady state).
2. The horizontal gradients are negligible, compared to the vertical ones.
3. Advection is constant and equal to the sedimentation rate.
4. Mixing processes are depth-independent in each layer and follow Fick’s law.

Following Burdige and Gieskes (1983), the source (or sink) term $R(z)$, the rate expression for either precipitation or dissolution, is modelled as a first order process:

\begin{align*}
\text{precipitation:} & \quad R(z) = K_p \cdot P(z) \\
\text{dissolution:} & \quad R(z) = K_d \cdot S(z)
\end{align*}

where $K_p$ and $K_d$ are the constant, depth-independent precipitation (oxidation) and dissolution (reduction) rates, respectively.

Upon substitution of (3) and (4) into (1) and (2), we obtain the following set of equations for each layer.

A. *For the oxidized zone* ($0 \leq z \leq L_1$)

\[ P_1 = 0 \quad \text{and} \quad S_1 - S_0, \text{the surface concentration} \]

B. *For the oxidizing zone* ($L_1 \leq z \leq L_2$)

\[ D_{21} \frac{\partial^2 P_2}{\partial z^2} - w \frac{\partial P_2}{\partial z} - K_p P_2 = 0 \\
D_{22} \frac{\partial^2 S_2}{\partial z^2} - w \frac{\partial S_2}{\partial z} + \frac{\phi}{1-\phi} K_p P_2 = 0 \]

C. *For the reducing zone with biodiffusion* ($L_2 \leq z \leq L_3$)

\[ D_{31} \frac{\partial^2 P_3}{\partial z^2} - w \frac{\partial P_3}{\partial z} + \frac{1-\phi}{\phi} K_d S_3 = 0 \\
D_{32} \frac{\partial^2 S_3}{\partial z^2} - w \frac{\partial S_3}{\partial z} - K_d S_3 = 0 \]
D. For the reducing zone without biodiffusion \((1.3 < z < \infty)\)

\[
\begin{align*}
D_{41} \frac{\partial^2 P_4}{\partial z^2} - w \frac{\partial P_4}{\partial z} + \frac{1 - \phi}{\phi} K_d S_4 &= 0 \\
- w \frac{\partial S_4}{\partial z} - K_d S_4 &= 0
\end{align*}
\]  

(9) (10)

where \(D_{41} = D_B + D_I + D_S\), and \(D_{42} = D_B\) in layer i. This notation allows the mixing coefficients to vary from layer to layer. The solutions, together with the proper matching conditions between layers, are given in the appendix.

The Burdige and Gieskes (1983) model was developed for deep-sea sediments, where the thickness of each layer is measured in centimeters rather than in millimeters. Therefore, the redox boundary was assumed deep enough to neglect bioturbation and bioirrigation. With this supplementary assumption, the set of eqs (5) to (10) would reduce to Burdige and Gieskes (1983) eqs (7) to (10).

Burdige and Gieskes (1983) further assumed that advection is negligible, compared to diffusion. That is,

\[4 \cdot D_S \cdot K_p \gg w^2 \quad \text{and} \quad 4 \cdot D_S \cdot K_d \gg w^2\]

Coastal sedimentation rates are two to three orders of magnitude larger than the values used by Burdige and Gieskes (1983). This simplification will therefore not be made.

APPLICATION OF THE MODEL

Derivation of precipitation and dissolution rate constants.—The rate expression for the oxidation of \(\text{Mn(II)}\) in a solution containing a reactive solid phase is often written as:

\[-d[\text{Mn(II)}]/dt = k[\text{Mn(II)}][O_2][OH^-]^2[\text{solid}]\]  

(11)

where \([\text{Mn(II)}], [O_2], [OH^-]\), and \([\text{solid}]\) indicate the concentrations of dissolved manganese, oxygen, hydroxyl ions, and the amount of active surface available, respectively, and \(k\) is the oxidation rate constant (Sung and Morgan, 1981). The active surface in aerobic sediments is mostly oxidized manganese. Eq (11) reduces to a pseudo-first-order equation

\[-d[\text{Mn(II)}]/dt = k'[\text{Mn(II)}] \]

