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To cite this version:

Brian D. Wood, Fabrice Golfier, Michel Quintard. Dispersive transport in porous media with biofilms: local mass equilibrium in simple unit cells. International Journal of Environment and Waste Management, 2011, 7 (1/2), pp.24-48. 10.1504/IJEWM.2011.037364 . hal-03469263

HAL Id: hal-03469263

https://hal.science/hal-03469263v1

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To link to this article : DOI:10.1504/IJEWM.2011.037364
URL : http://dx.doi.org/10.1504/IJEWM.2011.037364

To cite this version :
Wood, Brian D. and Golfier, Fabrice and Quintard, Michel *Dispersive transport in porous media with biofilms: local mass equilibrium in simple unit cells.* (2011) International Journal of Environment and Waste Management, vol. 7 (n° 1/2). pp. 24-48. ISSN 1478-9876

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Dispersive transport in porous media with biofilms: local mass equilibrium in simple unit cells

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Abstract: In this work, we continue our study of upscaling biofilm processes in porous media from the pore scale to the Darcy scale. We adopt a continuum-level description of biofilms at the pore scale on the basis of work reported in Wood et al. (2002b). We upscale from the pore scale to the Darcy scale using the method of volume averaging and we predict the effective dispersion tensor with two- and three-dimensional closure problems. Our results indicate that, for a one-equation local mass equilibrium theory, the primary influence of the biofilm is that the effective diffusion coefficient is smaller than it would be without the presence of biofilm. This effect is important primarily at low Péclet numbers.

Keywords: biofilm; dispersion; local mass equilibrium; averaging; homogenisation.

Reference to this paper should be made as follows: Wood, B.D., Golfier, F. and Quintard, M. (2011) 'Dispersive transport in porous media with biofilms: local mass equilibrium in simple unit cells', *Int. J. Environment and Waste Management*, Vol. 7, Nos. 1/2, pp.24–48.

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1 Introduction

The study of biofilms in porous media have had a long history from the environmental engineering perspective (Meunier and Williamson, 1981; Rittmann, 1980; Williamson and McCarty, 1976a, 1976b; Young and McCarty, 1969) and more recently have been of interest to the subsurface as part of various remediation schemes (de Blanc et al., 1996; Chen et al., 1992; Field et al., 1995; Scow and Hicks, 2005; Singh et al., 2006; White et al., 1998). This interest in microbially mediated reaction in the porous media has led to the development of a large number of mathematical models to describe the transport of biologically reactive dissolved solutes (Baveye and Valocchi, 1989; Moltz et al., 1986; Widdowson et al., 1988; Wood et al., 1994, 1995) a thorough review of mathematical representations of biofilms in porous media has been presented by de Blanc et al. (1996) and Murphy and Ginn (2000).

Most biofilm models have generally been developed by

- first identifying the important mass transport, mass transfer and reaction processes that may be involved for the system under consideration and then
- directly formulating a macroscale (Darcy scale) mathematical model by mass balancing the hypothesised processes.

Although this process does result in a macroscale transport equation for the processes hypothesised, it does not provide any direct link between the microscale structure and properties to the effective macroscale representation.

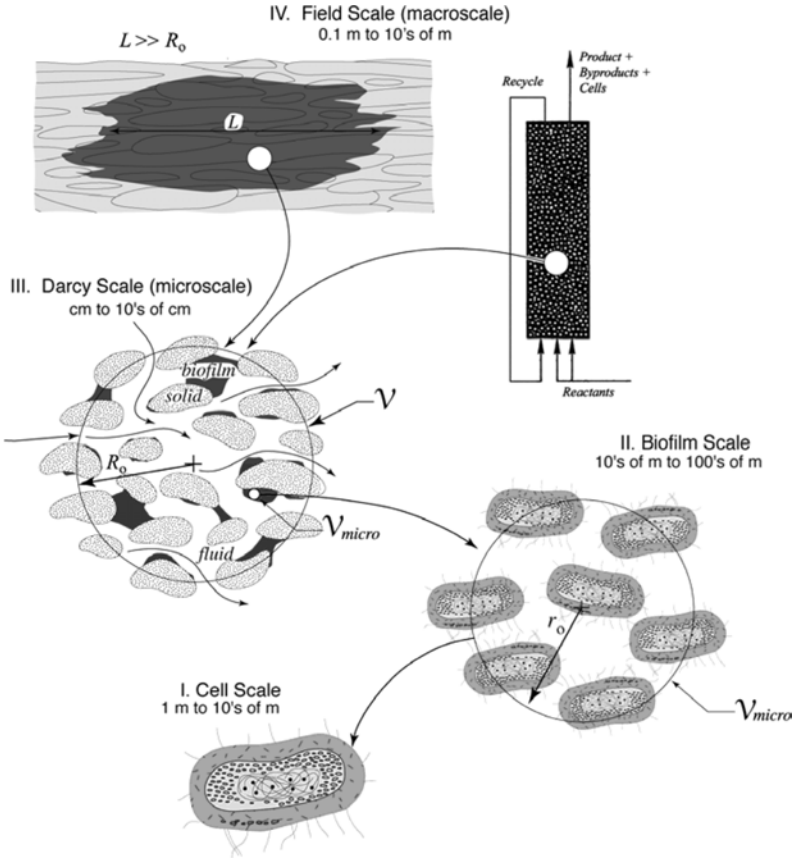
In recent past, several studies have conducted a more detailed analysis of biological processes in porous media where a pore-scale representation of mass transport has been upscaled to develop the macroscale transport representation (Dykaar and Kitanidis, 1996;

Lasseux et al., 2004; Wood and Whitaker, 1998; Aspa et al., 2011). In these studies, the detailed physical and biological processes that occur in porous media are explicitly accounted for in the models that are developed and efforts are made to relate the pore-scale physics to the conservation equations developed at the Darcy scale. In these studies the detailed physical and biological processes that occur in porous media are explicitly accounted for in the models that are developed and efforts are made to relate the pore-scale physics to the conservation equations developed at the Darcy scale.

For our starting point, we will examine the hierarchical porous medium illustrated in Figure 1. In this figure, a sequence of discrete length scales from the cell to the field are illustrated, indicating that the macroscale manifestation of mass transport at the largest scale (Level IV, the 'field' scale) is coupled to the processes at the smallest scales of interest (in this case, Level I, the 'cell' scale). In previous work, we have conducted upscaling from the cell scale to the biofilm (the volume v_{micro} in Figure 1 for the case of single or multiple substrate transport with a specific transport mechanism for chemical transport across the cell wall (Wood and Whitaker, 1998, 1999, 2000; Wood et al., 2002b)). In this work, we begin with a microscale description of the transport processes within the pore space of a porous medium (associated with a characteristic support volume $\mathcal{V}_{\mathrm{micro}}$) and homogenise this description to obtain a macroscale transport equation (associated with a characteristic support volume $\mathcal{V}$). We maintain a particular focus on examining how the presence of biofilms influences hydrodynamic dispersion under the conditions of local mass equilibrium. Homogenising for this work is conducted via the method of volume averaging (Whitaker, 1999) and we predict the effective longitudinal dispersion coefficient that arises from the homogenisation using a closure scheme in a simple unit cell. Our focus is on systems where the rate of reaction does not significantly affect the effective dispersive and convective fluxes and where there are assumed to be no significant deviations from local mass equilibrium between the bulk fluid and the biofilm phases. A few previous studies have considered the upscaling of chemical transport in porous media containing biofilms (Dykaar and Kitanidis, 1996; Lasseux et al., 2004; Wood et al., 2002a) and this paper is an extension of that work. We note here that the geometrical structure of biofilm itself is sometimes observed to be complex and in these instances it maybe useful to interject a level of upscaling between Levels II and III in Figure 1. This problem is discussed in significant detail in the paper by Aspa et al. (2011).

The paper is organised as follows. In Section 2, we establish the microscale equations that apply at the sub-pore scale within the fluid and biofilm phases, respectively. In Section 3, we define the upscaling operators and outline the homogenisation process. In Section 4, we consider the case of local mass equilibrium between the fluid and biofilm phases and we outline the constraints required, so that a one-equation, local mass equilibrium model is valid. In Section 5, we discuss the closure problem and how balance equations for concentration deviations can be developed to predict the effective hydrodynamic dispersion tensor for the one-equation, local mass equilibrium model. Finally, in Section 6, we present some numerical computations for the effective longitudinal dispersion coefficient and we provide some discussion and conclusions about these results.

