

Supporting Information

Geomembranes containing powdered activated carbon have the potential to improve containment of chlorinated aromatic contaminants

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	Pages
S1. Derivation of k for Diffusion-Limited Kinetics Model	S2-S3
S2. Materials and Manufacturers	S4
S3. PAC Particle Size Distribution	S5
S4. Effect of Stirring on PCB Breakthrough Curves	S6
S5. Analytical Methods	S7
S6. Effect of Acetone Content on HDPE-Solution Partition Coefficients	S8
S7. PAC Sorption Isotherms	S9
S8. Microscope Images of PAC-Containing Membranes	S10
S9. References	S11

Section S1. Derivation of k for Diffusion-Limited Kinetics Model

When sorptive particle concentrations within the membrane are low, lateral diffusion from the bulk membrane to the particle surface may limit the kinetics of sorption. Diffusion-limited kinetics can be derived using the steady-state Fick's law expression in radial coordinates for uptake by particles as described by Ferrari et al. (1)

$$\frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = 0 \quad (10)$$

where C is concentration (mol/m^3) and r (m) is the direction of diffusion to the surface of a spherical particle. Equation 9 is solved using the boundary conditions

$$\begin{aligned} \text{at } r = R, C &= 0 \\ \text{at } r = S, C &= C_m(x, t) \end{aligned} \quad (S1)$$

where $C_m(x, t)$ (mol/m^3) is the concentration of the membrane at a given depth x (m) and time t (s), R (m) is the radius of the particle, S (m) is the radius of diffusion around the particle as defined by

$$\phi = \frac{R^3}{S^3} \quad (S2)$$

where ϕ (dimensionless) is the volume fraction of particles in the membrane. Figure S1 defines the unit cell with radius of diffusion, S , schematically.

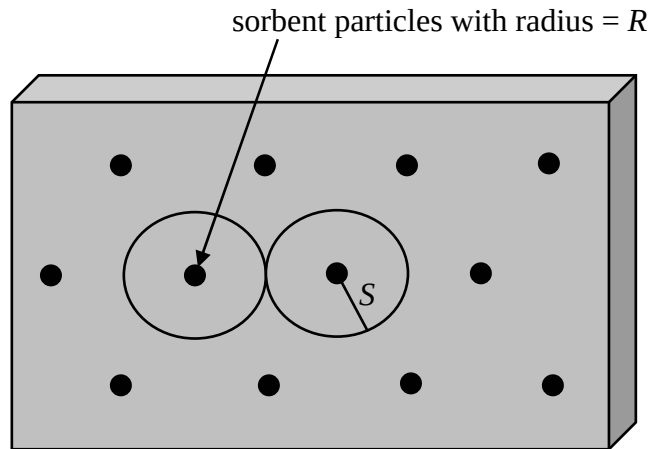


Figure S1. Unit cell for diffusion to membrane-bound particle.

Combining Equations 9, S1, and S2 gives a steady-state concentration profile around a single particle

$$C = \frac{C_m(x, t)}{1 - \phi^{1/3}} \left(1 - \frac{R}{r} \right) \quad (S3)$$

The steady-state flux of solute molecules to the particle surfaces is

$$j|_{r=R} = -D \frac{dC}{dr} \Big|_{r=R} = \frac{DC_m(x,t) \left(\frac{1}{R} \right)}{\left(1 - \phi^{1/3} \right)} \quad (\text{S4})$$

where D (m^2/s) is the diffusion coefficient of the solute in the membrane. The reaction-diffusion equation for a membrane with a kinetically-limited reaction is (2)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC \quad (9)$$

where k is the first-order reaction rate, defined for the case of diffusion-limited kinetics by

$$k = \frac{j|_{r=R}}{C_m(x,t)} \cdot \frac{\text{spherical particle surface area}}{\text{unit cell membrane volume}} \quad (\text{S5})$$

which reduces to

$$k = \frac{3D}{R^2 \left(1 - \phi^{1/3} \right) \left(\frac{1}{\phi} - 1 \right)} \quad (11)$$

when combined with the steady-state flux given in Equation S4.