(12)

when pH and the concentrations of oxygen and reactive solid surface are kept constant. The pseudo-first-order rate constant \(k'\) corresponds to the precipitation rate constant \(k_p\) used in developing our model. \(k_p\) is therefore not a true constant but varies in response to the local concentration of oxygen, pH, and reactive solid. It will therefore vary from one environment to another. Likewise, in a real sediment, \(k_p\) will decrease with depth because of the decreasing concentrations of oxygen and solid phase manganese. This has been shown to be true in Lauren-
tian Trough sediments, where \( k_p \) decreases with depth parallel to the decreasing concentration of solid phase manganese (Edenborn, Paquin, and Chateaupeuf, 1985).

With this in mind, the model for manganese diagenesis will now be applied to data from bioturbated sediments of the Laurentian Trough (fig. 2), for which estimates of all the parameters required by the model (except the two rate constants) are available. Solid-phase and porewater distributions of manganese, in combination with estimates of the transport parameters, in three replicate cores from station 23 (Gobeil and others, 1987), will be used for the purpose of deriving the rate constants. The three cores display the same general pattern for the manganese distributions, but the individual profiles are stretched or compressed relative to each other (fig. 3). Thus each core differs in the depth at which the transition from manganese-rich to manganese-poor sediment takes place and in the depth where the sharp gradient in dissolved manganese occurs. The concentration level of dissolved manganese below this gradient is similar in all cores, as is the background concentration of solid-phase manganese below the enriched layer.

Fig. 2. Chart showing the western portion of the Laurentian Trough and the location of stations 20, 23, and 24.
Fig. 3. Depth profiles of the concentrations of solid phase and dissolved Mn and Cd from three replicate box cores obtained at station 23 in August 1984 (after Gobeil and others, 1987).
For the purpose of defining the depth-zonation of the model, we interpret the bottom of the manganese-rich layer as the depth to which bioturbation and bioirrigation are effective (L3) (Sundby and Silverberg, 1985). Furthermore, we interpret the minimum in the solid cadmium profile (fig. 3) to represent the depth of the redox-boundary (L2), the initial sharp decrease in total Cd being associated with aerobic degradation of fresh organic matter (Gebeil and others, 1987). Subsequent micro-electrode measurements of the penetration depth of oxygen on cores from this station have given values for the depths of the redox boundary that are in good agreement with those estimated from the cadmium profiles (Silverberg and others, 1987).

The thickness of the top-most oxidized layer, (L1), is set arbitrarily to 0.1 cm. Unlike pelagic sediments, a surface layer in which the solid-phase manganese concentration is constant with depth is rarely apparent in these coastal sediments (Sundby, Silverberg, and Cheselelet, 1981; Sundby and Silverberg, 1985).

Since we are modeling only the fraction of solid manganese that participates in the redox cycle, we obtain the concentration of "reactive" manganese by subtracting the constant background concentration of solid-phase manganese below the enriched layer from the total manganese concentrations. For the surface sediment, this gives us \( S_0 \), the concentration of reactive manganese at depth 1.1. As mentioned above, the model ignores possible precipitation reactions in the fourth layer (the formation of rhodochrosite (MnCO₃) and alabandite (MnS)).

The sedimentation rate \( (w) \) is estimated from Pb-210 sediment profiles as well as from sediment trap measurements, and the best estimate of the bioturbation coefficient \( (D_B) \) is taken as the geometric mean of the values obtained from the depth distributions of short-lived thoriium isotopes (Silverberg and others, 1986). Bioirrigation coefficients \( (D_I) \) are not known with certainty for these sediments, but calculations based upon the consumption rate of oxygen indicate an effective diffusion coefficient three to five times that of molecular diffusion (Silverberg and others, 1987). Therefore, a value of 300 cm² yr⁻¹ has been chosen for \( D_I \). High densities of benthic organisms are known to be limited to the upper 5 to 10 cm of the sediment, so that bioirrigation in the fourth layer has been ignored. Finally, a value of 0.851 (the mean porosity over the top 3 cm) has been chosen to represent the porosity term.

