Predicting the Congener-Specific Environmental Behaviour of Perfluorinated Acid Contaminants Using Semi-Empirical Computational Methods

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Introduction

- Perfluorinated acids (PFAs) are contaminants detected worldwide in a range of abiotic and biotic environmental matrices
- Two major classes of PFAs include the perfluorinated sulfonic acids (PFSAs) and perfluorinated carboxylic acids (PFCAs)

- Both classes are considered persistent, bioaccumulative, and subject to long-range transport
- Both classes have low rates of hydrolysis, direct photolysis, and biodegradation/metabolism in environmental systems (1,2)
- Current research and regulatory efforts focussed on the straight-chain members of each PFA class and homologue group, primarily because these congeners are the major components of technical mixtures and are also available as pure standards
- Numerous potential branched congeners in each PFA class are a poorly understood family of contaminants whose environmental and toxicological properties may be more important than the straight-chain members
- Current work applied established quantitative structure and reactivity (QSAR) models for other multi-class emerging and legacy contaminants to estimate key parameters related to the congener-specific environmental fates of PFSAs and PFCAs

Methods

- Number of PFA congeners increases exponentially with perfluorinated chain length
- Practical to compute properties for all congeners only up to ~C₂₈ (there are 161 C₁ through C₈ congeners)
- Then look for statistical relations between chain length and C₁ through C₈ properties to extend our understanding to ≥C₉
- Semiempirical molecular descriptors were calculated for all C₁ through C₈ PFSAs and PFCAs and the straight-chain C₉, C₁₀, and C₁₁ PFCAs congeners
- Initial geometry optimization using MM2 followed by energy minimization and computations using AM1 and PM3 basis sets

Figure 1. Relationship between number of congeners in each homologue group and the perfluoroalkyl chain length (PCL). The actual number of congeners in each homologue group was determined for C₁ through C₈ and extrapolated for C₉ through C₁₁. A second-order polynomial regression equation of the form $\log_{10}(n) = -0.5 + 0.248 \times \text{PCL} + 0.00758 \times \text{PCL}^2$ ($r^2 = 0.9999$) is shown.

Results

1. Bioconcentration Factors (BCFs)

- Model developed with regressions between computed molecular areas and volumes and BCFs reported for straight-chain C₆ to C₈ PFSAs and C₇ to C₁₁ PFCAs (3)
- Used to estimate BCFs for all C₁ through C₈ PFSAs and PFCAs congeners ⇒ PFSAs ~10-fold higher BCFs than PFCAs

Area-based approaches result in a more continuous C₁ to C₈ BCF distribution and significant homologue mixing **versus** volume-based approach = homologue isolation

Figure 2. Estimated BCFs of all C₁ through C₈ (a) PFSAs and (b) PFCAs congeners based on correlations with the calculated Connolly accessible area (CAA), Connolly molecular area (CMA), and Connolly solvent excluded volume (CSEV) using the PM3 semiempirical basis set (AM1 data not shown for brevity). Values represent the mean BCF value from the correlations. Error bars signify lower and upper error limits based on the regression relationships.

Summary statistics for the PFSAs and PFCAs C₁ through C₈ BCF training sets can be reliably predicted ⇒ allows reliable estimation of homologue-specific BCF distributions for ≥C₉

Figure 3. Predicted mean, minimum, maximum, and standard deviation of estimated BCFs for C₁ through C₁₁ (a) PFSAs and (b) PFCAs congeners using the calculated Connolly accessible area (CAA; (i) and (iv)), Connolly molecular areas (CMA; (ii) and (v)), and Connolly solvent excluded volumes (CSEV; (iii) and (vi)) with the AM1 and PM3 semiempirical basis sets. Regression lines were developed based on calculated BCFs for all C₁ through C₈ PFCAs congeners.

Results

2. Atmospheric Reaction with Hydroxyl Radicals (k_{OH})

- Model developed with well-established regressions between ionization potentials (IPs) and k_{OH} values for a wide range of aliphatic compounds (4-6)
- Calibrated for PFAs using published experimental k_{OH} data for the C₁-C₄ straight chain PFCAs (7), C₁-C₃ fluorotelomer alcohols/aldehydes (8-10), and C₄ perfluoroalkyl sulfonamide derivatives (11,12)
- Used to estimate atmospheric lifetimes (τ_{OH}) for all C₁ through C₈ PFSAs and PFCAs and the straight-chain C₉, C₁₀, and C₁₁ PFCAs congeners ⇒ PFSAs and PFCAs have ≈ τ_{OH}

Figure 4. Estimated atmospheric lifetimes of the C₁ through C₈ PFSAs and PFCAs and C₉, C₁₀, and C₁₁ straight-chain PFCAs congeners using the AM1 (a) and (b) and PM3 (c) and (d) basis sets.