Section S2. Materials and Manufacturers

High-density polyethylene beads (HDPE, DOWLEX IP-40) were supplied by Dow. Poly(vinyl alcohol) (PVA, Elvanol 71-30) was provided by DuPont. Powdered activated carbon (PAC, J.T. Baker) was sieved (150 mesh) before use. Ultrapure water was used in all experiments (Milli-Q, Millipore). 1,2,4-Trichlorobenzene (1,2,4-TCB, 99+%) and 2,3',4',5-tetrachlorobiphenyl (2,3',4',5-PCB, 99.0%) were purchased from Sigma-Aldrich and AccuStandard, respectively. Hexane (65% n-hexane) and anhydrous sodium sulfate (99.4%) were obtained from Fisher Scientific. Acetone (99.5%), sodium chloride (100.0%), and sulfuric acid (95.9%) were obtained from Mallinckrodt Baker. Epoxies used to fix and seal membranes into the diaphragm cell apparatus were from Loctite (5-Minute Quick Set) and 3M (DP-125).

Section S3. PAC Particle Size Distribution

The size distribution of PAC particles used in HDPE and HDPE/PVA composite membranes is shown in Figure S2. The mass-averaged particle diameter is $40\ \mu\text{m}$ ($R=20\ \mu\text{m}$), but the presence of a particle size distribution may lead to a higher “effective” particle diameter.

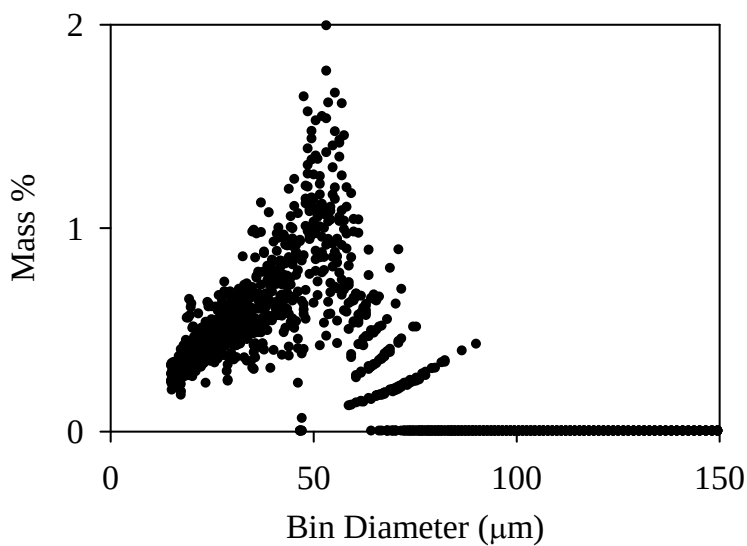


Figure S2. Distribution of the total mass of a sieved PAC sample by particle diameter.

Section S4. Effect of Stirring on 2,3',4',5-PCB Breakthrough Curves

Replicate 2,3',4',5-PCB experiments were conducted to ensure the accuracy of the observed breakthrough curves. Figure S3 shows four HDPE breakthrough curves for 2,3',4',5-PCB in 40:60 acetone:water. Membrane thicknesses and upstream concentrations ranged from 140 to 200 μm and from 4.7 to 7.1 μM , respectively. Mixing was investigated as a potential source of error in the system. One of the assumptions crucial to extrapolating D and H , the membrane-solution partition coefficient (dimensionless), values from breakthrough experiments is that the sole layer of diffusive resistance is the HDPE membrane (i.e., the diffusive boundary layer in the solution phase is infinitely thin). Stirring rates were varied and measured during two of the experiments, resulting in a difference in observed permeability of less than a factor of 2. D , H and P , permeability (m^2/s), calculated from each of these replicate breakthrough curves are listed in Table 1.