Figure 1 A hierarchical structure for biofilms in multiscale porous media systems



2 Microscale equations

In this work, we treat the biofilm phase as a region that does not have significant convective fluxes; when significant convective fluxes are present within the biofilm itself, a convective term will appear for the ω-phase as described by Aspa et al. (2011). The mass balance equations are defined at the microscale and they apply everywhere within the macroscale volume $\mathcal{V}$ illustrated by Level IV in Figure 1. The governing conservation equations applying at the microscale (Figure 2) for a single limiting substrate, denoted as chemical species A, can be stated succinctly by Wood and Whitaker (1998) Wood et al. (2002a).

$$\frac{\partial c_{A\gamma}}{\partial t} + \mathbf{v}_\gamma \cdot \nabla c_{A\gamma} = \nabla \cdot (\mathcal{D}_{A\gamma} \nabla c_{A\gamma}), \quad \text{in the } \gamma\text{-phase} \tag{1}$$

$$B.C.1 \quad -\mathbf{n}_{\omega k} \cdot \mathbf{D}_{A\omega} \cdot \nabla c_{A\omega} = 0, \quad \text{at } A_{\omega\kappa} \tag{2}$$

$$B.C.2 \quad -\mathbf{n}_{\gamma k} \cdot \mathcal{D}_{A\gamma} \cdot \nabla c_{A\gamma} = 0, \quad \text{at } A_{\gamma\kappa} \tag{3}$$

$$B.C.\,3 \quad -\mathbf{n}_{\gamma\omega}\cdot\mathbf{D}_{A\omega}\cdot\nabla c_{A\omega} = -\mathbf{n}_{\gamma\omega}\cdot\mathcal{D}_{A\gamma}\nabla c_{A\gamma}, \quad \text{at } A_{\gamma\omega} \tag{4}$$

$$B.C.\,4 \quad c_{A\gamma} = c_{A\omega}, \quad \text{at } A_{\gamma\omega} \tag{5}$$

$$B.C.\,5 \quad c_{A\gamma} = \mathcal{F}_{\gamma}(t), \quad \text{at } A_{\gamma e} \tag{6}$$

$$B.C.\,6 \quad c_{A\omega} = \mathcal{F}_{\omega}(t), \quad \text{at } A_{\omega e} \tag{7}$$

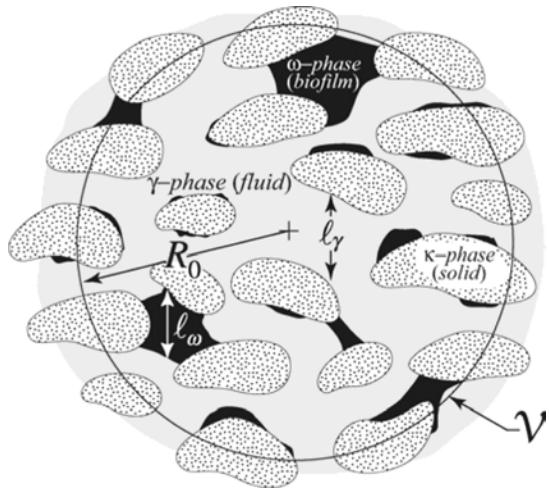
$$\frac{\partial c_{A\omega}}{\partial t} = \nabla\cdot(\mathbf{D}_{A\omega}\cdot\nabla c_{A\omega}) + R_{A\omega}, \quad \text{in the } \omega\text{-phase} \tag{8}$$

where

$$R_{A\omega} = -\rho_x \mu_{A,\text{eff}} \frac{c_{A\omega}}{c_{A\omega} + K_{A,\text{eff}}}. \tag{9}$$

The parameters appearing in these equations are defined as follows. The substrate concentrations in the fluid and biofilm phases are given by $c_{A\gamma}$ and $c_{A\omega}$, respectively. The pore-fluid velocity is represented by $\mathbf{v}_{\gamma}$. The diffusion coefficient in the fluid phase is given by $\mathcal{D}_{A\gamma}$, whereas in the biofilm phase diffusion is described by a tensor, $\mathbf{D}_{A\omega}$ The reaction rate in the biofilm phase is given by $R_{A\omega}$, and the reaction rate involves the microbial concentration (ρ_x), the effective specific growth rate ($\mu_{A,\text{eff}}$) and the effective half-saturation constant ($K_{A,\text{eff}}$). For the initial and boundary conditions, $A_{\gamma\omega}$ indicates the fluid-biofilm interface, $A_{\gamma e}$ indicates the interface of the fluid with the bounds of the macroscale volume, $\mathcal{V}$ and $A_{\omega e}$ indicates the interface of the biofilm and the bounds of the macroscale volume $\mathcal{V}$. The functions $\mathcal{F}_{\gamma}(t)$ and $\mathcal{F}_{\omega}(t)$ represent (generally unknown) Dirichlet boundary conditions that apply on $A_{\gamma e}$ and $A_{\omega e}$.

Figure 2 A representative region for the Darcy-scale volume $\mathcal{V}$. The fluid and biofilm phases are assumed each to be homogeneous and continuous at the microscale except at the phase boundaries



The evolution of the microbial biomass phase is given by a semi-empirical relationship of the form (Wood and Whitaker, 1999)

$$\frac{\partial \rho_x}{\partial t} = Y \rho_x \mu_{A,\text{eff}} \frac{c_{A\omega}}{c_{A\omega} + K_{A,\text{eff}}} - k_d \rho_x \tag{10}$$

where Y is the yield coefficient (mass of cells produced per unit mass of substrate consumed) and k_d is the first-order decay coefficient. In this expression, we have neglected biofilm sloughing and attachment (or detachment) of cells from the fluid phase; in a more general treatment, such processes may be important.

In many cases, the reaction rate term is given by a multiplicative Monod form that may depend on one or more chemical species

$$R_{A\omega} = -\rho_x \mu_{A,\text{ eff}} \frac{c_{A\omega}}{c_{A\omega} + K_{A,\text{eff}}} \frac{c_{B\omega}}{c_{B\omega} + K_{B,\text{eff}}} \ldots \tag{11}$$

and this creates a need for a transport equation for each chemical species involved (e.g., Wood and Whitaker (2000)). For the purposes of this work, we will focus on a single limiting substrate. The transport equations for additional species involved, if necessary, can be developed along similar lines. Note that in these instances, the Monod form can often be linearised (Wood and Whitaker, 1998, 2000) and the linearised form is suitable under many conditions (Wood et al., 2007).

3 Developing the averaged equations

To develop the *macroscale* equation for mass transport in the biofilm-porous medium system, the *microscale* equations given by equations (1), (8) and (10) are averaged over a representative volume, $\mathcal{V}$ (Figure 2). This averaging requires the use of the following operators for defining the *superficial* average (where v is the averaging volume, V_γ is the fluid phase volume and V_ω is the biofilm volume).

$$\langle c_{A\gamma} \rangle = \frac{1}{\mathcal{V}} \int_{V_\gamma} c_{A\gamma} \mathrm{d}V, \quad \langle c_{A\omega} \rangle = \frac{1}{\mathcal{V}} \int_{V_\omega} c_{A\omega} \mathrm{d}V. \tag{12}$$

Similar operators can be established for the *intrinsic* averages by defining the volume fractions of the fluid and biofilm phases

$$\langle c_{A\gamma} \rangle^\gamma = \frac{1}{V_\gamma} \int_{V_\gamma} c_{A\gamma} \mathrm{d}V, \quad \langle c_{A\omega} \rangle^\omega = \frac{1}{V_\omega} \int_{V_\omega} c_{A\omega} \mathrm{d}V \tag{13}$$

where the volumes V_γ and V_ω are related to the volume $\mathcal{V}$ by

$$\varepsilon_\gamma = \frac{V_\gamma}{\mathcal{V}}, \quad \varepsilon_\omega = \frac{V_\omega}{\mathcal{V}} \tag{14}$$

hence

$$\left\langle c_{A\gamma}\right\rangle = \varepsilon_\gamma \left\langle c_{A\gamma}\right\rangle^\gamma , \quad \left\langle c_{A\omega}\right\rangle = \varepsilon_\omega \left\langle c_{A\omega}\right\rangle^\omega . \tag{15}$$

In addition, one needs the following two theorems to interchange the averaging and spatial differentiation operators

$$\left\langle \nabla c_{A\omega}\right\rangle = \nabla \left\langle c_{A\omega}\right\rangle + \frac{1}{\mathcal{V}} \int_{A_{\omega\gamma}} \mathbf{n}_{\omega\gamma} c_{A\omega} \, \mathrm{d}A + \frac{1}{\mathcal{V}} \int_{A_{\omega\kappa}} \mathbf{n}_{\omega\kappa} c_{A\omega} \, \mathrm{d}A \tag{16}$$

$$\left\langle \nabla c_{A\gamma}\right\rangle = \nabla \left\langle c_{A\gamma}\right\rangle + \frac{1}{\mathcal{V}} \int_{A_{\gamma\omega}} \mathbf{n}_{\gamma\omega} c_{A\gamma} \, \mathrm{d}A + \frac{1}{\mathcal{V}} \int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} c_{A\gamma} \, \mathrm{d}A. \tag{17}$$

These two theorems are analogous to a three-dimensional Leibnitz rule for integration (Anderson and Jackson, 1967; Gray et al., 1993; Howes and Whitaker, 1985; Slattery, 1967; Whitaker, 1967).

Finally, we will find it useful to define the *deviation concentration* as the difference between the microscale and average concentrations

$$\tilde{c}_{A\gamma} = \left\langle c_{A\gamma}\right\rangle^\gamma - c_{A\omega}, \quad \tilde{c}_{A\omega} = \left\langle c_{A\omega}\right\rangle^\omega - c_{A\omega} \tag{18}$$

and similar definitions hold for the velocity and the biofilm cell density

$$\tilde{\mathbf{v}}_\gamma = \left\langle \mathbf{v}_\gamma\right\rangle^\gamma - \mathbf{v}_\gamma \tag{19}$$

$$\tilde{\rho}_x = \left\langle \rho_x\right\rangle^\omega - \rho_x . \tag{20}$$

With these definitions, the average of equations (1), (8) and (10) is reasonably straightforward, although the development is algebraically somewhat tedious. We will not present the entire development here; details of this kind of development are available in a large number of previously published works (e.g., Whitaker, 1999; Wood and Whitaker, 1998, 2000). Forming the average of the two transport equations given by equations (1), (8) and (10), the (unclosed) macroscale equations are found to be

