Supplemental Information: Benthic biolayer structure controls whole stream reactive transport

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CONTENTS

I. MOBILE-IMMOBILE BIOLAYER (MIM-B) MODEL

A. Vertical Average

In order to upscale the reactive transport problem, we employ a dual porosity approach and separate the transport equation (1) in the main manuscript into an equation that describes advection-dispersion in the river,

$$\partial_t C_s + v\partial_x C_s - D(z)\nabla^2 C_s = 0, \tag{S1a}$$

and an equation for diffusion-reaction in the hyporheic zone

$$\partial_t C_h - D_h \partial_z(\partial_z C_h) = -k(z)C_h. \tag{S1b}$$

The concentrations in the river and hyporheic zone are denoted by C_s and C_h, respectively. Both domains are coupled through concentration and flux continuity at the interface located at $z = 0$,

$$C_h(x, z = 0, t) = C_s(x, 0, t) \tag{S2}$$

$$D\partial_z C_s|_{z=0} = D_h \partial_z C_h|_{z=0} \tag{S3}$$

We define now the vertical average over the stream as

$$\overline{C}_s = \frac{1}{d}\int_0^h dz C_s. \tag{S4}$$

Thus, vertical averaging of Eq. (S1a) gives

$$\partial_t\left(\overline{C}_s + \frac{1}{d}M_h\right) + \overline{v}\partial_x\overline{C}_s - D^*\partial_x^2\overline{C}_s = -\frac{1}{d}\int_{-h}^0 dz k(z)C_h, \tag{S5}$$

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where we defined the total mass in the hyporheic zone as

$$M_h = \int_{-h}^{0} dz C_h. \tag{S6}$$

The term on the right side of (S5) represents a sink term for the stream domain due to reactions in the hyporheic zone. The derivation of the vertical average in the stream gives rise to the shear dispersion coefficient, which quantifies the impact of velocity variability with depth on longitudinal dispersion [1].

B. Closure

In order to close Eq. (S5), we need to express the right side in terms of $\overline{C}_s$. As a first step, we approximate the interface condition (S2) by

$$C_h(x, z = 0, t) = \overline{C}_s(x, t), \tag{S7}$$

which assumes that concentration in the stream is uniform in the vertical. Furthermore, we note that the solution of Eq. (S1b) can be written as

$$C_h = \int_{0}^{t} dt' dz g(z, t - t') \overline{C}_s(x, t'), \tag{S8}$$

where the Green function $g(z, t)$ satisfies

$$\partial_t g - D_h \partial_z (\partial_z g) = -k(z) g. \tag{S9}$$

for the boundary condition $g(z = 0, t) = \delta(t)$. Thus, we can write (S6) as

$$M_h = \int_{0}^{t} dt' \varphi_h(t - t') \overline{C}_s(x, t'), \tag{S10}$$

where the memory function

$$\varphi_h(t) = \int_{-h}^{0} dz g(z, t), \tag{S11}$$

denotes the mass in the hyporheic zone in response to an instanteous solute pulse at the interface between stream and streambed.

C. Biolayer

We now consider the reaction profile $k(z) = k_b \mathbb{I}(-b < z < 0)$. Thus, Eq. (S5) can be written as

$$\partial_t \left(\overline{C}_s + \frac{1}{d} M_h \right) + \overline{v} \partial_x \overline{C}_s - D^* \partial_x^2 \overline{C}_s = -\frac{k_b}{d} M_b, \tag{S12}$$

where

$$M_b = \int_{-b}^{0} dz C_h. \tag{S13}$$

In order to close the problem, we solve Eq. (S1b) for the concentration in the hyporheic zone. For convenience, we define a local coordinate system such that the interface between the biolayer and the sublayer is located at $z' = 0$,

and the interface between stream and streambed is located a $z' = b$, and the lower boundary of the hyporheic zone is located at $z' = b - h \equiv -\ell$. In the following we omit the primes for compactness of notation.