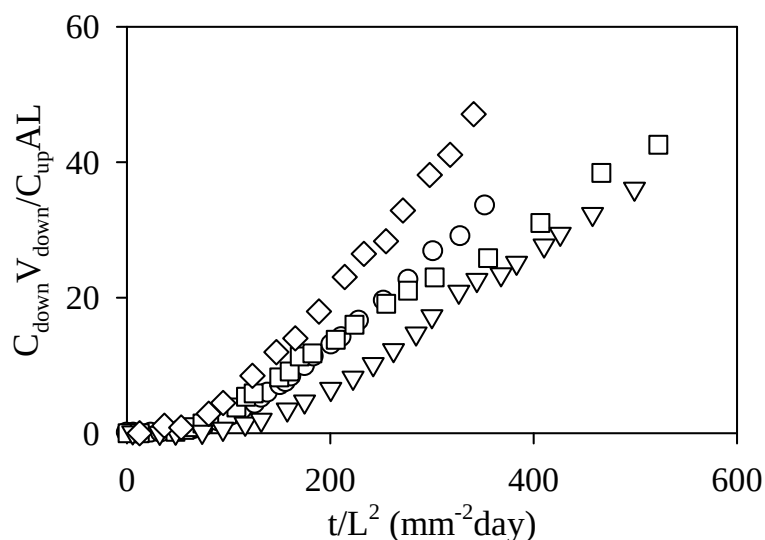


Figure S3. Replicate 2,3',4',5-PCB breakthrough curves in 40:60 acetone:water in HDPE. Experiments with a stirring rate of 940 s^{-1} ($\circ, \square$) are compared with experiments with upstream stirring rates of 690 s^{-1} (∇) and 1300 s^{-1} ($\diamond$).

Section S5. Analytical Methods

For 2,3',4',5-PCB experiments, 1-mL samples were extracted in two sequential aliquots of hexane for 2 minutes each. The hexane phase was then shaken for 2 minutes each with 1 mL sodium chloride solution (38 g sodium chloride in 900 mL Milli-Q water), 1 mL 10% sulfuric acid solution, and 1 mL sodium chloride solution again. Finally, the hexane phase was dried with ~2 g anhydrous sodium sulfate. The extraction efficiency of this procedure was 85-90%. For 1,2,4-TCB experiments in solutions containing 10%, 20%, and 40% acetone, 10- μ L samples were extracted in 1 mL hexane by vortex mixing (Touch Mixer 232, Fisher Scientific) for 30 seconds. For 1,2,4-TCB experiments in water, 0.5-mL samples were extracted in 1 mL hexane by vortex mixing for 1 minute. 1,2,4-TCB extraction efficiencies were 91% and 83-93%, respectively, for extraction from 40:60 acetone:water and from water.

Hexane extracts were analyzed on a Hewlett Packard 5890A gas chromatograph equipped with an electron capture detector (oven temperature at 100°C for 2 min, 15°C/min to 160°C, 5°C/min to 235°C, hold for 3 min, 15°C/min to 270°C, hold for 2 min). Two-microliter samples were injected to a splitless inlet at 225°C on an HP-5 column (30 m $\times$ 0.32 mm i.d. $\times$ 0.25 μ m film thickness). The instrument was calibrated using a set of six to ten 2,3',4',5-PCB or 1,2,4-TCB standards in hexane. The limits of detection for 1,2,4-TCB and 2,3',4',5-PCB extracts in hexane were 0.02 μ M and 0.4 μ M, respectively, as determined from the area of a chromatography peak 3 $\times$ larger than the noise of the instrument.

A Strobotac type 1531-A variable-frequency strobe light (General Radio Company) was used to estimate stirring rates in 2,3',4',5-PCB breakthrough experiments. The strobe light was aimed toward the upstream stir plate in a dark room. The frequency was adjusted until the stir bar appeared to be still, indicating that the stir bar had made a full rotation between flashes of light. Frequency was adjusted through a broad spectrum to ensure that the frequency capturing one full rotation (e.g., not a half rotation or two rotations) was properly identified.

The particle size distribution of the sieved PAC, suspended in Isoton II Diluent (Beckman Coulter) was measured on a Beckman Coulter Multisizer 3 with a 400 μ m aperture tube.

Digital photos of the PAC-containing HDPE and PVA membranes were taken using the 10 $\times$, 20 $\times$, and 40 $\times$ lenses of a Nikon Eclipse E600 microscope equipped with an MTI 3CCD camera.

Section S6. Effect of Acetone Content on HDPE-Solution Partition Coefficients

Membrane-water partition coefficients for 1,2,4-TCB and 2,3',4',5-PCB in aqueous solutions containing up to 40% acetone are shown in Figure S4. As expected, H decreases with increasing acetone content in the solution. The 2,3',4',5-PCB data are extrapolated to 0% acetone to estimate the partition coefficient between HDPE and sediment porewater in the environment.