As seen in table 1, estimates for all the parameters in the model are available except the two rate constants, which can be obtained by fitting the model to the three profiles of solid and dissolved manganese in figure 3. We originally attempted to least-square fit the model to actual data using a larger data set. As was the case in Burdige and Gieskes (1983), the presence of secondary maxima made the least-square approach difficult to use. The results were highly dependent on the choice of the initial guesses needed for the numerical algorithm. Orders of magnitude variations in the rate constants were found, and solid
phase and pore water profiles could not both be fit satisfactorily. Therefore, the rate constants were obtained instead by varying systematically each of the two parameters over a wide range of values. The combination that best reproduced the data from a single core was then retained and tested with data from other cores.

The model does not consider chemical reactions within the reduced zone and will not produce the decrease in the distribution of dissolved manganese with depth that would be expected if manganese were precipitating deeper in the sediment. Therefore, when fitting the model, we used the measured maximum concentrations of dissolved manganese to represent the constant value to be reached by the model within the reducing zone. Within these limitations, an excellent fit to all three cores is obtained when \( k_p = 5 \times 10^4 \text{ yr}^{-1} \) and \( k_d = 2.5 \times 10^2 \text{ yr}^{-1} \) (fig. 4).

For core 1, the modeled concentration of dissolved manganese in the reduced layer is slightly higher than the measured concentration (fig. 4A). The concentration of solid-phase manganese in the surface layer is also highest in this particular core. The modeled concentration of dissolved manganese can be made to correspond more closely to the measured maximum concentration by decreasing the bioturbation coefficient, which affects the rate of burial of dissolved manganese into the reducing zone (fig. 4D) or by decreasing the bioirrigation coefficient, which affects the upward transport of dissolved manganese (fig. 4E). These modifications, which amount to a 30 percent decrease of the bioturbation coefficient or a 50 percent increase in the effective diffusion coefficient, result in profiles of solid-phase manganese that are more uniform. The extent of these modifications is small, however, considering the uncertainties in the estimates for these transport parameters.

Comparison with measured values of the precipitation rate constant.—

The model can now be tested by comparing the estimate for the
precipitation rate constant with measured values of this parameter in sediments from the same station in the Laurentian Trough. Edenborn, Paquin, and Chateauneuf (1985) obtained values for a pseudo-first-order oxidation rate constant (eq 12) that ranged from $10^4$ to $10^5$ yr$^{-1}$ by measuring the rate of precipitation of dissolved manganese in the reduced sediment porewater in the presence of sediment from the oxidizing layer. In agreement with eqs (11) and (12), the value of this parameter decreased with depth in parallel with the decreasing concentration of solid-phase manganese. The measured values bracket the result of the model calculation ($5 \times 10^4$ yr$^{-1}$), which is very encouraging,
given the assumptions made in the model and the uncertainties in some of the rate estimates.

Whereas the model results agree with actual measurements made on sediments from the same station, the rate constants are very high compared to those obtained by modeling pelagic sediments and other coastal sediments (table 2). The discrepancy could well be related to differences in local conditions of pH, oxygen, and reactive solid.