We separate Eq. (S9) for the hyporheic zone into two coupled equations, one for the biolayer and one for the sublayer. The equation for the Green function g_b in the biolayer is

$$\frac{\partial g_b}{\partial t} - D_h \frac{\partial^2 g_b}{\partial z^2} = -k_b g_b(z, t) \tag{S14a}$$

for the initial condition $g_b(z, t = 0) = 0$ and the boundary condition $g_b(z = b, t) = \delta(t)$. The equation for the concentration g_0 in the sublayer is

$$\frac{\partial g_0}{\partial t} - D_h \frac{\partial^2 g_0}{\partial z^2} = 0. \tag{S14b}$$

At the interface at $z = 0$, we have concentration and flux continuity, meaning $g_b = g_0$ and $\partial g_b / \partial z = \partial g_0 / \partial z$. The boundary condition for g_0 at $z = -\ell$ is $\partial g_0 / \partial z = 0$.

In order to solve for the Green functions, we consider the system (S14) in Laplace space,

$$\lambda g_b^* - D_h \frac{\partial^2 g_b^*}{\partial z^2} = -k_b g_b^*(z, t) \tag{S15a}$$

for the boundary condition $g_b^*(z = b, \lambda) = 1$. The equation for the concentration g_0 in the sublayer is

$$\frac{\partial g_0^*}{\partial t} - D_h \frac{\partial^2 g_0^*}{\partial z^2} = 0. \tag{S15b}$$

At the interface at $z = 0$, we have

$$g_b^* = g_0^*, \qquad\qquad \frac{\partial g_b}{\partial z} = \frac{\partial g_0^*}{\partial z}. \tag{S16}$$

Thus, the Laplace transform of $g_0(z, t)$ in the sublayer can be expressed in terms of the concentration $g_b^*(z = 0, t)$ as

$$g_0^*(z, t) = G^*(z, \lambda) g_b^*(z = 0, \lambda) \tag{S17}$$

where the Green function $G^*(z, \lambda)$ satisfies (S15b) for the boundary condition $G = 1$ at $z = 0$. It is given by

$$G^*(z, \lambda) = \frac{\cosh(\sqrt{\lambda \tau_0}(1 + z/\ell))}{\cosh(\sqrt{\lambda \tau_0})}, \tag{S18}$$

where we defined $\tau_0 = \ell^2 / D_h$.

The fundamental solution for $g_b^*(z, \lambda)$ is

$$g_b^*(z, \lambda) = A \exp(-zB) + C \exp(zB), \qquad\qquad B = \sqrt{(\lambda + k_b)/D_h}. \tag{S19}$$

where the constants A and C are determined from the Dirichlet boundary condition at $z = 0$ and the Neumann boundary condition at $z = b$. Note that concentration continuity at $z = 0$ is automatically fulfilled by (S17). Thus, we obtain the solution

$$g_b^*(z, \lambda) = \frac{\cosh(\sqrt{(\lambda + k_b)\tau_b}\, z/bb) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \sinh(\sqrt{(\lambda + k_b)\tau_b}\, z/w)}{\cosh(\sqrt{(\lambda + k_b)\tau_b}) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \sinh(\sqrt{(\lambda + k_b)\tau_b})}. \tag{S20}$$

The total mass φ_b in the biolayer in response to an instantaneous unit pulse at the interface at $z = b$ is given by its Laplace transform as

$$\varphi_b^*(\lambda) = \int_0^b dz\, g_b^*(z, \lambda) = \sqrt{\frac{D_h}{\lambda + k_b}} \frac{\sinh(\sqrt{(\lambda + k_b)\tau_b}) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \left[\cosh(\sqrt{(\lambda + k_b)\tau_b}) - 1\right]}{\cosh(\sqrt{(\lambda + k_b)\tau_b}) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \sinh(\sqrt{(\lambda + k_b)\tau_b})} \tag{S21}$$