Unclosed macroscale species A transport equation, γ-phase (fluid)

$$\begin{aligned}
&\underbrace{\frac{\partial\left(\varepsilon_\gamma \left\langle c_{A\gamma}\right\rangle^\gamma\right)}{\partial t}}_{\text{Accumulation}} + \underbrace{\nabla\cdot\left(\varepsilon_\gamma \left\langle \mathbf{v}_\gamma\right\rangle^\gamma \left\langle c_{A\gamma}\right\rangle^\gamma\right)}_{\text{Convection}} \\
&= \underbrace{\nabla\cdot\left[\varepsilon_\gamma \mathcal{D}_{A\gamma}\left(\nabla\left\langle c_{A\gamma}\right\rangle^\gamma + \frac{1}{V_\gamma}\int_{A_{\gamma\omega(t)}} \mathbf{n}_{\gamma\omega}\tilde{c}_{A\gamma}\,\mathrm{d}A + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa(t)}} \mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,\mathrm{d}A\right)\right]}_{\text{Diffusion}} \\
&\quad + \underbrace{\frac{1}{\mathcal{V}}\int_{A_{\omega\gamma}(t)} \mathbf{n}_{\gamma\omega}\cdot(\mathcal{D}_{A\gamma}\nabla c_{A\gamma})\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\omega\kappa(t)}} \mathbf{n}_{\gamma\kappa}\cdot(\mathcal{D}_{A\gamma}\nabla c_{A\gamma})\,\mathrm{d}A}_{\text{Interfacial flux}} - \underbrace{\nabla\cdot\left\langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma}\right\rangle}_{\substack{\text{Dispersive}\\ \text{Transport}}}.
\end{aligned} \tag{21}$$

Unclosed macroscale species A transport equation, ω-phase (biofilm)

$$\underbrace{\frac{\partial\left(\varepsilon_\omega \left\langle c_{A\omega}\right\rangle^\omega\right)}{\partial t}}_{\text{Accumulation}} = \underbrace{\nabla\cdot\left[\varepsilon_\omega \mathbf{D}_{A\omega}\cdot\left(\nabla\left\langle c_{A\omega}\right\rangle^\omega + \frac{1}{V_\omega}\int_{A_{\omega\gamma}(t)}\mathbf{n}_{\omega\gamma}\tilde{c}_{A\omega}\,\mathrm{d}A + \frac{1}{V_\omega}\int_{A_{\omega\kappa}(t)}\mathbf{n}_{\omega\kappa}\tilde{c}_{A\omega}\,\mathrm{d}A\right)\right]}_{\text{Diffusion}}$$
$$\underbrace{+\frac{1}{\mathcal{V}}\int_{A_{\omega\gamma}(t)}\mathbf{n}_{\omega\gamma}\cdot(\mathbf{D}_{A\omega}\cdot\nabla c_{A\omega})\,\mathrm{d}A + \frac{1}{\mathcal{V}}\int_{A_{\omega\kappa}(t)}\mathbf{n}_{\omega k}\cdot(\mathbf{D}_{A\omega}\cdot\nabla c_{A\omega})\,\mathrm{d}A}_{\text{Interfacial Flux}}$$
$$\underbrace{-\varepsilon_\omega\left\langle\rho_x\right\rangle^\omega \mu_{A,\mathrm{eff}}\frac{\left\langle c_{A\omega}\right\rangle^\omega}{\left\langle c_{A\omega}\right\rangle^\omega + K_{A,\mathrm{eff}}}}_{\text{Reaction}}. \tag{22}$$

Unclosed macroscale equation for biofilm growth, ω-phase

$$\underbrace{\frac{\partial\left(\varepsilon_\omega\left\langle\rho_x\right\rangle^\omega\right)}{\partial t}}_{\text{Accumulation}} = \underbrace{\varepsilon_\omega Y\left\langle\rho_x\right\rangle^\omega \mu_{A,\mathrm{eff}}\frac{\left\langle c_{A\omega}\right\rangle^\omega}{\left\langle c_{A\omega}\right\rangle^\omega + K_{A,\mathrm{eff}}}}_{\text{Biofilm Growth}} - \underbrace{k_d\varepsilon_\omega\left\langle\rho_x\right\rangle^\omega}_{\text{Decay}}. \tag{23}$$

The development of equations (21)–(23) have required several assumptions to obtain the forms listed. To be explicit, the assumptions that we have made to this point are as follows.

- Convection of species *A* due to the growth of the biofilm phase (and associated movement of the fluid–biofilm interface) can be neglected relative to the rate of diffusive transport in the fluid and biofilm phases.
- The time rates of change of the averaged concentration fields $\left\langle c_{A\gamma}\right\rangle^\gamma$ and $\left\langle c_{A\omega}\right\rangle^\omega$ are large compared with the time rate of change of the biofilm volume fraction ε_ω.
- The intrinsic averages $\left\langle c_{A\gamma}\right\rangle^\gamma$ and $\left\langle c_{A\omega}\right\rangle^\omega$ can be removed from area integrals. This requires a condition of separation of length scales, usually expressed by ℓ_γ, $\ell_\omega \ll R_0 \ll L$ (Chapter 1.3, Whitaker, 1999).
- For the biomass growth rate, the term $\left\langle\tilde{\rho}_x\tilde{c}_{A\omega}\right\rangle$ can be neglected relative to the term $\left\langle\rho_x\right\rangle^\omega\left\langle c_{A\omega}\right\rangle^\omega$.
- Finally, for the linearisation of the reaction term, it is sufficient to specify that, within an averaging volume, the standard deviation of the concentration field is sufficiently small relative to the average concentration (Wood, 2007). This is usually expressed by imposing the constraint that the concentration deviations are suitably small (Appendix A, Wood and Whitaker, 1998), i.e., $\tilde{c}_{A\gamma} \ll \left\langle c_{A\gamma}\right\rangle^\gamma$, $\tilde{c}_{A\omega} \ll \left\langle c_{A\omega}\right\rangle^\omega$.

In the next section, we will briefly describe one additional assumption regarding the state of interphase mass transfer and this assumption will allow us to develop a one-equation model for the macroscale transport equation. One-equation models are often used in

applications; however, in many cases the systems are poised such that it may be necessary to consider disequilibrium between the fluid and the biofilm phases. In this work, we consider only the case where local mass equilibrium applies and a one-equation model can be developed.

4 Local mass equilibrium

In the most general form, there should be two separate mass transport equations for the problem of biofilms in porous media. Such a model is similar to the mobile–immobile models that have been prevalent in the literature (e.g., Coats and Smith, 1964; van Genuchten and Wierenga, 1976). One of these two macroscale equations would describe the mass transport in the fluid phase and the other equation would describe mass transport in the biofilm phase. Equations (21) and (22) each include an *interfacial flux* term that represents the macroscale mass interchange between the fluid and the biofilm. In the development of a two-region model for this system, the two macroscale equations would be coupled at the biofilm–fluid interface by these interfacial flux terms.

In some systems of practical interest, the characteristic time for transport in the biofilm phase can be considered to be of the same order of magnitude as the characteristic time for transport within the fluid phase. An example of such a situation might be the case of thin biofilms in groundwater transport under natural gradient conditions. Under such circumstances, one might expect that there exists local mass equilibrium between the fluid and biofilm phases. In this case, the two macroscale concentrations would be related by an equilibrium expression of the form

$$\left\langle c_{A\gamma}\right\rangle^{\gamma} = \left\langle c_{A\omega}\right\rangle^{\omega}, \quad \text{at thermodynamic equilibrium.} \tag{24}$$

When local equilibrium is valid, one of the two transport equations given by equations (21) and (22) becomes essentially redundant, because the second macroscale concentration is instead specified by the relation given by equation (24). A one-equation model for the transport of chemical species *A* applies under these conditions.

The constraints that are required to be met such that equation (24) is valid are possible to derive, but the development is complex. Here, we will establish the essential features of the derivation, but the essential details are presented in the Appendix. To begin, we define the following *spatial average* concentration

$$(\varepsilon_{\gamma} + \varepsilon_{\omega})\left\langle c_{A}\right\rangle = \varepsilon_{\gamma}\left\langle c_{A\gamma}\right\rangle^{\gamma} + \varepsilon_{\omega}\left\langle c_{A\omega}\right\rangle^{\omega}. \tag{25}$$

Note that at equilibrium, we now have the relationship among concentrations

$$\left\langle c_{A}\right\rangle = \left\langle c_{A\gamma}\right\rangle^{\gamma} = \left\langle c_{A\omega}\right\rangle^{\omega}, \quad \text{at thermodynamic equilibrium.} \tag{26}$$

When equilibrium conditions *do not* apply, we expect some differences between the three macroscale concentrations. Note that by adding the quantities $\varepsilon_{\omega}\left\langle c_{A\gamma}\right\rangle^{\gamma}$ and $\varepsilon_{\gamma}\left\langle c_{A\omega}\right\rangle^{\omega}$, respectively, to equation (25), we can define these differences by

$$\left\langle c_{A\gamma}\right\rangle^{\gamma} = \left\langle c_{A}\right\rangle + \frac{\varepsilon_{\omega}}{\varepsilon_{\gamma} + \varepsilon_{\omega}}\left(\left\langle c_{A\gamma}\right\rangle^{\gamma} - \left\langle c_{A\omega}\right\rangle^{\omega}\right) \tag{27}$$

$$\langle c_{A\omega}\rangle^{\omega} = \langle c_A\rangle - \frac{\varepsilon_\gamma}{\varepsilon_\gamma+\varepsilon_\omega}\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right). \tag{28}$$

To assess the case of local mass equilibrium, we first start by developing an expression for the spatial average concentration, $\langle c_A\rangle$, that applies even when local mass equilibrium is not valid. The most efficient way to do this is to add the two averaged equations given by equations (21) and (22) together and then use equations (27) and (28) to put the expression in terms of $\langle c_A\rangle$. This result is