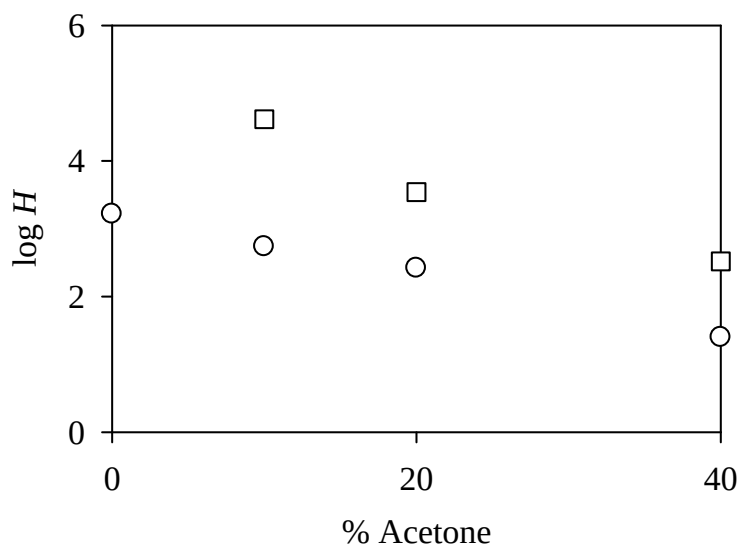


Figure S4. HDPE membrane-solution partition coefficients for 1,2,4-TCB (○) and 2,3',4',5-PCB (□) in water and in aqueous solutions containing up to 40% acetone.

The H values determined by fitting breakthrough curves to Equation 1 (Table 1) and those determined from equilibrium experiments (Figure S4) did not always agree. This result may be an artifact of leakage from the equilibrium experiments, although controls indicate that leakage was not a primary factor. A series of 2,3',4',5-PCB breakthrough experiments at various mixing rates were conducted to determine whether improper upstream mixing affected the apparent H in breakthrough experiments (Table 1 and Section S4). The resulting breakthrough curves showed a small effect of mixing on apparent D , but H was unaffected. Thus, we cannot explain with certainty the cause of the difference, but we do recognize the trend of increasing discrepancy with increasing H . This is a pattern discovered in our previous work (3), for which there is not a satisfying explanation as there is no apparent affect of mixing on H (Table 2). We have previously found, however, that modeling breakthrough experiments requires use of the H determined from breakthrough experiments.

Section S7. PAC Sorption Isotherms

Equilibrium data for the sorption of 1,2,4-TCB and 2,3',4',5-PCB onto PAC are given in Figures S3 and S4, respectively.

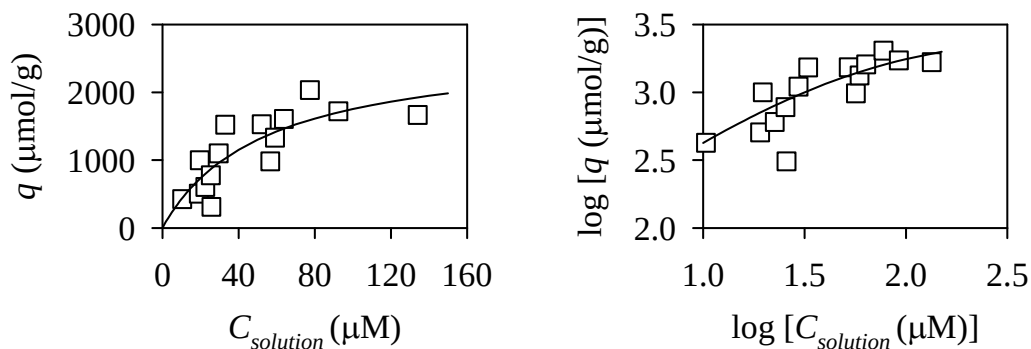


Figure S5. Equilibrium sorption data ($\square$) for 1,2,4-TCB sorption to PAC in water and a Langmuir isotherm fit with $q_{\text{max}}=3000\pm1000$ $\mu\text{mol/g}$ and $b=0.02\pm0.02$ L/ μmol (—).