Furthermore, we obtain for the concentration $g_0^*(z, \lambda)$ in the sublayer,

$$g_0^*(z, \lambda) = \frac{G^*(z, \lambda)}{\cosh(\sqrt{(\lambda + k_b)\tau_b}) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \sinh(\sqrt{(\lambda + k_b)\tau_b})} \tag{S22}$$

Thus we obtain for the mass φ_0 in the sublayer in terms of its Laplace transform

$$\varphi_0^*(\lambda) = \int_{-\ell}^0 dz\, g_0^*(z, \lambda) = \sqrt{\frac{D_h}{\lambda}} \frac{\tanh(\sqrt{\lambda \tau_0})}{\cosh(\sqrt{(\lambda + k_b)\tau_b}) + \sqrt{\frac{\lambda}{\lambda + k_b}} \tanh(\sqrt{\lambda \tau_0}) \sinh(\sqrt{(\lambda + k_b)\tau_b})} \tag{S23}$$

The Laplace transform $\varphi_h^*(\lambda)$ of the memory function φ_h, which denotes the total mass in the hyporheic zone in response to Delta pulse at the stream-streambed interface, is thus given by

$$\varphi_h^*(\lambda) = \varphi_b^*(\lambda) + \varphi_0^*(\lambda). \tag{S24}$$

D. Mass balance

We integrate now over the reactive biolayer, which gives for the mass φ_b the conservation equation

$$\frac{d\varphi_b}{dt} = -D_h \frac{\partial g_b(z = 0)}{\partial z} + D_h \frac{\partial g_b(z = b)}{\partial z} - k_b \varphi_b. \tag{S25}$$

The first and second terms denote mass transfer across the interfaces with the sublayer and the stream, the third term is a sink term due to reaction. Using flux continuity over the interface at $z = 0$, we can express the right side in terms of the total mass m_0 in the sublayer as

$$\frac{d\varphi_b}{dt} = -\frac{d\varphi_0}{dt} - D_h \frac{\partial g_b(z = b)}{\partial z} - k_b \varphi_b, \tag{S26}$$

The total reacted mass m_R is obtained from

$$\frac{dm_R(t)}{dt} = k_b \varphi_b(t) \tag{S27}$$

and therefore

$$m_R^\infty = k_b \varphi_b^*(\lambda = 0). \tag{S28}$$

From the explicit expression (S21), we obtain

$$m_R^\infty = \sqrt{k_b D_h} \tanh(\sqrt{k_b \tau_b}). \tag{S29}$$

For times $t \gg \tau_b$, we can approximate the mass balance equation (S26) as

$$\frac{d\varphi_b}{dt} = -\frac{d\varphi_0}{dt} + \frac{D_h}{b^2} \varphi_b - k_b \varphi_b, \tag{S30}$$

where we set $\partial g_b / \partial z \approx -\varphi_b / b^2$. We can furthermore write

$$\frac{1 + Da}{\tau_b} \frac{d\varphi_b}{dt} = -\frac{\tau_b}{1 + Da} \frac{d\varphi_0}{dt} + \varphi_b, \tag{S31}$$

For $t \gg \tau_b$, we obtain in leading order

$$\varphi_b = \frac{\tau_b}{1 + Da} \frac{d\varphi_0}{dt}. \tag{S32}$$

This means, the mass in the biolayer scales as the time-derivative of the mass in the sublayer.

E. Stream concentration

We solve Equation (S12) for the boundary condition $\overline{C}_s(x = 0, t) = \delta(t)$. To this end, we transform (S12) to Laplace space,

$$\lambda \overline{C}_s^* + d^{-1}[\lambda \varphi_h^*(\lambda) + k_b \varphi_b^*(\lambda)]\overline{C}_S^*(x, \lambda) + \overline{v} \partial_x \overline{C}_S^*(\lambda) - D^* \partial_x^2 \overline{C}_s^*(\lambda) = 0. \tag{S33}$$

The boundary condition reads as

$$\overline{C}_s(x = 0, \lambda) = 1. \tag{S34}$$

The solution is

$$\overline{C}_s^*(x, \lambda) = \exp\left[-\frac{x\overline{v}_s}{2D^*}\left(\sqrt{1 + 4\frac{(\lambda + d^{-1}[\lambda \varphi_h^*(\lambda) + k_b \varphi_b^*(\lambda)])D^*}{\overline{v}_s^2}} - 1\right)\right]. \tag{S35}$$

F. Constant reactivity in hyporheic zone

We consider the scenario that the entire hyporheic zone is characterized by a constant reactivity, which is used in the main text to define a constant equivalent reactivity for the streambed.