Macroscale equation, spatial average concentration form

$$\begin{aligned}(\varepsilon_\gamma+\varepsilon_\omega)\frac{\partial\langle c_A\rangle}{\partial t} &+ \nabla\cdot\left(\varepsilon_\gamma\langle \mathbf{v}_\gamma\rangle^{\gamma}\langle c_A\rangle\right)\\ &= \nabla\cdot\left(\mathbf{D}'_A\cdot\nabla\langle c_A\rangle\right) - \varepsilon_\omega\langle\rho_x\rangle^{\omega}\frac{\mu_{A,eff}\langle c_A\rangle}{\langle c_A\rangle + K_{A,\mathrm{eff}}} + \Omega\end{aligned} \tag{29}$$

where

$$\begin{aligned}\mathbf{D}'_A\cdot\nabla\langle c_A\rangle &= (\varepsilon_\gamma\mathcal{D}_{A\gamma}\mathbf{I} + \varepsilon_\omega\mathbf{D}_{A\omega})\cdot\nabla\langle c_A\rangle\\ &+\left[\varepsilon_\omega\mathbf{D}_{A\omega}\cdot\left(\frac{1}{V_\omega}\int_{A_{\omega\gamma(t)}}\mathbf{n}_{\omega\gamma}\tilde{c}_{A\omega}\,\mathrm{d}A + \frac{1}{V_\omega}\int_{A_{\omega\kappa(t)}}\mathbf{n}_{\omega\kappa}\tilde{c}_{A\omega}\,\mathrm{d}A\right)\right]\\ &+\left[\varepsilon_\gamma\mathcal{D}_{A\gamma}\left(\frac{1}{V_\gamma}\int_{A_{\gamma\omega(t)}}\mathbf{n}_{\gamma\omega}\tilde{c}_{A\gamma}\,\mathrm{d}A + \frac{1}{V_\gamma}\int_{A_{\gamma\kappa(t)}}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\,\mathrm{d}A\right)\right]\\ &-\left\langle\tilde{\mathbf{v}}_\gamma\tilde{c}_{A\gamma}\right\rangle\end{aligned} \tag{30}$$

and Ω represents the terms of the equation that involve the difference in the two phase concentrations as follows.

$$\begin{aligned}\Omega = \nabla\cdot&\left(\frac{\varepsilon_\gamma\varepsilon_\omega}{\varepsilon_\gamma+\varepsilon_\omega}\langle\mathbf{v}_\gamma\rangle^{\gamma}\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right)\right)\\ &+\nabla\cdot\left[\frac{\varepsilon_\gamma\varepsilon_\omega}{\varepsilon_\gamma+\varepsilon_\omega}(\mathcal{D}_{A\gamma}\mathbf{I} - \mathbf{D}_{A\omega})\cdot\nabla\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right)\right]\\ &+\left(\frac{\varepsilon_\gamma\varepsilon_\omega}{\varepsilon_\gamma+\varepsilon_\omega}\right)\mu_{A,\mathrm{eff}}\langle\rho_x\rangle^{\omega}\frac{\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right)}{\langle c_A\rangle + K_{A,\mathrm{eff}} - \left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right)}\left(\frac{K_{A,\mathrm{eff}}}{\langle c_A\rangle + K_{A,\mathrm{eff}}}\right).\end{aligned} \tag{31}$$

When local mass equilibrium applies, we have the condition $\langle c_A\rangle = \langle c_{A\gamma}\rangle^{\gamma} = \langle c_{A\omega}\rangle^{\omega}$, and Ω is identically zero. It is possible to make a careful analysis of the conditions for which Ω can be neglected relative to other terms in the macroscale equation (Lasseux et al., 2004; Wood and Whitaker, 1998), but such analyses are lengthy and usually quite complex. We provide a rough outline for developing an estimate of the quantity $\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right)$ in the Appendix. There, we establish the result

$$\left(\left\langle c_{A\gamma}\right\rangle^{\gamma}-\left\langle c_{A\omega}\right\rangle^{\omega}\right)=\mathbf{O}\left(\frac{\mathsf{D}'_{A}}{\mathcal{D}_{A\gamma}}\frac{\ell_{\gamma\omega}^{2}}{L^{2}}\Delta\left\langle c_{A}\right\rangle\right). \tag{32}$$

This estimate allows the comparison of each of the terms comprising Ω with the macroscale dispersion term. To begin, we make the order-of-magnitude estimate

$$\nabla\cdot\mathbf{D}'_{A}\cdot\nabla\left\langle c_{A}\right\rangle=\mathbf{O}\left(\frac{\mathsf{D}'_{A}\Delta\left\langle c_{A}\right\rangle}{L^{2}}\right) \tag{33}$$

where

$$\mathsf{D}'_{A}=\sqrt{\frac{1}{2}\mathbf{D}'_{A}:\mathbf{D}'_{A}}. \tag{34}$$

Similar kinds of order-of-magnitude estimates can be produced for each term comprising Ω. With these estimates, we can develop unitless constraints indicating conditions when Ω can be requiring that each term in Ω be substantially smaller than the term $\nabla\cdot\mathbf{D}'_{A}\cdot\nabla\left\langle c_{A}\right\rangle$. Upon making these comparisons, we find restrictions take the form

$$\left(\frac{\varepsilon_{\gamma}\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\right)\frac{(\mathcal{D}_{A\gamma}-\mathsf{D}_{A\omega})}{\mathsf{D}'_{A}}\left(\frac{\ell_{\gamma\omega}}{L}\right)^{2}\ll 1 \tag{35}$$

$$\left(\frac{\varepsilon_{\gamma}\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\right)\mathrm{Da}\ll 1 \tag{36}$$

$$\left(\frac{\varepsilon_{\gamma}\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\right)\left(\frac{\ell_{\gamma\omega}}{L}\right)\mathrm{Pe}\ll 1 \tag{37}$$

where $v_{\gamma}=\sqrt{\left\langle\mathbf{v}_{\gamma}\right\rangle^{\gamma}\cdot\left\langle\mathbf{v}_{\gamma}\right\rangle^{\gamma}}$, and $\mathsf{D}_{A\omega}$ is defined analogously to equation (34). In these expressions, we have identified the Péclet and Damköhler numbers by

$$\mathrm{Pe}=\frac{v_{\gamma}\ell_{\gamma\omega}}{\mathcal{D}_{A\gamma}} \tag{38}$$

$$\mathrm{Da}=\frac{\mu_{\mathrm{eff}}\left\langle\rho_{x}\right\rangle^{\omega}\ell_{\gamma\omega}^{2}}{K_{A,\mathrm{eff}}\mathcal{D}_{A\gamma}}. \tag{39}$$

When these constraints are met, then the assumption of local mass equilibrium is valid. We can choose the fluid-phase concentration, $\left\langle c_{A\gamma}\right\rangle^{\gamma}$, to be the macroscale concentration of choice (since all three concentrations defined are then equal) and we can express the one-equation model for the transport equation in the form

Macroscale equation, local mass equilibrium form

$$(\varepsilon_\gamma + \varepsilon_\omega)\frac{\partial (c_{A\gamma})^\gamma}{\partial t} + \nabla \cdot \left(\varepsilon_\gamma \left\langle \mathbf{v}_\gamma \right\rangle^\gamma \left\langle c_{A\gamma} \right\rangle^\gamma\right) = \nabla \cdot \left(\mathbf{D}'_A \cdot \nabla \left\langle c_{A\gamma} \right\rangle^\gamma\right)$$
$$- \varepsilon_\omega \left\langle \rho_x \right\rangle^\omega \frac{\mu_{\mathrm{A,eff}} \left\langle c_{A\gamma} \right\rangle^\gamma}{\left\langle c_{A\gamma} \right\rangle^\gamma + K_{\mathrm{A,eff}}}. \tag{40}$$

Here, the effective dispersion tensor is given by

$$\mathbf{D}'_A \cdot \nabla \left\langle c_{A\gamma} \right\rangle^\gamma = (\varepsilon_\gamma \mathcal{D}_{A\gamma} \mathbf{I} + \varepsilon_\omega \mathbf{D}_{A\omega}) \cdot \nabla \left\langle c_{A\gamma} \right\rangle^\gamma$$
$$+ \left[\varepsilon_\omega \mathbf{D}_{A\omega} \cdot \left(\frac{1}{V_\omega}\int_{A_{\omega\gamma(t)}} \mathbf{n}_{\omega\gamma} \tilde{c}_{A\omega}\, \mathrm{d}A + \frac{1}{V_\omega}\int_{A_{\omega\kappa(t)}} \mathbf{n}_{\omega\kappa} \tilde{c}_{A\omega}\, \mathrm{d}A\right)\right]$$
$$+ \left[\varepsilon_\gamma \mathcal{D}_{A\gamma} \left(\frac{1}{V_\gamma}\int_{A_{\omega\gamma(t)}} \mathbf{n}_{\gamma\omega} \tilde{c}_{A\gamma}\, \mathrm{d}A + \frac{1}{V_\gamma}\int_{A_{\omega\kappa(t)}} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma}\, \mathrm{d}A\right)\right] - \left\langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \right\rangle. \tag{41}$$

The challenge at this point is to prove that equation (41) can be *closed* by eliminating the two deviation concentrations $\tilde{c}_{A\gamma}$ and $\tilde{c}_{A\omega}$. This problem is discussed in the next section.

5 Closure

Closure problems are ancillary conservation equations that serve to describe how the microscopic and macroscopic of a multiphase system are related; this is done by providing balance equations that predict the deviation quantities $\tilde{c}_{A\gamma}$ and $\tilde{c}_{A\omega}$. Generally, these ancillary problems are solved over a *representative* unit cell. The term 'representative' is meant to apply in a mathematically *weak* sense; the intent is that the macroscopic parameters (such as the effective dispersion tensor) do not depend on the pointwise values of the deviation concentration fields, but, rather, on area or volume integrals of these fields. Beyond this, however, it is difficult to generate a unique and precise definition for the term representative. In a loose sense, the term indicates a form of spatial stationarity for the deviation concentration fields. In other words, as long as the effective parameter does not depend strongly upon the microscale spatial structure of the porous medium, then there exists the possibility that a representative region exists. Ultimately, however, this dependence has only be examined heuristically.

