Supporting Information

For

Remediation of Perfluorooctylsulfonate Contamination

by In-Situ Sequestration:

Direct Monitoring of PFOS Binding to Polyquaternium Polymers

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**Experimental Methods**

**Synthesis of 1,3-Di(1H,1H,2H,2H-perfluoro-7-methyloctyl)imidazolium Iodide**

One equivalent of 1H,1H,2H,2H-perfluoro-7-methyloctyl iodide was added to 3 equivalents of imidazole in ethyl acetate, and the reaction mixture was heated under argon at 77 °C (boiling point of ethyl acetate) for 48 h (Figure S1). The cooled reaction mixture was then extracted with 1 M NaCO₃, followed by three washes with deionized water to remove the unreacted imidazole. The organic phase was dried with Na₂SO₄ and the solvent evaporated under reduced pressure, resulting in the mono-substituted imidazole. The crude mono-substituted imidazole was dissolved in toluene, and 1.2 equivalents of 1H,1H,2H,2H-perfluoro-7-methyloctyl iodide was added. The reaction mixture was stirred and heated to boiling for 48 h. The disubstituted product precipitated from the reaction mixture and was collected by filtration. The product was washed with cold toluene (≈0 °C) and then dried under vacuum at room temperature. Its structure was confirmed by \(^1\)H NMR and mass spectrometry. \(^1\)H NMR: Rf(CH₂ (3.1 ppm, 4H, m), CH₂CH₂ (4.9 ppm, 4H, t), NCHN (9.8 ppm, 1H, s), and NCHC (8.1 ppm, 2H, d). The exact mass as measured with a Bruker BioTOF II ESI/TOF-MS was 861.0421, which matches the expected value of 861.0443.

![Reaction scheme](image)

**Figure S1.** Reaction scheme for the synthesis of the fluorophilic imidazolium iodide.
Synthesis of 1,3-Di(1H,1H,2H,2H-perfluoro-7-methyloctyl)imidazolium Tetrakis[3,5-bis-(perfluoroctyl)phenyl]borate

Sodium tetrakis[3,5-bis(perfluoroctyl)phenyl]borate was synthesized as reported previously.\(^1\)

1,3-Di(1H,1H,2H,2H-perfluoro-7-methyloctyl)imidazolium tetrakis[3,5-bis(perfluoroctyl)-phenyl]borate was synthesized by metathesis from 1,3-di(1H,1H,2H,2H-perfluoro-7-methyloctyl)imidazolium iodide and sodium tetrakis[3,5-bis(perfluoroctyl)phenyl]borate. One equivalent of each salt was dissolved in perfluorohexanes. The mixture was extracted three times with water, and the perfluorohexane portion was collected and dried with MgSO\(_4\). The solvent was removed by evaporation and the product dried under reduced pressure for 48 h, resulting in a wax-like colorless solid. Its structure was confirmed by \(^1\)H NMR spectroscopy (perfluorohexane with a D\(_2\)O capillary). \(^1\)H NMR: 1,3-Di(1H,1H,2H,2H-perfluoro-7-methyloctyl)imidazolium \([\text{Rf}_7\text{CH}_2 (2.37 \text{ ppm, 4H, t}), \text{CH}_2\text{CH}_2 (3.91 \text{ ppm, 4H, t}), \text{NCHN (7.42 ppm, 1H, s}), \text{and NCHC (6.68 ppm, 2H, d})]\) and tetrakis[3,5-bis(perfluoroctyl)phenyl]borate \([\text{Rf}_6\text{CCHCRf}_6 (7.64 \text{ ppm, 4H, s}) \text{ and Rf}_6\text{CCHCCHCRf}_6 (7.73 \text{ ppm, 8H, s})]\). This solid was used directly for the preparation of ion-selective membranes.