We set $k(z) = k_e = $ constant. In this case, the transport equation (2) simplifies to

$$\partial_t \left[\overline{C}_e + \frac{1}{d}\int_0^t \varphi_e(t - t')\overline{C}_s(t')\right] + \overline{v}\partial_x \overline{C}_e - \overline{D}^* \partial_x^2 \overline{C}_e = -\frac{k_e}{d}\int_0^t dt' \varphi_e(t - t')\overline{C}_e(t'), \tag{S36}$$

where the reactive memory function is given by

$$\varphi_e(t) = \phi(t)\exp(-k_e t), \tag{S37}$$

and in Laplace space

$$\varphi_e^*(\lambda) = \phi^*(\lambda + k_e). \tag{S38}$$

The conservative memory function $\phi(t)$ is defined in Laplace space by

$$\phi^*(\lambda) = \sqrt{\frac{D}{\lambda}}\tanh(\sqrt{\lambda \tau_h}). \tag{S39}$$

The solution of (S36) for the boundary condtion $\overline{C}_0^*(x = 0, t) = \delta(t)$ reads in Laplace space as

$$\overline{C}_e^*(x, \lambda) = \exp\left[-\frac{x\overline{v}}{2D^*}\left(\sqrt{1 + 4\frac{[\lambda + H^{-1}(\lambda + k_e)\phi^*(\lambda + k_e)]D^*}{\overline{v}^2}} - 1\right)\right]. \tag{S40}$$

G. Effective reaction rate in the streambed

The effective reaction rate k_e is obtained from expression (5) in the main text. In Laplace space,

$$k_e \varphi_e^*(0) \equiv k_b \varphi_h^*(0). \tag{S41}$$

Using expressions (S21), (S23) and (S24), as well as (S38) and (S39) gives Equation (6) in the main text.

H. Effective reaction rate at the reach scale

The effective reach scale reaction rate is defined by expression (8) in the main text, which reads in Laplace space as

$$k_r \int_0^x dx' \overline{C}_0^*(x', 0) \equiv k_b \int_0^x dx' \overline{C}_s^*(x', \lambda). \tag{S42}$$

Using the explicit expressions (S35) and (S40) gives Equation (9) in the main text.

II.   LITERATURE COMPARISON

We compared simulated and modeled Da to values of Da estimated from field experiments, to understand the expected range of Da in natural streams. We limited the comparison to studies that met the following criteria:

- profiles of first-order solute reactions were reported as a function of depth in the hyporheic zone,

- no production of mass was inferred (i.e., all values of $k(z)$ were non-zero),

- $k(z)$ decreased to a nominal value by the deepest measurement location, indicating the presence of a benthic biolayer and an inert sublayer.

For each solute, we determined whether the reported $k(z)$ was best approximated by a strip or by an exponential profile. Profiles that showed a sharp transition to values near $k(z) = 0$ were considered to be a slab with $z = -b$ equal to the transition depth, and k_b equal to the arithmetic average of $k(z)$ for all depths above $z = -b$. For profiles that showed a gradual decrease to near-zero values by the lowest measurement location, we determined k_b and b by fitting an exponential profile to $k(z)$. If dispersion coefficients and retardation coefficients R were reported as a function of depth, we approximated D_h as a constant value equal to the harmonic mean of $D_h(z)$ measured at all depths above $z = -b$ [2]. Similarly, we approximated a constant R as the arithmetic average of all R above $z = -b$. For consistency with our model assumptions, advective velocities reported in the biolayer were set to zero, meaning Da estimates are biased slightly higher than in conditions reported in Knapp *et al.* [3] and Schaper *et al.* [4] since downwelling conditions in each study suggest a shorter residence time in the biolayer. We calculated Da as

$$Da = \frac{k_b b^2}{R D_h}$$

All literature values are reported in Table I and plotted in Figure 3 in the main text.