As an example, an early and very successful model for diffusion in an isotropic porous medium was developed by Rayleigh (1892) using a periodic array of spheres embedded in cubes as the model for the porous medium. This model provides excellent agreement between the theory and the values of the effective diffusion tensor measured experimentally (Quintard, 1993; Whitaker, 1999). The use of the same model for predicting the effective *dispersion* tensor in a porous medium with flow still provides a reasonable agreement with the available experimental data, the results predicted by the theory do underestimate the magnitude of the dispersion tensor, particularly at high

values of the Péclet number (Wood, 2007). Apparently, there is something important about the correlation structure of particles in randomly packed porous medium that leads to features that are not captured by simpler models constructed of a periodic array of spheres.

5.1 Deviation equations

The essential purpose of the closure problem is to eliminate the deviation quantities $\tilde{c}_{A\gamma}$ and $\tilde{c}_{A\omega}$ that appear in the macroscale effective dispersion tensor (equation (41)). The definition of the deviations themselves provides a suggestion for how to develop a balance equation. The deviations can be rewritten in the form

$$\tilde{c}_{A\gamma} = c_{A\gamma} - \left\langle c_{A\gamma} \right\rangle^{\gamma} \tag{42}$$

$$\tilde{c}_{A\omega} = c_{A\omega} - \left\langle c_{A\omega} \right\rangle^{\omega} \tag{43}$$

and this suggests that subtracting the averaged equation from the microscale equation will generate a balance equation for the deviation. For development of the closure problem, we will assume that variations of the volume fractions ε_γ and ε_ω can be neglected. Subtracting the macroscale (volume averaged) equations (21) and (22) from the microscale equations (1) and (8) yields

Closure problem

$$\begin{aligned}\frac{\partial \tilde{c}_{A\gamma}}{\partial t} + \tilde{\mathbf{v}}_\gamma \cdot \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma} + \mathbf{v}_\gamma \cdot \nabla \tilde{c}_{A\gamma} &= \nabla \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) + \varepsilon_\gamma^{-1} \nabla \cdot \left\langle \tilde{\mathbf{v}}_\gamma \tilde{c}_{A\gamma} \right\rangle \\ &\quad - \nabla \cdot \left[\mathcal{D}_{A\gamma} \left(\frac{1}{V_\gamma} \int_{A_{\gamma\omega}(t)} \mathbf{n}_{\gamma\omega} \tilde{c}_{A\gamma} \, \mathrm{d}A + \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}(t)} \mathbf{n}_{\gamma\kappa} \tilde{c}_{A\gamma} \, \mathrm{d}A \right) \right] \\ &\quad - \frac{1}{V_\gamma} \int_{A_{\gamma\omega}(t)} \mathbf{n}_{\gamma\omega} \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) \, \mathrm{d}A - \frac{1}{V_\gamma} \int_{A_{\gamma\kappa}(t)} \mathbf{n}_{\gamma\kappa} \cdot (\mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma}) \, \mathrm{d}A\end{aligned} \tag{44}$$

$$B.C.\ 1 \quad -\mathbf{n}_{\omega\kappa} \cdot \mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega} = \underbrace{\mathbf{n}_{\omega\kappa} \cdot \mathbf{D}_{A\omega} \cdot \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma}}_{\text{dispersive source}}, \quad \text{at } A_{\omega\kappa} \tag{45}$$

$$B.C.\ 2 \quad -\mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{A\gamma} \cdot \nabla \tilde{c}_{A\gamma} = \underbrace{\mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{A\gamma} \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma}}_{\text{dispersive source}}, \quad \text{at } A_{\gamma\kappa} \tag{46}$$

$$B.C.\ 3 \quad \mathbf{n}_{\gamma\omega} \cdot \mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega} = \mathbf{n}_{\gamma\omega} \cdot \mathcal{D}_{A\gamma} \nabla \tilde{c}_{A\gamma} + \underbrace{\mathbf{n}_{\gamma\omega} \cdot (\mathcal{D}_{A\gamma} \mathbf{I} - \mathbf{D}_{A\omega}) \cdot \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma}}_{\text{dispersive source}}, \quad \text{at } A_{\gamma\omega} \tag{47}$$

$$B.C.\ 4 \quad \tilde{c}_{A\gamma} = \tilde{c}_{A\omega}, \quad \text{at } A_{\gamma\omega} \tag{48}$$

$$B.C.\ 5 \quad \tilde{c}_{A\gamma} = \tilde{\mathcal{F}}_\gamma(t), \quad \text{at } A_{\gamma e} \tag{49}$$

$$B.C.\ 6 \quad \tilde{c}_{A\omega} = \tilde{\mathcal{F}}_\omega(t), \quad \text{at } A_{\omega e} \tag{50}$$

$$\frac{\partial \tilde{c}_{A\omega}}{\partial t} = \nabla \cdot (\mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega})$$

$$-\nabla \left[\mathbf{D}_{A\omega} \cdot \left(\frac{1}{V_\omega} \int_{A_{\omega\gamma}(t)} \mathbf{n}_{\omega\gamma} \tilde{c}_{A\omega} \, \mathrm{d}A + \frac{1}{V_\omega} \int_{A_{\omega\kappa}(t)} \mathbf{n}_{\omega\kappa} \tilde{c}_{A\omega} \, \mathrm{d}A \right) \right]$$

$$-\frac{1}{V_\omega} \int_{A_{\omega\gamma}(t)} \mathbf{n}_{\omega\gamma} \cdot (\mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega}) \, \mathrm{d}A - \frac{1}{V_\omega} \int_{A_{\omega\kappa}(t)} \mathbf{n}_{\omega\kappa} \cdot (\mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega}) \, \mathrm{d}A. \tag{51}$$

Here, we have used the definition of the concentration deviations to derive the boundary conditions. In boundary condition 3 (equation (47)), we have used the concept of local mass equilibrium to derive this expression. Finally, note that we have implicitly dropped the reaction term relative to the remaining terms in the deviation equation. As mentioned in the introduction, we are interested in cases where the reaction rate does not influence the effective dispersion tensor. This requires that

$$R_A - \varepsilon_\omega^{-1} \langle R_A \rangle \ll \nabla \cdot (\mathbf{D}_{A\omega} \cdot \nabla \tilde{c}_{A\omega}) \tag{52}$$

and it has been shown by Wood and Whitaker (1998) that this restriction is met when

$$\frac{\ell_\omega^2 \mu_{\mathrm{eff}} \langle \rho_x \rangle^\omega}{\mathbf{D}_{A\omega} K_{A,\mathrm{eff}}} \ll 1. \tag{53}$$

We will assume that this constraint, which takes the form of a microscale Damkhöler number, is met for the remainder of the development of the closure problem.

Although in many instances, the full transient evolution of the effective parameters is of interest [e.g., in groundwater dispersion, cf. Wood et al. (2003a)], this is primarily dependent on the relative time scales involved at the microscale and macroscale. Under the conditions already imposed for local mass equilibrium to be valid, it is reasonable to assume a separation of time scales

$$t^* \ll T^* \tag{54}$$

and this separation of time scales is conventionally known as *quasi-steady* conditions. Noting the Péclet number restriction that we have already imposed in equation (37), it is easy to develop an estimate for the macroscale time scale of the form

$$T^* = \frac{L^2}{\mathbf{D}'_A}. \tag{55}$$

Similarly, we have for the microscale

$$t^* = \frac{\ell_\gamma^2}{\mathcal{D}_{A\gamma}}, \quad t^* = \frac{\ell_\omega^2}{\mathbf{D}_{A\omega}}. \tag{56}$$

Combining these last three equations, yields

$$\frac{\ell_\gamma^2}{L^2} \ll \frac{\mathcal{D}_{A\gamma}}{\mathbf{D}'_A}, \quad \frac{\ell_\omega^2}{L^2} \ll \frac{\mathcal{D}_{A\omega}}{\mathbf{D}'_A}. \tag{57}$$

In light of the macroscale constraint imposed previously by equation (35), under the conditions of local mass equilibrium the microscale constraint requires only the separation of length-scales, ℓ_γ, $\ell_\omega << L$ imposed in Section 4. We will assume from hereon that this constraint is met and that the closure problem can be treated as quasi-steady.

5.2 Closure variables

The closure problem is linear and its solution to the closure problem can be solved in principle by developing the Greens function solution kernel for the set of differential equations given by equations (44)–(51). In general, this results in a *nonlocal* solution that depends on spatial convolutions of the dependent variables. Such solutions have been investigated in the context of volume averaging and they can be useful when, for example, strong heterogeneity exists or the fully transient closure is desired (Chastanet and Wood, 2008; Golfier et al., 2007; Wood, 2007). For the quasi-steady problem under the length-scale constraints that have been imposed already, it is not difficult to show that the solution to the closure problem must take the following form (cf. Wood, 2007)

$$\tilde{c}_{A\gamma} = \mathbf{b}_{A\gamma} \cdot \nabla \left\langle c_{A\gamma} \right\rangle^{\gamma} \tag{58}$$

$$\tilde{c}_{A\omega} = \mathbf{b}_{A\omega} \cdot \nabla \left\langle c_{A\omega} \right\rangle^{\omega} \tag{59}$$

where $\mathbf{b}_{A\gamma}$ and $\mathbf{b}_{\Lambda\omega}$ represent integrals of the kernel functions that define the solution. Note that this shows only the solution *form*, but does not provide the solution itself. In general, a closed-form analytic solution to the closure problem is not possible and we must use numerical methods to integrate the closure problems. However, the general solution form given by equations (58) and (59) are useful in that they allow a decoupling of the macroscale and microscale equations. To see this, substitute equations (58) and (59) into the closure problem specified before. One finds after some simplification.