<table>
<thead>
<tr>
<th>Location</th>
<th>k (yr(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower limit for marine sediments based on lab data</td>
<td>3.2</td>
<td>Boudreau and Scott (1978)</td>
</tr>
<tr>
<td>Eastern equatorial Pacific</td>
<td>10.7–12</td>
<td>Burdge and Gieskes (1983)</td>
</tr>
<tr>
<td>Long Island Sound</td>
<td>50</td>
<td>Elderfield and others (1981)</td>
</tr>
<tr>
<td>Laurentian Trough (from biodiffusion model)</td>
<td>50,000</td>
<td>This study</td>
</tr>
</tbody>
</table>

**The effect of bioturbation on the concentration of dissolved manganese in sediment porewater.** — A second test of the model is its ability to reproduce the range of values of dissolved manganese observed in sediment from the Laurentian Trough. For that purpose, we will apply the model to a data set, obtained in 1980, for stations 20, 23, and 24 (fig. 5; Sundby and Silverberg, 1985). The order-of-magnitude range of the maximum concentration of dissolved manganese was difficult to explain by invoking the equilibrium with a solid manganese phase as the control of the dissolved manganese concentration.

The concentration of solid phase manganese in the surface layer sediments is similar at these stations, as is the dissolved oxygen concentration in the bottom water. We therefore feel justified in applying the model values of the rate constants obtained from station 23 to the two other stations as well. When those constants are included, estimates for all the parameters required by the model are available (table 3), and we can derive the profiles of solid and dissolved manganese.

The results of the model calculations are shown in figure 6. The maximum concentration of dissolved manganese predicted by the model for station 20 is very close to the observed value (The decreasing concentration with depth cannot be reproduced by the model since it ignores reactions in the reduced layer). For the other two stations the predicted dissolved manganese concentrations are slightly lower than the observed values. However, by assuming a slightly lower bioturbation coefficient for station 23 (fig. 6D) and extending the depth of bioturbation from 2 to 4 cm for station 24, the calculated profiles are in excellent agreement with the observed profiles. This latter assumption of deeper bioturbation is a reasonable one since station 24 is known to be characterized by particularly deep bioturbation (Ouellet, 1982).
Fig. 5. Data obtained in 1980 at stations 20, 23, and 24 (after Sundby and Silverberg, 1985). Note the large shift of the maximum dissolved manganese concentration between station 20 and station 24. The intensity of bioturbation increases in the same direction.

| Table 3 |

| Parameters used for modeling the 1980 data from stations 20, 23, and 24 |
|---------------------------------|---|---|---|
|                                | St. 20 | St. 23 | St. 24 |
| Depth of oxidized layer L1 (cm) | 0.1 | 0.1 | 0.1 |
| Depth of redox boundary L2 (cm)  | 1.0 | 1.0 | 1.0 |
| Depth of bioturbation L3 (cm)    | 2.0 | 2.0 | 2.0 |
| Sedimentation rate (cm yr⁻¹)     | 0.15 | 0.23 | 0.67 |
| Molecular diffusion Dₙ (cm² yr⁻¹) | 91  | 91  | 91  |
| Bioturbation coefficient Dₘ (cm² yr⁻¹) | 1.27 | 4.64 | 14.07 |
| Bioirrigation coefficient Dᵢ (cm² yr⁻¹) | 100 | 300 | 500 |
| Porosity                        | 0.85 | 0.85 | 0.85 |
| Dry sediment density (g cm⁻³)    | 2.65 | 2.65 | 2.65 |
| Solid phase manganese content S₀ (％ wt) | 0.165 | 0.349 | 0.260 |
| Measured maximum of dissolved Mn (μM) | 75 | 210 | 390 |
CONCLUSION

The success of the model in reproducing the field observations is a strong indication that the profiles of dissolved manganese in the sediments of the Laurentian Trough represent a dynamic balance between the rate of production and the rate of removal of dissolved manganese. Hence it is not necessary to invoke solubility control to explain the observations. The production rate of dissolved manganese within sediments depends on the rate at which bioturbation transports dissolvable manganese down into the reducing zone. The higher the rate of bioturbation, the higher the production rate of dissolved manganese. As a result, the balance is shifted toward higher concentrations of dissolved manganese.
ACKNOWLEDGMENTS

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, the Government of Quebec (FCAC funds), and the Université du Québec à Rimouski.