Table I: Literature values of Da

Chemical	Source	D_H ($\times 10^{-6}$ m^2 s^{-1})	R	profile shape	k_0 ($\times 10^{-4}$ s^{-1})	B ($\times 10^{-2}$ m)	Da
metoprolol	Schaper et al., 2019	1.0	4.5	exp	16.1	8.6	$5.5 \times 10^{+01}$
gabapentin	Schaper et al., 2019	1.0	1.4	exp	6.8	11.6	$1.3 \times 10^{+01}$
gabapentin-lactam	Schaper et al., 2019	1.0	1.3	slab	0.8	5.0	2.8×10^{-01}
valsartan	Schaper et al., 2019	1.0	1.9	slab	1.7	5.0	8.1×10^{-01}
sotalol	Schaper et al., 2019	1.0	1.9	exp	3.7	10.5	$8.0 \times 10^{+00}$
metformin	Schaper et al., 2019	1.0	15.3	exp	1.9	38.5	$4.3 \times 10^{+02}$
guanylurea	Schaper et al., 2019	1.0	2.6	exp	4.0	18.5	$3.6 \times 10^{+01}$
benzotriazole	Schaper et al., 2019	1.0	4.0	exp	2.8	14.5	$2.4 \times 10^{+01}$
4-formylaminoantipyrine	Schaper et al., 2019	1.0	2.4	slab	1.5	5.0	9.3×10^{-01}
methylbenzotriazole	Schaper et al., 2019	1.0	3.3	exp	1.5	17.0	$1.5 \times 10^{+01}$
candesartan	Schaper et al., 2019	1.0	1.7	slab	1.7	5.0	7.2×10^{-01}
olmesartan	Schaper et al., 2019	1.0	1.4	slab	1.3	5.0	4.6×10^{-01}
tramadol	Schaper et al., 2019	1.0	2.2	slab	0.5	5.0	3.0×10^{-01}
carbamazepine	Schaper et al., 2019	1.0	3.6	slab	0.2	5.0	1.8×10^{-01}
dihydroxy-carbamazepine	Schaper et al., 2019	1.0	2.2	exp	0.9	10.5	$2.3 \times 10^{+00}$
diatrizoic acid	Schaper et al., 2019	1.0	1.1	slab	0.3	5.0	8.6×10^{-02}
dissolved organic carbon	Schaper et al., 2019	1.0	1.0	exp	1.1	16.4	$3.1 \times 10^{+00}$
raz $\rightarrow$ rru (Site C)	Knapp et al., 2017	0.4	2.2	exp	11.3	3.5	$7.6 \times 10^{+00}$
nitrate	Li et al., 2017	0.1	1.0	exp	0.1	3.6	1.1×10^{-01}

[1] H. B. Fischer, J. E. List, C. R. Koh, J. Imberger, and N. H. Brooks, *Mixing in inland and coastal waters* (Academic press, 1979).

[2] M. Dentz, P. Gouze, A. Russian, J. Dweik, and F. Delay, Advances in Water Resources **49**, 13 (2012).

[3] J. L. A. Knapp, R. González-Pinzón, J. D. Drummond, L. G. Larsen, O. A. Cirpka, and J. W. Harvey, Water Resources Research **53**, 1575 (2017).

[4] J. L. Schaper, M. Posselt, C. Bouchez, A. Jaeger, G. Nuetzmann, A. Putschew, G. Singer, and J. Lewandowski, Environmental Science & Technology **53**, 4224 (2019).