5.2.1 Simplified closure problem

$$\tilde{\mathbf{v}}_\gamma + \mathbf{v}_\gamma \cdot \nabla \mathbf{b}_{A\gamma} = \nabla \cdot (\mathcal{D}_{A\gamma} \nabla \mathbf{b}_{A\gamma})$$

$$-\frac{1}{V_\gamma}\int_{A_{\gamma\omega}} \mathbf{n}_{\gamma\omega} \cdot (\mathcal{D}_{A\gamma} \nabla \mathbf{b}_{A\gamma}) \mathrm{d}A - \frac{1}{V_\gamma}\int_{A_{\gamma\kappa}} \mathbf{n}_{\gamma\kappa} \cdot (\mathcal{D}_{A\gamma} \nabla \mathbf{b}_{A\gamma})\, \mathrm{d}A \tag{60}$$

$$B.C.1 \quad -\mathbf{n}_{\gamma\kappa} \cdot \mathcal{D}_{A\gamma} \nabla \mathbf{b}_{A\gamma} = \underbrace{\mathbf{n}_{\gamma\kappa} \mathcal{D}_{A\gamma}}_{\text{dispersive source}}, \quad \text{at } A_{\gamma\kappa} \tag{61}$$

$$B.C.2 \quad -\mathbf{n}_{\omega\kappa} \cdot \mathsf{D}_{A\omega} \nabla \mathbf{b}_{A\omega} = \underbrace{\mathbf{n}_{\omega\kappa} \mathsf{D}_{A\omega}}_{\text{dispersive source}}, \quad \text{at } A_{\omega\kappa} \tag{62}$$

$$B.C.3 \quad -\mathbf{n}_{\gamma\omega} \cdot \mathsf{D}_{A\omega} \nabla \mathbf{b}_{A\omega} = -\mathbf{n}_{\gamma\omega} \cdot \mathcal{D}_{A\gamma} \nabla \mathbf{b}_{A\gamma} - \underbrace{\mathbf{n}_{\gamma\omega} (\mathcal{D}_{A\gamma} \mathsf{I} - \mathsf{D}_{A\omega})}_{\text{dispersive source}}, \quad \text{at } A_{\gamma\omega} \tag{63}$$

$$B.C.4 \quad \mathbf{b}_{A\gamma} = \mathbf{b}_{A\omega}, \quad \text{at } A_{\gamma\omega} \tag{64}$$

$$\textit{Periodicity } 1 \quad \mathbf{b}_{A\gamma}(\mathrm{x}) = \mathbf{b}_{A\gamma}(\mathrm{x} + \mathrm{l}_i), \quad i = 1, 2, 3 \tag{65}$$

$$\textit{Periodicity } 2 \quad \mathbf{b}_{A\omega}(\mathrm{x}) = \mathbf{b}_{A\omega}(\mathrm{x} + \mathrm{l}_i), \quad i = 1, 2, 3 \tag{66}$$

$$\textit{Constraint } 1 \quad \left\langle \mathbf{b}_{A\gamma} \right\rangle^{\gamma} = 0 \tag{67}$$

$$\textit{Constraint } 2 \quad \left\langle \mathbf{b}_{A\omega} \right\rangle^{\omega} = 0 \tag{68}$$

$$\nabla \cdot (\mathsf{D}_{A\omega} \cdot \nabla \mathbf{b}_{A\omega}) = \frac{1}{V_\omega} \int_{A_{\omega\gamma}} \mathbf{n}_{\omega\gamma} \cdot \mathsf{D}_{A\omega} \nabla \mathbf{b}_{A\omega} \mathrm{d}A + \frac{1}{V_\omega} \int_{A_{\omega\kappa}} \mathbf{n}_{\omega\kappa} \cdot \mathsf{D}_{A\omega} \nabla \mathbf{b}_{A\omega} \mathrm{d}A. \tag{69}$$

Note that here we have

- adopted periodic boundary conditions (where l_i is a lattice vector defining the periodic structure) in place of the original Dirichlet conditions given by equations (6) and (7)
- added two constraints on the $\mathbf{b}_{A\gamma}$ and $\mathbf{b}_{A\omega}$ fields.

These uses of periodic conditions for the solution of the closure problem have been discussed extensively elsewhere [e.g., Ochoa-Tapia et al., 1994; Pickup et al., 1994; Wood et al., 2003a, 2007].

In short, it is necessary to supply *some* boundary conditions at the edges of the unit cell and periodic boundaries supply the *weakest* condition that is independent of the average concentration. The two constraints are required so that the *level* of the $\mathbf{b}_{A\gamma}$ and $\mathbf{b}_{A\omega}$ fields is specified; without these constraints, the problem is solved to within an arbitrary but undetermined constant. With these simplifications in place, equations (60)–(69) can be solved to determine the $\mathbf{b}_{A\gamma}$ and $\mathbf{b}_{A\omega}$ fields and, subsequently, the effective dispersion tensor. Using the general solutions given by equations (58) and (59), the effective dispersion tensor relationship given in Section 4 (equation (41)) can now be expressed in its closed form.

$$\begin{aligned}
\mathsf{D}'_A \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma} = \Big[& (\varepsilon_\gamma \mathcal{D}_{A\gamma} \mathsf{I} + \varepsilon_\omega \mathsf{D}_{A\omega}) \\
& + \varepsilon_\omega \mathsf{D}_{A\omega} \cdot \left(\frac{1}{V_\omega} \int_{\mathcal{A}_{\omega\gamma(t)}} \mathbf{n}_{\omega\gamma} \mathbf{b}_{A\omega} \mathrm{d}A + \frac{1}{V_\omega} \int_{A_{\omega\kappa(t)}} \mathbf{n}_{\omega\kappa} \mathbf{b}_{A\omega} \mathrm{d}A \right) \\
& + \varepsilon_\gamma \mathcal{D}_{A\gamma} \left(\frac{1}{V_\gamma} \int_{\mathcal{A}_{\omega\gamma(t)}} \mathbf{n}_{\gamma\omega} \mathbf{b}_{A\gamma} \mathrm{d}A + \frac{1}{V_\gamma} \int_{A_{\omega\kappa(t)}} \mathbf{n}_{\gamma\kappa} \mathbf{b}_{A\gamma} \mathrm{d}A \right) \\
& - \nabla \cdot \langle \tilde{\mathbf{v}}_\gamma \mathbf{b}_{A\gamma} \rangle \Big] \cdot \nabla \langle c_{A\gamma} \rangle^{\gamma}.
\end{aligned} \tag{70}$$

The numerical solution to equations (60)–(69) is described in the next section.

6 Results and discussion

6.1 Solution to the closure problem

As discussed in the introduction to this section, the solution to the closure problem is usually conducted over some representative unit cell. Simple unit cells can often provide

substantial information about a macroscale phenomenon even in cases where more complex unit cells may ultimately be necessary for capturing phenomena arising from correlations in the porous media structure. For the presentation of results, it is useful to define the particle Péclet number by

$$\mathrm{Pe}_p = \frac{v_\gamma \mathcal{D}_h}{\mathcal{D}_\gamma} \tag{71}$$

where D_h is the hydraulic diameter given by

$$D_h = 4\frac{\varepsilon_\gamma}{a_v} \tag{72}$$

and $a_v = (A_{\gamma\omega} + A_{\gamma\kappa})/\mathcal{V}$ is the area of fluid interface (fluid-solid or fluid-biofilm) per unit volume of porous medium. For the case of hydrodynamic dispersion, a simple unit cell can provide reasonable results, particularly for the longitudinal component for particle Péclet numbers less than about 1000. Note that we have previously put a restriction of the macroscale Péclet number and this constraint was

$$\left(\frac{\varepsilon_\gamma \varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega}\right)\frac{v_\gamma L}{\mathsf{D}'_A} \ll 1. \tag{73}$$

This constraint can be rearranged in the form

$$\frac{1}{4}\left(\frac{\varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega}\right)\frac{4\varepsilon_\gamma}{a_v}\frac{v_\gamma}{\mathcal{D}_\gamma} La_v \frac{\mathcal{D}_\gamma}{\mathsf{D}'_A} \ll 1 \tag{74}$$

and this leads to a constraint of the form

$$\frac{1}{4}\left(\frac{\varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega}\right)\left(\frac{\mathcal{D}_\gamma}{\mathsf{D}'_A}\right) La_v \mathrm{Pe}_p \ll 1. \tag{75}$$

In this work, we have not considered the influence of fluid shear on the biofilm structure. It is reasonable, then, to restrict our analysis to systems in which the particle Reynolds number ($\mathrm{Re}_p = \rho_\gamma v_\gamma D_h/\mu_\gamma$) is less than 1; if water is the fluid of interest, this is equivalent to a Péclet number of about 1000.

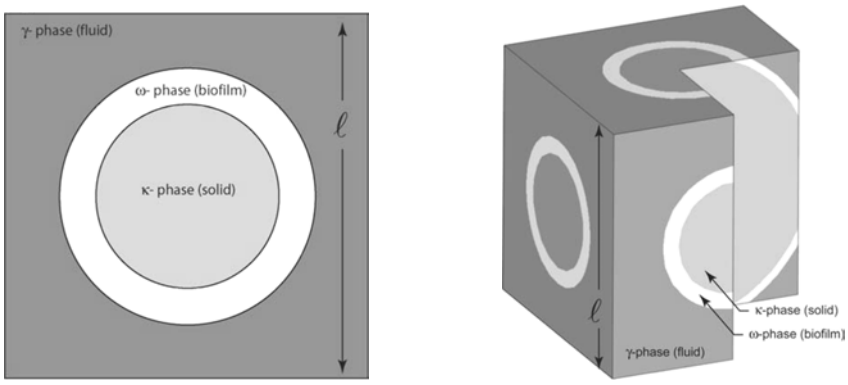
The simplified closure problem was coded using a production level finite-element solver (COMSOL Multiphysics, Comsol, Inc., Los Angeles) in both two- and three-dimensional unit cells (Figure 3). Although not reported here, convergence analyses were conducted for these simulations to assure that the physics were appropriately resolved. Equations (60)–(69) were solved using a weak formulation to a pre-specified relative convergence criterion. The integrations required for the determination of the effective dispersion tensor, as indicated by equation (70), were conducted using a fourth-order quadrature method as a post-processing step.

