# Measurement of Octanol-Water and Butanol-Water Partition Coefficients for Per- and Poly-fluorinated Alkyl Substances.

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## Introduction

Per-and-poly-fluorinated alkyl substances (PFAS) are a diverse class of synthetic compounds found ubiquitously in the environment. Certain PFAS are demonstrated to bioaccumulative, toxic, and resistant to degradation. Octanol-water partition coefficients ($K_{OW}$) are useful properties that can be used to predict the environmental fate, bioaccumulation, and toxicity of chemicals. However, log $K_{OW}$ values predicted by various computational models are inconsistent, likely because those models were calibrated using data from neutral and non-perfluorinated organic chemicals. For example, the EPA's CompTox Chemical Dashboard lists a range of model-predicted log $K_{OW}$ values for PFOA (perfluorooctanoic acid) from 3.1-7.8. Experimental data for octanol-water partition values of PFAS are rare and in some cases derived from indirect measurements. The paucity of reliable partitioning data for PFAS is a critical data gap that hinders the development of predictive models. As such, the purpose of this work is to experimentally measure $K_{OW}$ values for a range of PFASs within the homologue series of carboxylates, sulfonates, sulfonamides, and fluorotelomer sulfonates (see structures below in descending order). In addition, the butanol-water partition coefficient ($K_{BW}$) was determined for some PFAS to determine if previously established relationships between log $K_{OW}$ and log $K_{BW}$ hold true for PFAS.

## Methods
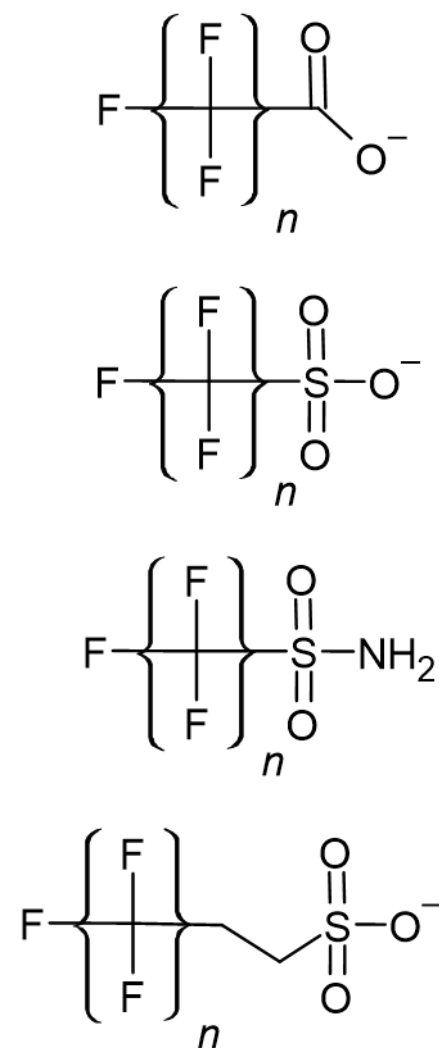
The procedure followed the OECD guidelines for determining octanol-water partition coefficients by the slow-stir method. Briefly, select PFAS were dissolved separately into water-saturated solvent (either octanol or butanol). After the chemical was disolved, 100-300 mL of the solvent solution was added to a slow stir apparatus (pictured above to the right) containing 3.5 L of solvent-saturated deionized water. For some experiments, the water was acidified with HCl, for the purpose of exploring pH dependency on partitioning. The experiments were temperature controlled at 25.0 °C using a water jacket. After a minimum of three days of gentle stirring, organic and aqueous samples were taken and analyzed by high-performance liquid chromatography coupled to a single quadrupole mass spectrometer by electrospray ionization. A minimum of eight separate determinations of log $K_{OW}$ and log $K_{BW}$ were made over at least four separate days from two independent tests. For the partition coefficient measurement to be valid, the slope of the partitioning coeffient as a function of time was required to be statistically not different than zero (p≤0.05). Measurements of pH were taken throughout each experiment, except for PFOSA.