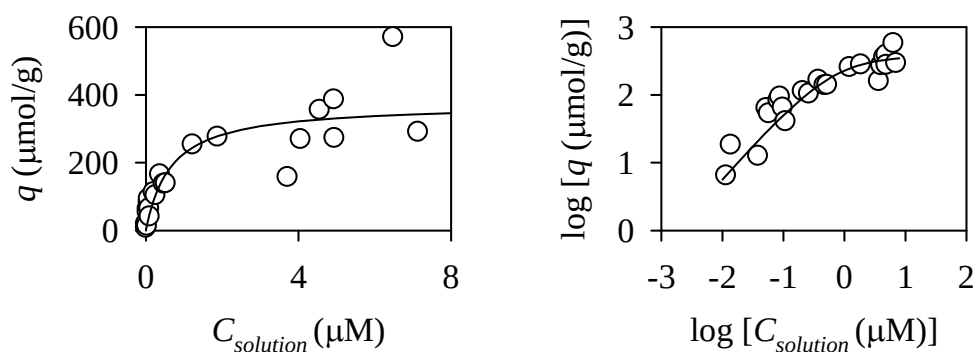


Figure S6. Equilibrium sorption data ($\circ$) for 2,3',4',5-PCB sorption to PAC in 40:60 acetone:water and a Langmuir isotherm fit with $q_{\text{max}}=370\pm80$ $\mu\text{mol/g}$ and $b=1\pm1$ L/ μmol (—).

Section S8. Microscope Images of PAC-Containing Membranes

Images of several PAC-containing membranes are shown in Figure S7. PAC particles in the HDPE membrane with 0.29 g PAC/cm³ (not shown) were too dense to allow light through for a photograph.

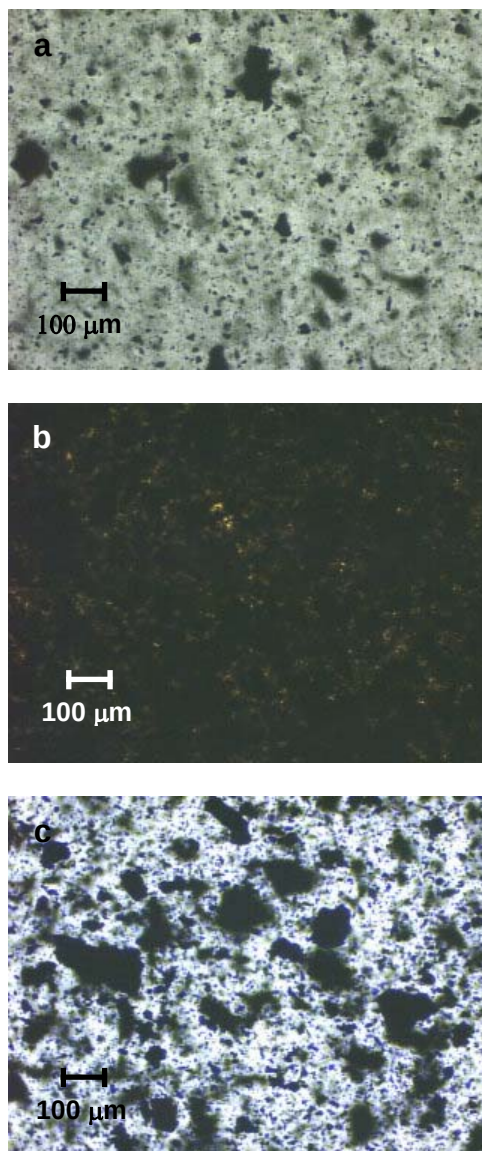


Figure S7. 10× magnified images of HDPE membranes containing 0.04 g PAC/cm³ (a) and 0.14 g PAC/cm³ (b) and PVA containing 0.05 g PAC/cm³.

Section S9. References

- (1) Ferrari, M.C.; Carranza, S.; Bonnacaze, R.T.; Tung, K.K.; Freeman, B.D.; Paul, D.R. Modeling of oxygen scavenging for improved barrier behavior: Blend films. *J. Membrane Sci.* **2009**, 329, 183-192.
- (2) Cussler, E.L. *Diffusion: Mass transfer in fluid systems*; Cambridge University Press: New York, NY, 1984.
- (3) Shimotori, T.; Cussler, E.L.; Arnold, W.A. High-density polyethylene membrane containing Fe⁰ as a contaminant barrier. *J. Environ. Eng.* **2006**, 132, 803-809.