The solution to equations (60)–(69) is complicated by the integral terms. These terms are nonlocal and this couples the solution at any one point in the domain to the solution at every other point. In the discretised forms that arise in numerical schemes for these equations, the appearance of the nonlocal integral terms creates a linear system in which the array of unknowns is a full rather than sparse matrix. This dramatically increases both

computational time for matrix inversion and total memory requirements for storage of the solution. This problem is particularly acute in three-dimensional systems, where the degrees of freedom required to accurately discretise the equations are large to begin with.

We investigated the importance of these integral terms for the two-dimensional unit cell illustrated in Figure 3. The effective dispersion tensor predicted for the simple two-dimensional unit cell is shown as a function of particle Péclet number in Figure 4. For these simulations, the parameters were as follows: $\ell = 1 \times 10^{-3}$ m, $\varepsilon_\gamma = 0.615$, $\varepsilon_\omega = 0.188$, $a_v = 2199\ \mathrm{m}^{-1}$, $D_h = 0.0011$ m and $\mathcal{D}_{A\gamma} = \mathcal{D}_{A\omega} = 1\times10^{-9}\,\mathrm{m}^2/\mathrm{s}$, where the diffusion tensor for the biofilm phase is assumed to be isotropic, $\mathsf{D}_{A\omega} = \mathcal{D}_{A\omega}\mathsf{I}$.

Figure 3 Simple unit cells used for the closure problem computational domain: (a) two-dimensional cell and (b) three-dimensional cell (with cut away for interior visualisation)



(a) (b)

The results of these two-dimensional computations indicate that, for the range of Pe_p investigated

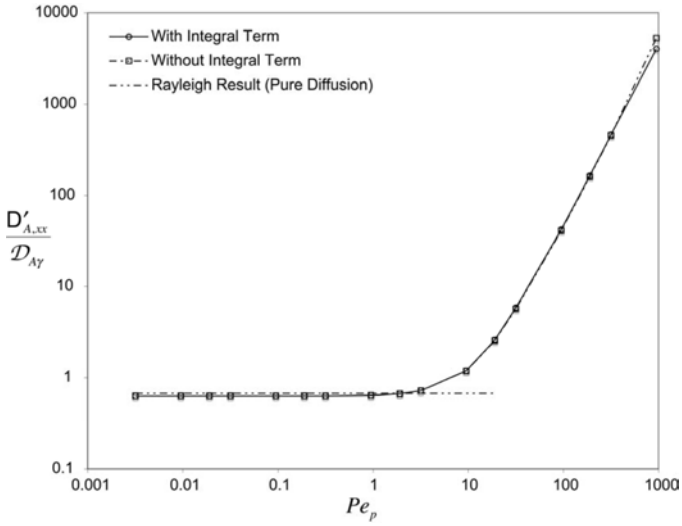
- the dispersion tensor for the case of local mass equilibrium evolves qualitatively like the conventional dispersion tensor in porous media without biofilms
- the integral terms for this case (symmetric unit cell, $\mathrm{Pe}_p < 1000$) are negligible compared with other quantities in the closure problem
- the results at low values of Pe_p compare favourably with the analytical expression of Rayleigh (1892) for diffusion in an array of spheres.

For the three-dimensional unit cells, we found a similar relationship. For these simulations, the parameters were as follows: $\ell = 2.34 \times 10^{-4}$ m, $\varepsilon_\gamma = 0.235$, $\varepsilon_\omega = 0.035$, $a_v = 8572\ \mathrm{m}^{-1}$, $D_h = 1.1 \times 10^{-4}$ m and $\mathcal{D}_{A\gamma} = 1\times10^{-9}\,\mathrm{m}^2/\mathrm{s}$, where the diffusion tensor for the biofilm phase is assumed to be isotropic, $\mathsf{D}_{A\omega} = \mathcal{D}_{A\omega}\mathsf{I}$. In Figure 5, we show the effective dispersion plotted as a function of the Péclet number for two different ratios of the diffusion coefficient for the two phases ($\mathcal{D}_{A\omega}/\mathcal{D}_{A\gamma} = 1$ and $\mathcal{D}_{A\omega}/\mathcal{D}_{A\gamma} = 0.25$). In the high Péclet number range ($\mathrm{Pe}_p > 10$), mechanical dispersion is the dominant process determining $\mathsf{D}'_{A,xx}$. In this range, the diffusive resistance of the biofilm appears to have little influence. The longitudinal dispersion coefficient takes roughly the form

$$\mathsf{D}'_{A,xx} = \alpha \mathrm{Pe}_p^{\delta} \tag{76}$$

where $\delta \approx 1.2$. This is consistent with a wide variety of experimental data from the mechanical dispersion regime and from previous studies of dispersion via volume averaging with closure (Wood, 2007).

Figure 4 Effective dispersion tensor for the two-dimensional unit cell illustrated in Figure 3 computed with and without the integral terms



In the low Péclet number range ($Pe_p < 10$), we find that the diffusion coefficient of the biofilm can have a significant influence, primarily by lowering the effective diffusion coefficient. When the diffusion coefficient of the biofilm and fluid are set equal to one another, we expect to recover the effective diffusion coefficient that would be predicted by the well-known results of Maxwell (1873) and Rayleigh (1892). Our results for the limiting case $Pe_p \to 0$ are consistent with the predictions from these theories for three-dimensional isotropic media.

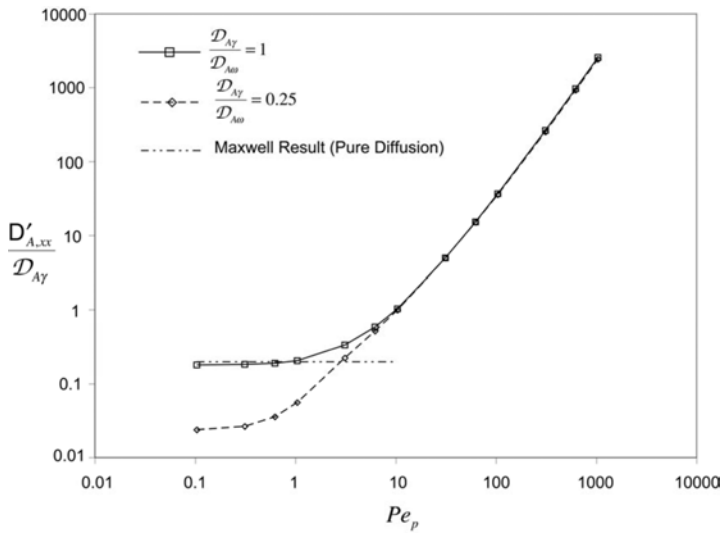
In summary, for the one-equation, local mass equilibrium model studied here, the influence of the biofilm phase on the dispersion process can be important in the low Péclet number regime ($Pe_p < 10$). For larger Péclet numbers, the effect of the biofilm is overwhelmed by mechanical dispersion. In the results presented here, the influence of the biofilm volume on the mechanical dispersion was small due to the small volume fraction of the biofilm phase; for larger volume fractions, some effect of the biofilm volume on the mechanical portion of the dispersion tensor might occur.

The constraints for the validity of the one-equation, local mass equilibrium model have been presented in this work. Note that there are more likely to be many cases of practical interest in which these constraints are not met and the one-equation, local mass equilibrium model cannot be used. Two such cases include

- the case where the reaction rate is not small compared with the rate of diffusion within the biofilm [the constraint given by equation (36) is not met]
- the case where convection in the fluid phase is large compared with diffusion through the biofilm [the constraint given by equation (37) is not met].

In the first case, a one-equation effectiveness factor model, similar to that described by Wood et al. (2007), might be possible. In the second case, a two-equation model would be necessary and in general this may require a fully nonlocal-in-time approach. These models will be considered in future developments.

Figure 5 Effective dispersion tensor for the three-dimensional unit cell illustrated in Figure 3 computed without the integral terms



Acknowledgements

This research was supported by the National Science Foundation under grant CBET 0449452 (‘Microbial Transport and Adhesion – A Multiscale Approach’).

