Measurement of n-Alcohol/Water Partition Coefficients for Nonionic Perfluorocarbons

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Abstract

Per- and poly-fluorinated compounds (PFAS) are a group of chemicals created by humans, that have become a growing concern in the environment. To predict and model the movement of PFAS chemicals through the environment, partition coefficients such as n-octanol-water (K_{OW}), organic carbon-water (K_{OC}), and Henry's law constants (H) are needed. Measurements for K_{OW} are limited for PFASs and using the OECD-123 Slow Stir method, we have measured the log K_{OW}s of octafluoronaphthalene (3.53 sd=0.076, n=12), decafluorobiphenyl (4.58 sd=0.036, n=5), and decachlorobiphenyl (PCB209) (8.16 sd=0.13, n=5). Measurements are underway on four aliphatic fluorocarbons: perfluorodecalin, perfluorooctane, perfluorodecane, and perfluoropentadecane. The measured K_{OW}s will be compared to predictions from a variety of predictive methods including EPISuite, OPERA, ACD, and Chemaxon. n-Butanol/water partition coefficients (K_{BW}) are also being measured to determine if the K_{OW}-K_{BW} pairs reside on the linear free energy relationship between these partition coefficients developed using non-fluorinated organic chemicals. We have measured the log K_{BW}s of hexachlorobenzene (4.04 sd=0.055, n=4), and octafluoronaphthalene (3.00 sd=0.053, n=6).

Introduction

n-Octanol/water partition coefficients (K_{OW}s) are an important parameter used to assess environmental fate, bioaccumulation, and effects of organic chemicals

- Traditionally, the K_{OW} is measured
- If not measured, K_{OW} is estimated
  - EPI-Suite, ACD/Labs, ChemAxon, SPARC, …
- For highly fluorinated chemicals, measurements are lacking.

Objectives

- Measure K_{OW}s for a few nonionic perfluorinated organic chemicals
- Measure K_{BW}s for a few nonionic perfluorinated organic chemicals
- Compare measurements of K_{OW}s to values estimated using software models
- Evaluate if $K_{OW} - K_{BW}$ pairs align with linear free-energy relationship developed using non-fluorinated chemicals.

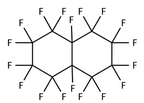
Slow Stir Measurement Method

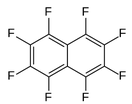
Available Techniques

- Slow Stir: OECD 123

Chemicals

- Hexachlorobenzene (HCB)
- Decachlorobiphenyl (PCB209)
- Decafluorobiphenyl (DFBP)
- Octafluoronaphthalene (OFNE)
- Perfluorooctane (PFO)
- Perfluorodecane (PFD)
- Perfluorodecalin (PFDC)



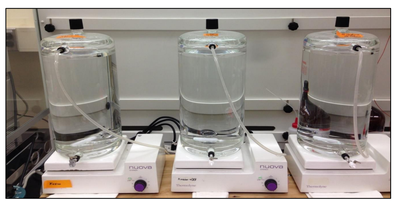


Approaches

- Sample both Octanol and H_2O layers of stir
- Using analytical techniques and GCMS instrumentation, quantify the concentration of analyte in each phase

- Aqueous Sample Volume Varied Based on Compound
- Higher K_{OW} value chemicals required larger H_2O samples for GCMS detection

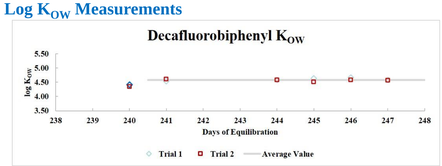
Chemical	Sample size	Extraction Solvent
HCB	5 mL	Hexane
DFBP	50 mL	Hexane
OFNE	50 mL	Pentane
DCBP	500 mL	Pentane
PFO	N.D.	Pentane
PFD	N.D.	Pentane
PFDC	N.D.	Pentane