Preparation of PFOS-Selective Membranes

Fluoropore membrane filters (polytetrafluoroethylene, 0.45 um pore size, 50 um thick, 85% porosity) were cut with a 19 mm O.D. circular punch. The cut filters were mounted onto custom poly(chlorotrifluoroethylene) electrode bodies sandwiched between two Viton washers (Figure S2). The filter disk was filled with 40 \(\mu\)L of the membrane solution (which turned opaque as a result of the liquid addition), and the electrode was assembled. The membrane was contacted on the top by an inner filling solution composed of 15 \(\mu\)M KCl and 10 \(\mu\)M potassium perfluoroctyl-1-sulfonate (KPFOS), and the inner compartment of the electrode body and was sealed with a
rubber septum. A AgCl coated Ag wire was inserted through the septum to contact the inner filling solution.

Electrodes were placed so that the outer surface of the membrane was in contact with a stirred solution of 10 mM NaHCO₃ (pH=7.0, adjusted with 1.0 M HCl) and 50 µM KPFOS. The membranes were allowed to equilibrate for two days. For further information on the buffer preparation, see page S7.

**Figure S2.** Schematic of custom-made poly(chlorotrifluoroethylene) electrode bodies; design of the electrode bodies by Xin V. Chen.

**Potentiometric Measurements**

Potential measurements were performed using a Lawson Labs EMF 16 channel potentiometer (Malvern, PA) controlled by EMF Suite 1.02 software. All measurements were performed in stirred solutions at room temperature (23 ± 2 °C). Potentials were measured relative to a Mettler
Toledo DX200 free-flowing double junction (with a 1.0 M LiOAc bridge electrolyte and AgCl saturated 3.0 M KCl inner reference electrolyte). A Hanna Instruments pH glass electrode was used to monitor pH. Calibration of the pH electrode was carried out using buffered solutions of pH 10, 7, and 4. A schematic of the experimental setup is pictured in Figure S3.

![Experimental setup](image)

**Figure S3.** Experimental setup used for the measurement of binding of PFOS to polyquaternium polymers.

**Nikolskii-Eisenman Equation**

The Nikolskii-Eisenman equation describes the response of an ion-selective electrode that also includes selectivity against an interfering ion (j) as follows:

\[
E = E^0 + \frac{RT}{zF} \ln (a_{PFOS} + K_{PFOS/j} a_j^{1/2})
\]  

(S1)

where \( K_{PFOS/j} \) is the selectivity coefficient of the ion-selective electrode for PFOS over ion j, \( a_j \) is the activity of ion j, and \( z_j \) is the charge of ion j. For the PFOS-selective electrodes described here, the limit of detection, \([PFOS]_{\text{limit}}\), in not caused by interfering ions, but it is determined by KPFOS flux from the inner filling solution to the sample solution. Therefore, eqn. S1 can be simplified by substituting the concentration for activity and PFOS for ion j (resulting in \( K_{PFOS/PFOS} = 1 \)):

\[
E = E^0 + \frac{RT}{zF} \ln ([PFOS] + [PFOS]_{\text{limit}})
\]  

(S2)
Eqn. S2 was used for all fits of data when polycations and soil were absent. [PFOS]_limit was determined to be 4.6 ± 1.5 µM (95% confidence interval).

**Calculation of the Free Concentration of PFOS in a System Containing Polyquaternium Polymers**

Continuing the derivation from eqns 3 and 4, it follows that formation of [PFOS-R] causes a decrease of [R]_free:

\[
[R]_\text{free} = [R]_\text{total} - [\text{PFOS-R}] \tag{S3}
\]

Replacing [R]_free in eqn 4 with the right hand side of eqn S3 and solving the resulting equation for [PFOS]_free gives:

\[
\text{[PFOS]}_\text{free} = \frac{[\text{PFOS}]_\text{total}}{K ([R]_\text{total} - [\text{PFOS-R}])} \tag{S4}
\]

Furthermore, [PFOS-R] can be related to [PFOS]_free since formation of [PFOS-R] leads to the reduction of [PFOS]_free:

\[
[R]_\text{total} = [\text{PFOS}]_\text{total} - [\text{PFOS}]_\text{free} \tag{S5}
\]