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Appendix

In this appendix, we provide a rough estimate for the concentration difference, $(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega})$. To start, we subtract the unclosed macroscale equation for the ω-phase concentration from the analogous equation for γ phase (after first dividing both sides of each equation by the respective volume fraction). Assuming that the κ-phase is impenetrable, this results in

$$
\begin{aligned}
&\frac{\partial}{\partial t}\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right)+\nabla\cdot\left(\langle \mathbf{v}_{\gamma}\rangle^{\gamma}\langle c_{A\gamma}\rangle^{\gamma}\right)\\
&=\nabla\cdot\left(\mathcal{D}_{A\gamma}\nabla\langle c_{A\gamma}\rangle^{\gamma}-\mathbf{D}_{A\omega}\cdot\nabla\langle c_{A\omega}\rangle^{\omega}\right)\\
&\quad\nabla\cdot\left[\mathcal{D}_{A\gamma}\left(\frac{1}{V_{\gamma}}\int_{A_{\gamma\omega}(t)}\mathbf{n}_{\gamma\omega}\tilde{c}_{A\gamma}\mathrm{d}A+\frac{1}{V_{\gamma}}\int_{A_{\gamma\kappa}(t)}\mathbf{n}_{\gamma\kappa}\tilde{c}_{A\gamma}\mathrm{d}A\right)\right]\\
&\quad-\nabla\cdot\left[\mathbf{D}_{A\omega}\cdot\left(\frac{1}{V_{\omega}}\int_{A_{\omega\gamma}(t)}\mathbf{n}_{\omega\gamma}\tilde{c}_{A\omega}\mathrm{d}A+\frac{1}{V_{\omega}}\int_{A_{\omega\kappa}(t)}\mathbf{n}_{\omega\kappa}\tilde{c}_{A\omega}\mathrm{d}A\right)\right]\\
&\quad-\varepsilon_{\gamma}^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_{\gamma}\tilde{c}_{A\gamma}\rangle+\langle\rho_{x}\rangle^{\omega}\mu_{A,\mathrm{eff}}\frac{\langle c_{A\omega}\rangle^{\omega}}{\langle c_{A\omega}\rangle^{\omega}+K_{A,\mathrm{eff}}}\\
&\quad+\frac{1}{\mathcal{V}}\int_{A_{\omega\gamma}(t)}\mathbf{n}_{\gamma\omega}\cdot\left(\varepsilon_{\gamma}^{-1}\mathcal{D}_{A\gamma}\nabla c_{A\gamma}+\varepsilon_{\omega}^{-1}\mathbf{D}_{A\omega}\cdot\nabla c_{A\omega}\right)\mathrm{d}A.
\end{aligned}
\tag{77}
$$

Using the boundary condition given by equation (4), the closure relation given by equations (58) and (59)

$$\tilde{c}_{A\gamma}=\mathbf{b}_{A\gamma}\cdot\nabla\langle c_{A\gamma}\rangle^{\gamma} \tag{78}$$

$$\tilde{c}_{A\omega}=\mathbf{b}_{A\omega}\cdot\nabla\langle c_{A\omega}\rangle^{\omega} \tag{79}$$

and the definitions of the macroscale deviations

$$\langle c_{A\gamma}\rangle^{\gamma}=\langle c_{A}\rangle+\frac{\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right) \tag{80}$$

$$\langle c_{A\omega}\rangle^{\omega}=\langle c_{A}\rangle-\frac{\varepsilon_{\gamma}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right) \tag{81}$$

this expression can be written

$$
\begin{aligned}
&\frac{\partial}{\partial t}\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right)+\frac{\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\nabla\cdot\left[\langle \mathbf{v}_{\gamma}\rangle^{\gamma}\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right)\right]\\
&=+\frac{\varepsilon_{\gamma}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\nabla\cdot\left(\mathcal{D}_{A\gamma}\mathbf{I}+\mathbf{D}^{\mathrm{o}}_{A\gamma\omega}\right)\cdot\nabla\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right)\\
&\quad+\frac{\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\nabla\cdot\left(\mathbf{D}_{A\omega}+\mathbf{D}^{\mathrm{o}}_{A\omega}\right)\cdot\nabla\left(\langle c_{A\gamma}\rangle^{\gamma}-\langle c_{A\omega}\rangle^{\omega}\right)\\
&\quad-\nabla\cdot\left(\langle \mathbf{v}_{\gamma}\rangle^{\gamma}\langle c_{A}\rangle\right)+\nabla\cdot\left(\mathcal{D}_{A\gamma}\mathbf{I}+\mathbf{D}^{\mathrm{o}}_{A\gamma\omega}+\mathbf{D}_{A\omega}+\mathbf{D}^{\mathrm{o}}_{A\omega}\right)\cdot\nabla\langle c_{A}\rangle\\
&\quad-\varepsilon_{\gamma}^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_{\gamma}\tilde{c}_{A\gamma}\rangle+\langle\rho_{x}\rangle^{\omega}\mu_{A,\mathrm{eff}}\frac{\langle c_{A\omega}\rangle^{\omega}}{\langle c_{A\omega}\rangle^{\omega}+K_{A,\mathrm{eff}}}\\
&\quad+\left(\frac{\varepsilon_{\gamma}\varepsilon_{\omega}}{\varepsilon_{\gamma}+\varepsilon_{\omega}}\right)^{-1}\frac{1}{\mathcal{V}}\int_{A_{\omega\gamma(t)}}\mathbf{n}_{\gamma\omega}\cdot\left(\mathcal{D}_{A\gamma}\nabla c_{A\gamma}\right)\mathrm{d}A.
\end{aligned}
\tag{82}
$$

Here, we have used the following notation

$$\mathbf{D}^{\mathrm{o}}_{A\gamma\omega} = \left(\frac{\varepsilon_\gamma \mathbf{D}_{A\omega} + \varepsilon_\omega \mathbf{I} \mathcal{D}_{A\gamma}}{\varepsilon_\gamma \varepsilon_\omega} \right) \cdot \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\omega}(t)} \mathbf{n}_{\gamma\omega} \mathbf{b}_{A\gamma} \mathrm{d}A \right) + \left(\varepsilon_\gamma^{-1} \mathbf{I} \mathcal{D}_{A\gamma} \right) \cdot \left(\frac{1}{\mathcal{V}} \int_{A_{\gamma\kappa}(t)} \mathbf{n}_{\gamma\omega} \mathbf{b}_{A\gamma} \mathrm{d}A \right) \tag{83}$$

$$\mathbf{D}^{\mathrm{o}}_{A\omega} = \left(\varepsilon_\omega^{-1} \mathbf{D}_{A\omega} \right) \cdot \left(\frac{1}{\mathcal{V}} \int_{A_{\omega\kappa}(t)} \mathbf{n}_{\omega\kappa} \mathbf{b}_{A\omega} \mathrm{d}A \right). \tag{84}$$

Rather than attempting to conduct an exhaustive comparison of the terms in this expression, we instead rely on the significant similar work that has been on estimating such terms. In particular, we follow Whitaker (1999) to suggest that this expression is dominated by the interfacial flux term and the diffusion term. If these two terms dominate, we can generate the estimate

$$\left(\frac{\varepsilon_\gamma \varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega} \right)^{-1} \frac{1}{\mathcal{V}} \int_{A_{\omega\gamma}(t)} \mathbf{n}_{\gamma\omega} \cdot \left(\mathcal{D}_{A\gamma} \nabla c_{A\gamma} \right) \mathrm{d}A = \mathbf{O}\left(\nabla \cdot \left(\mathcal{D}_{A\gamma} \mathbf{I} + \mathbf{D}^{\mathrm{o}}_{A\gamma\omega} + \mathbf{D}_{A\omega} + \mathbf{D}^{\mathrm{o}}_{A\omega} \right) \cdot \nabla \langle c_A \rangle \right). \tag{85}$$

For the interfacial term, we adopt the estimate (cf. Whitaker, 1999, Chapter 3)

$$\left(\frac{\varepsilon_\gamma \varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega} \right)^{-1} \frac{1}{\mathcal{V}} \int_{A_{\omega\gamma(t)}} \mathbf{n}_{\gamma\omega} \cdot \left(\mathcal{D}_{A\gamma} \nabla c_{A\gamma} \right) \mathrm{d}A = \mathbf{O}\left(\left(\frac{\varepsilon_\gamma \varepsilon_\omega}{\varepsilon_\gamma + \varepsilon_\omega} \right)^{-1} \frac{\mathcal{D}_{A\gamma}}{a_v^{-1} \delta} \left(\langle c_{A\gamma} \rangle^\gamma - \langle c_{A\omega} \rangle^\omega \right) \right) \tag{86}$$

where δ represents a diffusive boundary layer thickness. For the right-hand side

$$\left(\nabla \cdot \left(\mathcal{D}_{A\gamma} \mathbf{I} + \mathbf{D}^{\mathrm{o}}_{A\gamma\omega} + \mathbf{D}_{A\omega} + \mathbf{D}^{\mathrm{o}}_{A\omega} \right) \cdot \nabla \langle c_A \rangle \right) = \mathbf{O}\left(\frac{\mathbf{D}_{A,\mathrm{sum}}}{L^2} \Delta \langle c_A \rangle \right) \tag{87}$$

where

$$\mathbf{D}_{A,\mathrm{sum}} = \sqrt{\tfrac{1}{2} \left(\mathcal{D}_{A\gamma} \mathbf{I} + \mathbf{D}^{\mathrm{o}}_{A\gamma\omega} + \mathbf{D}_{A\omega} + \mathbf{D}^{\mathrm{o}}_{A\omega} \right) : \left(\mathcal{D}_{A\gamma} \mathbf{I} + \mathbf{D}^{\mathrm{o}}_{A\gamma\omega} + \mathbf{D}_{A\omega} + \mathbf{D}^{\mathrm{o}}_{A\omega} \right)}. \tag{88}$$

Combining these expressions gives

$$\left(\langle c_{A\gamma} \rangle^\gamma - \langle c_{A\omega} \rangle^\omega \right) = \mathbf{O}\left(\frac{\mathrm{D}_{A,\mathrm{sum}}}{\mathcal{D}_{A\gamma}} \frac{\ell_{\gamma\omega}^2}{L^2} \Delta \langle c_A \rangle \right). \tag{89}$$

Here, $\ell_{\gamma\omega}^2 = \delta a_v \varepsilon_\gamma \varepsilon_\omega / (\varepsilon_\gamma + \varepsilon_\omega)$. Finally, note that it is convenient to adopt the approximation

$$\mathsf{D}_{\mathrm{A,sum}} = \mathbf{O}\left(\mathsf{D}'_{\mathrm{A}}\right) \tag{90}$$

so that the estimate above can be given as

$$\left(\langle c_{A\gamma}\rangle^{\gamma} - \langle c_{A\omega}\rangle^{\omega}\right) = \mathbf{O}\left(\frac{\mathsf{D}'_{A}}{\mathcal{D}_{A\gamma}}\frac{\ell^{2}_{\gamma\omega}}{L^{2}}\Delta\langle c_{A}\rangle\right). \tag{91}$$

This estimate provides the basis for the estimates made in the body of the paper.