3. Abiotic Reductive Defluorination Rates (k_{red})

- Recent work shows qualitative proof-of-principle that C₂-C₈ PFSAs can be reductively defluorinated (13,14)
- Model developed with established relationships between the energy of the lowest unoccupied molecular orbital (e_{LUMO}) and surface-area normalized reduction rate constants (k_{red}) using zero-valent metal reductants (e.g., Fe, Mg) across a range of halogenated aliphatic and aromatic contaminants (15-17)
- In absence of quantitative PFA k_{red} "benchmarks", values were normalized to the minimum estimated k_{red} within each basis set among all C₁ through C₈ PFSAs and PFCAs congeners (k_{red,min})

Figure 5. Estimated average relative rates of abiotic reductive defluorination within each C₁ through C₁₁ homologue group for PFSAs and PFCAs. Regression lines were developed based on calculated BCFs for all C₁ through C₈ PFCAs congeners. Error bars show standard deviations in k_{red,min} within each homologue group.

Results

Both AM1 and PM3 basis sets predict higher reductive defluorination rates for the more branched PFSAs congeners in each homologue group

⇒ no similar trends expected for PFCAs (chain-length effect dominates)

Figure 6. Estimated relative rate constants for the abiotic reductive defluorination (k_{red}/k_{red,min}) of the C₁ through C₈ PFSAs and PFCAs and C₉, C₁₀, and C₁₁ straight-chain PFCAs congeners using the AM1 (a) and (b) and PM3 (c) and (d) basis sets.

Conclusions and Recommendations

- Findings provide guidance for:
 - developing new analytical methods for separating and identifying PFAs in environmental and technical mixtures
 - prioritizing efforts on synthesizing authentic standards
 - focussing toxicological studies on the congeners most likely to be of concern
- Molecular area approach to estimating BCFs suggests wide variability within homologue groups ⇒ while volume approach indicates low variability:
 - need to determine which model best applies via targeted synthesis of selected congeners and BCF testing
 - e.g., (C₆ PFSAs-23) perfluoro-1,1,2,2-tetramethylbutylsulfonic acid predicted to have BCF >120-fold higher using volume versus area
 - also, (C₆ PFCAs-28) perfluoro-2,2,3,3-tetramethylbutylcarboxylic acid predicted to have BCF >100-fold higher using volume versus area

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References

- ¹ Vanden Heuvel et al. (1991) *Toxicol Appl Pharmacol* 107, 450-459. ² Goetzke et al. (1992) *Chem Res Toxicol* 5, 512-519. ³ Martin et al. (2003) *Environ Toxicol Chem* 22, 196-204. ⁴ Gusten et al. (1984) *J Atmos Chem* 2, 83-93. ⁵ Gaffney and Levine (1979) *Int J Chem Kinet* 11, 1187-1209. ⁶ Atkinson (1986) *Chem Rev* 85, 69-201. ⁷ Hurley et al. (2004) *J Phys Chem A* 108, 615-620. ⁸ Ellis et al. (2003) *Environ Sci Technol* 37, 3816-3820. ⁹ Wallington et al. (2006) *Environ Sci Technol* 40, 924-930. ¹⁰ Selleva et al. (2004) *Phys Chem Chem Phys* 6, 1243-1252. ¹¹ O'Eon et al. (2006) *Environ Sci Technol* 40, 1862-1868. ¹² Martin et al. (2006) *Environ Sci Technol* 40, 864-872. ¹³ Hori et al. (2006) *Environ Sci Technol* 40, 1049-1054. ¹⁴ Ochoa-Herrera et al. (2008) *Environ Sci Technol* 42, 3260-3264. ¹⁵ Scherer et al. (1996) *Environ Sci Technol* 30, 3026-3033. ¹⁶ Chen et al. (2002) *SAR QSAR Environ Res* 13, 597-606. ¹⁷ Onanong et al. (2007) *Environ Sci Technol* 41, 1200-1205.