Insertion of the right hand side of eqn S5 for [PFOS-R] into eqn S4 gives

\[
\text{[PFOS]}_\text{free} = \frac{([\text{PFOS}]_\text{total} - [\text{PFOS}]_\text{free})}{K ([R]_\text{total} - [\text{PFOS}]_\text{total} + [\text{PFOS}]_\text{free})} \tag{S6}
\]

Solving eqn S6 for [PFOS]_free using the quadratic formula gives only one physically meaningful solution:

\[
\text{[PFOS]}_\text{free} = \frac{(-1 + K [\text{PFOS}]_\text{total} - K [R]_\text{total} + \sqrt{4 K [\text{PFOS}]_\text{total} + (1 - K [\text{PFOS}]_\text{total} + K [R]_\text{total})^2})/(2 K} \tag{S7}
\]

Eqn S7 is identical with eqn (5) of the main manuscript.
**Average Concentration of Charged Repeat Units within a Polyquaternium Polymer Chain**

In order to determine the concentration of binding sites of each polycationic polymer, the effective charged repeat unit concentration was calculated for both poly(diallyldimethylammonium) chloride (MW = 340,000; repeat unit MW = 161.67) and poly(dimethylamine-co-epichlorohydrin); (MW = 240,000; repeat unit MW = 137.61) based on the molecular weight and repeat unit molecular weight.

**NaHCO₃ as a Buffer**

Due to the environmental relevance of bicarbonate solutions, 10.0 mM NaHCO₃ was adjusted to pH=7.0 with 1.0 M HCl and was used as the buffer for all experiments. When storing solutions of this composition in stirred open beakers with direct exposure to the ambient atmosphere and monitoring the pH with a pH glass electrode, it was observed that over 50 hours the pH (initially adjusted to 7) increased by 2 pH units (Figure S4).

![Figure S4](image)

**Figure S4.** pH of a 10 mM NaHCO₃ solution after adjustment to pH=7. pH was measured using a pH glass electrode relative to a free-flowing double junction reference electrode.

However, this pH change did not have an effect on the PFOS measurements, which is consistent with the lack of any effect of carbonate or bicarbonate on the limit of detection of the electrode.
However, changes in pH alter the total ionic strength of these solutions. We conclude that bicarbonate solutions of pH 7 may represent environmental samples well, but are not good pH buffers or good ionic strength buffers in a strict sense.

Figure S5. Predicted $E$ versus the logarithm of the polycationic polymer concentration, expressed in terms of the total concentration of charged polymer repeat units. Solid black, dashed blue, and dotted red lines are predicted for $K = 5 \times 10^5$, $1 \times 10^2$, and $1 \times 10^4$, respectively. For these simulations, values of $[\text{PFOS}]_{\text{total}}$ and $E^{0+}$ were chosen as 41.6 µM and −63.8 mV, respectively.
Figure S6. $E$ values collected during the stepwise addition of poly(diallyldimethylammonium) chloride to a 25.4 µM KPFOS solution (10 mM NaHCO$_3$, pH = 7). Black x, blue diamonds, and green triangles represent experimental results for three separate electrodes. Solid black, dashed blue, and dotted green lines represents data fitted to eqn 9.
Figure S7. $E$ values collected during the stepwise addition of poly(dimethylamine-co-epichlorohydrin) to a 25.4 µM KPFOS solution (10 mM NaHCO$_3$, pH = 7). Black ×, blue diamonds, and green triangles represent experimental results for three separate electrodes. Solid black, dashed blue, and dotted green lines represents data fitted to eqn 9.