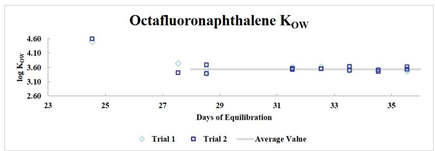


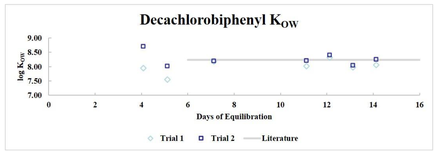
Slow stir apparatus

Log K_{OW} and Log K_{BW} Measurement Results

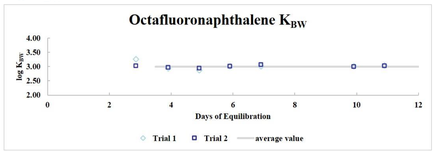
Log K_{OW} Measurements

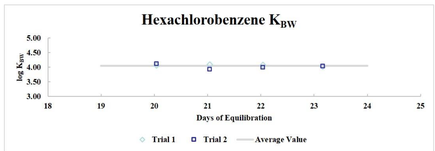






Log K_{BW} Measurements





Measured and predicted K_{OW}s and K_{BW}s

Chemical	Measured log K_{OW}	Measured log K_{BW}	Literature log K_{OW}	Predicted log K_{OW}s: EPI_Suite	OPERA	ACD/Labs	ACD/Labs Consensus
HCB	--	4.07 ± 0.030	5.73 ± 0.009	5.86	5.73	4.89	5.35
PCB209	8.11 ± 0.15	--	8.22 ± 0.17 (10)	10.20	8.38	8.10	8.30
DFBP	4.59 ± 0.026 (4)	--	--	5.76	5.73	5.81	4.44
OFNE	3.53 ± 0.008 (2)	2.99 ± 0.016 (2)	--	4.77	4.58	3.61	3.63
PFO	--	--	--	7.95	4.62	7.43	6.59
PFD	in progress	in progress	--	9.88	5.08	9.21	7.95
PFDC	--	--	--	7.80	8.35	6.03	5.62

Correlation between K_{BW} and K_{OW}

Background

- Partition coefficients in different solvent systems are correlated:

$$\log K_1 = a \cdot \log K_2 + b$$ Collander (1951 Acta Chem Scand 5:774-780)

Collander (1951)

$$\log K_{iso\text{-}pentanol} = 1.17 \log K_{iso\text{-}butanol} - 0.17$$
$$\log K_{octanol} = 1.24 \log K_{iso\text{-}butanol} - 0.42$$

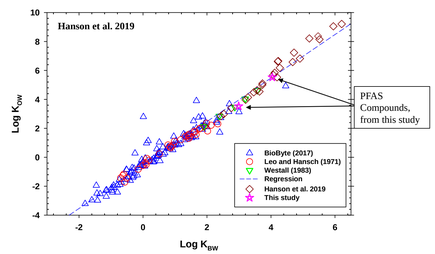
- Leo and Hansch (1971)

	(*n*	*r*)
$\log K_{oleyl\ alcohol} = 0.999 \log K_{n\text{-}octanol} - 0.575$	(37,	0.985)
$\log K_{n\text{-}pentanol} = 0.808 \log K_{n\text{-}octanol} + 0.0271$	(19,	0.987)
$\log K_{n\text{-}butanol} = 0.697 \log K_{n\text{-}octanol} + 0.381$	(57,	0.993)
$\log K_{2\text{-}butanone} = 0.493 \log K_{n\text{-}octanol} + 0.315$	(9,	0.987)
…		

Results

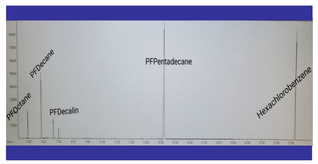
Evaluating Octafluoronaphthalene K_{BW} – K_{OW} Pair

K_{BW} = 2.99 ±0.016 K_{OW} = 3.53 ±0.008



Observations

Pair follows the linear free-energy relationship of non-fluorinated chemicals



Conclusions, Predictions, & Next Steps

- Aromatic fluorocarbons: Successful measurements of K_{OW} and K_{BW}
- Alphatic fluorocarbons: Measurements in progress
- Comparison of predicted K_{OW}s to measured K_{OW}s for aromatic fluorocarbons:
  - EPI Suite:
    - Predicted > measured by ten-fold for DFBP & OFNE
  - OPERA:
    - Predicted > measured by ten-fold for DFBP & OFNE
  - ACD/Labs:
    - DFBP: predicted > measured by ten-fold
    - OFNE: accurate prediction of measured value
  - ACD/Labs Consensus:
    - Accurate prediction of measured values for DFBP & OFNE
- Linear free relationship between partition coefficients
  - OFNE: K_{OW}-K_{BW} pair in agreement with relationship developed using non-fluorinated chemicals
- Nest Steps:
  - Complete measurements on aliphatic fluorocarbons
  - Transition to measurements on perfluorocarbon alcohols, amides …

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Acknowledgements

Plan: Chemical Safety for Sustainability Research Plan (CSS)
Research Area: Ecotoxicological Assessment and Monitoring (ETAM)
Task: CSS.6.6 — Improve ecological methods and models for predicting exposure, accumulation and effects of PFAS and other methodologically challenging compounds.
Product: CSS.6.6.1 — Methodically Challenging Chemicals (MCCs): Bioaccumulation of MCCs by Fish and Benthic Invertebrates

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