APPENDIX

Eqs (5) to (8) are all second order ordinary differential equations with constant coefficients. They are of one of two types:

\[ a \frac{d^2F}{dz^2} + b \frac{dF}{dz} + dF = 0 \quad (A1) \]

\[ p \frac{d^2G}{dz^2} + q \frac{dG}{dz} + rG = 0 \quad (A2) \]

The general solution of (A1) is

\[ F = \exp(\lambda z)[C_1 \exp(\delta z) + C_2 \exp(-\delta z)] \quad (A3) \]

where \( \lambda = -b/2a \), and \( \delta^2 = (b^2 - 4ad)/4a^2 \). \( C_1 \) and \( C_2 \) are arbitrary constants. The solution of (A2) will then be

\[ G = C_3 + C_4 \exp(-\gamma z) + [D_1 \exp(\delta z) + D_2 \exp(-\delta z)] \exp(\lambda z) \quad (A4) \]

where \( C_3 \) and \( C_4 \) are arbitrary constants, and \( \gamma = -q/p \). The constants \( D_1 \) and \( D_2 \) are given by

\[ D_1 = \frac{r \cdot C_1}{q(\lambda + \delta) - p(\lambda - \delta)^2} \quad D_2 = \frac{r \cdot C_2}{q(\lambda - \delta) - p(\lambda - \delta)^2} \]

Eq (10) is obtained by setting \( a \) to zero in (A1). Its solution is

\[ F = C_1 \exp(\alpha z) \quad (A5) \]

where \( \alpha = -d/b \). The corresponding solution for (A2) will be

\[ G = C_3 + C_4 \exp(2\lambda z) - D_1 \exp(\alpha z) \quad (A6) \]

where \( D_1 \) is now given by

\[ D_1 = \frac{-r \cdot C_4}{\alpha(p\alpha + q)} \]

The arbitrary constants are determined by the requirement that the concentrations and the fluxes must be continuous across the boundaries between layers. The matching conditions between layers \( i \) and \( i + 1 \) are

\[ P_i(L_i) = P_{i+1}(L_i) \quad (A7) \]

\[ S_i(L_i) = S_{i+1}(L_i) \quad (A8) \]

\[ w \cdot P_i(L_i) - D_{i+1} \cdot \frac{\partial P_i}{\partial z}(L_i) = w \cdot P_{i+1}(L_i) - D_{i+1} \cdot \frac{\partial P_{i+1}}{\partial z}(L_i) \quad (A9) \]

\[ w \cdot S_i(L_i) - D_{i+2} \cdot \frac{\partial S_i}{\partial z}(L_i) = w \cdot S_{i+1}(L_i) - D_{i+2} \cdot \frac{\partial S_{i+1}}{\partial z}(L_i) \quad (A10) \]
The general solutions (A3) to (A6) are then substituted into (5) to (10). The final solution is obtained by solving the system of twelve linear algebraic eqs (A7) to (A10) for the arbitrary constants. The manganese profiles in each layer will be:

A. **Oxidized zone** (0 ≤ z ≤ L1)

\[ P_1 = 0 \quad \text{and} \quad S_1 = S_0, \] the surface value

B. **Oxidizing zone** (L1 ≤ z ≤ L2)

\[ P_2 = A \cdot \exp(az) \cdot \sinh(bz), \]
\[ S_2 = F + (B/\alpha) \exp(az) + A \cdot [C \cdot \exp(bz) + D \cdot \exp(-bz)] \cdot \exp(az), \]

C. **Reducing zone with biodiffusion** (L2 ≤ z ≤ L3)

\[ P_3 = J + (1/\beta) \exp(\beta z) + [g \cdot G \cdot \exp(fz) + h \cdot H \cdot \exp(-fz)] \cdot \exp(\varepsilon z), \]
\[ S_3 = [G \cdot \exp(fz) + H \cdot \exp(-fz)] \cdot \exp(\varepsilon z), \]