Table S1. Potential of PFOS selective electrodes in the presence of 0.35 mM PFOS and increasing concentrations of Tinker soil.

| PFOS (mM) | Tinker Soil (g/L) | Electrode 1 (mV) | Electrode 2 (mV) | Electrode 3 (mV) |
|-----------|-------------------|------------------|------------------|------------------|
| 0.35      | 0.00              | 157              | 181              | 178              |
| 0.35      | 0.06              | 158              | 181              | 178              |
| 0.35      | 0.31              | 158              | 181              | 178              |
| 0.35      | 0.94              | 158              | 181              | 178              |
| 0.35      | 4.69              | 159              | 181              | 178              |
| 0.35      | 10.94             | 159              | 182              | 179              |
| 0.35      | 14.69             | 159              | 182              | 179              |
Figure S8. $E$ values collected during the stepwise addition of poly(diallyldimethylammonium) chloride/soil mixture to a 325 µM KPFOS solution (10 mM NaHCO₃, pH = 7). Black ×, blue diamonds, and green squares represent experimental data for three separate electrodes. Solid black, dashed blue, and dotted green lines represents data fitted to eqn 9 for $K = 2.7 \times 10^5$ M⁻¹.

Figure S9. $E$ values collected during the stepwise addition of poly(dimethylamine-co-epi-chlorohydrin)/soil mixture to a 325 µM KPFOS solution (10 mM NaHCO₃, pH = 7). Black ×, blue diamonds, and green squares represent data for three separate electrodes. Solid black, dashed blue, and dotted green lines represent data fitted to eqn 9 for $K = 6.4 \times 10^5$ M⁻¹.
Figure S10. Predicted $E$ versus the logarithm of the polycationic polymer concentration, expressed in terms of total concentration of charged polymer repeat units. Solid black and dashed blue lines are predicted for $K = 5 \times 10^5$, $[\text{PFOS}]_{\text{total}} = 41.6$ µM, and $E^{\infty} = -63.8$ mV. The solid black line is predicted assuming that 100% of the polymer is available for binding, and the dashed blue line is based on the assumption that only 10% of the polymer is available for binding.

Figure S11. $E$ values measured during the stepwise addition of a poly(diallyldimethylammonium) chloride/soil mixture to a 350 µM KPFOS solution (10 mM NaHCO$_3$, pH = 7.0). Black $\times$, blue diamonds, and green triangles represent experimental results for three separate electrodes. Solid black, dashed blue, and dotted green lines represent data fits using eqn 9.
**Figure S12.** $E$ values measured during the stepwise addition of a poly(dimethylamine-\textit{co}-epi-chlorohydrin)/soil mixture to a 350 µM KPFOS solution (10 mM NaHCO$_3$, pH = 7.0). Black $\times$, blue diamonds, and green triangles represent experimental results for three separate electrodes. Solid black, dashed blue, and dotted green lines represent data fits using eqn 9.

**Figure S13.** Plot showing the concentration of unbound PFOS versus the total amount of PFOS in a system. The dashed black line shows the EPA health advisory PFOS level ($\log_{10}[1.86 \text{ pM}] = -11.7$). The solid line in black stands for a system without polymer. All other lines are labeled with the concentration (in g/L) of the soil-bound poly(dimethylamine-\textit{co}-epichlorohydrin) polymer. Colored diamonds refer to experimental data points taken from Figure 8 and S12.
Table S2. $[R]_{\text{total}}$ needed to bind a targeted fraction of PFOS with $K = 9.3 \times 10^4$ M$^{-1}$.

| Fraction PFOS Bound | $[R]_{\text{total}}$ (M) | Binding Capacity (mol PFOS bound per mol of polymer repeat unit) |
|---------------------|--------------------------|---------------------------------------------------------------|
| 0.5                 | $1.07 \times 10^{-5}$   | $4.67 \times 10^{-5}$                                       |
| 0.9                 | $9.67 \times 10^{-5}$   | $9.31 \times 10^{-6}$                                       |
| 0.95                | $2.04 \times 10^{-4}$   | $4.66 \times 10^{-6}$                                       |
| 0.99                | $1.06 \times 10^{-3}$   | $9.34 \times 10^{-7}$                                       |

References

1. Boswell, P. G.; Bühlmann, P., Fluorous bulk membranes for potentiometric sensors with wide selectivity ranges: Observation of exceptionally strong ion pair formation. *J. Am. Chem. Soc.* **2005**, *127*, 8958-8959.