D. **Reducing zone without biodiffusion** (L3 ≤ z < ∞)

\[ P_4 = Q - K \cdot \ell \cdot \exp(-mz), \]
\[ S_4 = K \cdot \exp(-mz), \]

where \( z_i = z - L_i \). The numerous (and messy) constants are, in alphabetical order,

\[ \alpha = w/D_{22}, \quad \beta = w/D_{31}, \quad \delta = (1 - \phi)/\phi, \]
\[ a = w/2D_{21}, \quad b^2 = \frac{[w^2 + 4D_{22} \cdot K(ox)]}{4 \cdot D_{21}^2}, \quad e = w/2D_{22}, \]
\[ f^2 = \frac{[w^2 + 4 \cdot D_{32} \cdot K(\text{red})]}{4 \cdot D_{32}^2}, \quad g = \frac{\delta \cdot K(\text{red})}{p(w - D_{31}p)}, \]
\[ h = \frac{\delta \cdot K(\text{red})}{q(w - D_{31}q)}, \quad \ell = \frac{\delta \cdot K(\text{red})}{m(w + D_{41}m)}, \]
\[ m = K(\text{red})/w, \quad p = e + f, \quad q = e - f, \quad s = a + b, \quad t = a - b, \]
\[ A = A_1 \cdot K, \]
\[ A_1 = 2 \cdot \frac{D_{31}}{D_{21}} \cdot \exp(-a \cdot L_{21}) \cdot \left[ \frac{[s \cdot \exp(b \cdot L_{21}) + t \cdot \exp(-b \cdot L_{21})]}{[s \cdot \exp(b \cdot L_{21}) + t \cdot \exp(-b \cdot L_{21})]} \right], \]
\[ B = -S_0 \cdot K2/(B1 \cdot K2 - B2 \cdot K1), \quad B1 = [\exp(\alpha \cdot L_{21}) - 1]/\alpha, \]
\[ B2 = D_{22} \cdot \exp(\alpha \cdot L_{21}), \quad C = \frac{\delta \cdot K(ox)}{2s(w - D_{22}s)}, \quad D = \frac{-\delta \cdot K(ox)}{2t(w - D_{22}t)}, \]
\[ E = S_0 \cdot (B/\alpha - A \cdot (C + D)), \quad G = G1 \cdot K, \]
\[ G1 = -(q/2f) \cdot \exp(-p \cdot L_{32}), \quad H = H1 \cdot K, \]
\[ H1 = (p/2f) \cdot \exp(-q \cdot L_{32}), \quad I = H1 \cdot K, \]
\[ J1 = A1 \cdot K0 \sinh(b \cdot L_{21}) - (11/\beta) - g \cdot G1 - h \cdot H1, \]
\[ J2 = g \cdot p \cdot G1 \cdot \exp(f \cdot L_{32}) + h \cdot q \cdot H1 \cdot \exp(-f \cdot L_{32}), \quad J = J1 \cdot K, \]
\[ K = S_0/(B1 \cdot K2 - B2 \cdot K1), \quad K0 = \exp(a \cdot L_{21}), \]
\[ K1 = -G1 - H1 - A1 \cdot [(C + D) - K4 \cdot K0], \]
\[ K2 = K3 + A1 \cdot D_{22} \cdot [C \cdot s \cdot \exp(b \cdot L_{21}) + d \cdot t \cdot \exp(-b \cdot L_{21})] \cdot K0 \]
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\[ K_3 = -(G_1 \cdot p + H_1 \cdot q) \cdot D_{D_2} \]
\[ K_4 = C \cdot \exp(b \cdot L_{21}) + D \cdot \exp(-b \cdot L_{21}) \]
\[ L_{21} = L_2 - L_1, \quad L_{32} = L_3 - L_2, \quad Q = Q_1 + Q_2 \cdot \exp(e \cdot L_{32}) \]
\[ Q_1 = K \cdot f + J + (1/\beta) \cdot \exp(\beta \cdot L_{32}) \]
\[ Q_2 = g \cdot G \cdot \exp(f \cdot L_{32}) + h \cdot H \cdot \exp(-f \cdot L_{32}) \]

REFERENCES