## Log $K_{OW}$ vs. Number of Perfluorinated Carbons
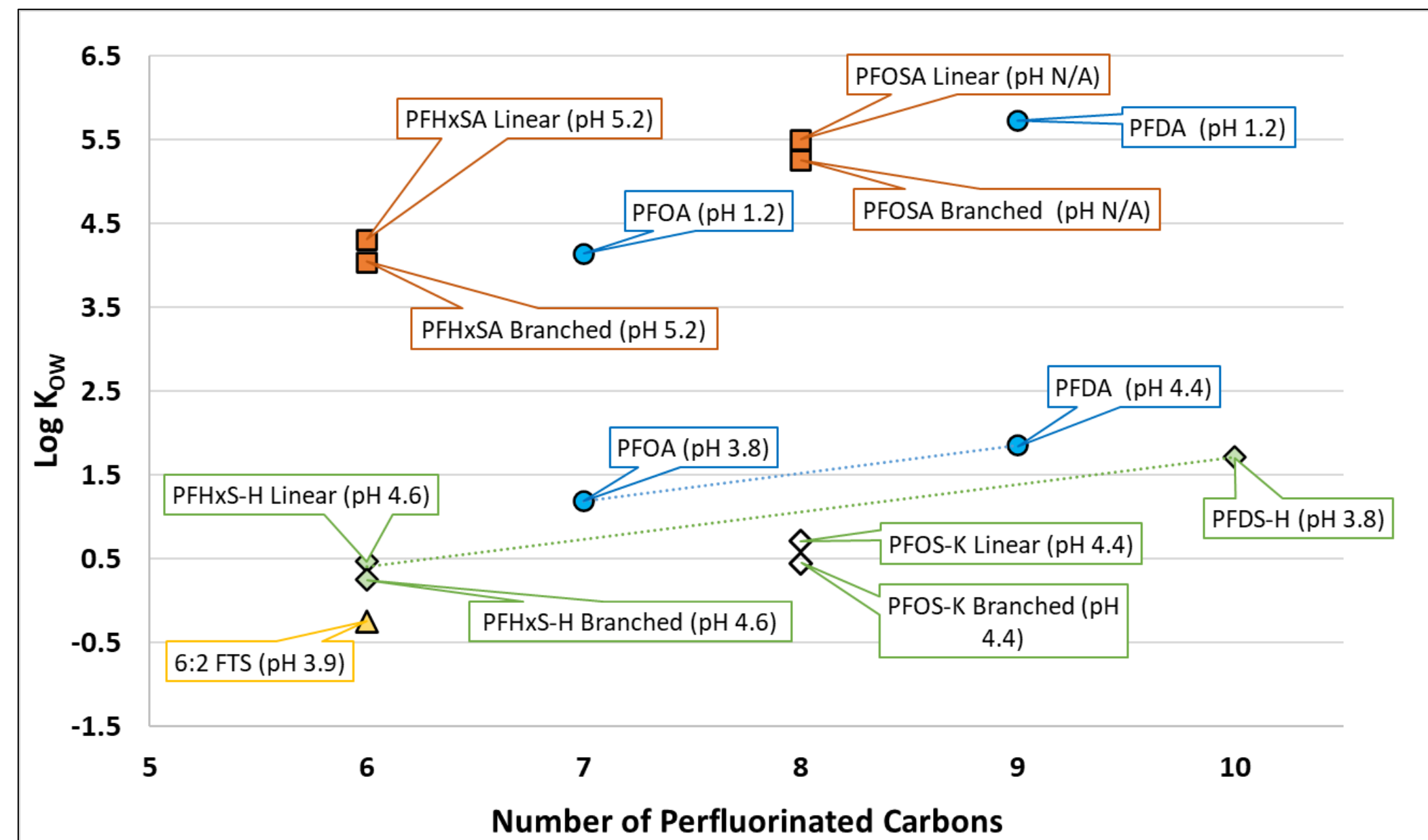


- Log $K_{OW}$ increases with increasing chain length.
- The mass balance of each experiment was an average of 96 ± 8% (95% C.I.) with a range of 76-110 %.
- On average the linear isomers had a log $K_{OW}$ value of 0.25 ± 0.03 (95% C.I.; n=4) greater than their branched counterparts (all branced species were integrated together).
- There was a significant increase (3-4 log units) in log $K_{OW}$ between experiments using unmodified water and acidified water.
- The PFOS-K results are suspect. PFOS-K was tested at octanol concentrations of 300, 25, and 8.3 mg/L resulting in log $K_{OW}$ values of 0.08, 0.56, and 0.71 (graphed), respectively.

## Measured log $K_{OW}$ vs. KOWWIN Predicted Values

| Chemical | Measured log $K_{ow}$ | Predicted log $K_{ow}$ | Δ log $K_{ow}$ |
|---|---|---|---|
| 6:2 FtS (pH 3.9) | -0.24 | 2.7 | 2.9 |
| L-PFHxS (pH 4.6) | 0.47 | 3.2 | 2.7 |
| L-PFOS (pH 4.4) | 0.71 | 4.5 | 3.9 |
| PFDS-H (pH 3.8) | 1.7 | 5.8 | 4.1 |
| PFOA (pH 3.8) | 1.2 | 4.8 | 3.6 |
| PFDA (pH 4.4) | 1.9 | 6.2 | 4.3 |
| PFOA (pH 1.2) | 4.2 | 4.8 | 0.61 |
| PFDA (pH 1.2) | 5.7 | 6.2 | 0.45 |
| L-PFHxSA (pH 5.2) | 4.3 | 4.5 | 0.16 |
| L-PFOSA (pH N/A) | 5.5 | 5.8 | 0.30 |

Measured log $K_{OW}$ values agree well with KOWWIN™ predicted values for compounds that are neutral (PFHxSA and PFOSA) or are assumed to be mostly neutral (PFOA and PFDA @ pH 1.2). KOWWIN™ predicts partition coefficients using the atom/fragment contribution method.

## Log $K_{BW}$ vs. Log $K_{OW}$



$$log (Kow) = 1.5log (Kbw) - 0.53$$
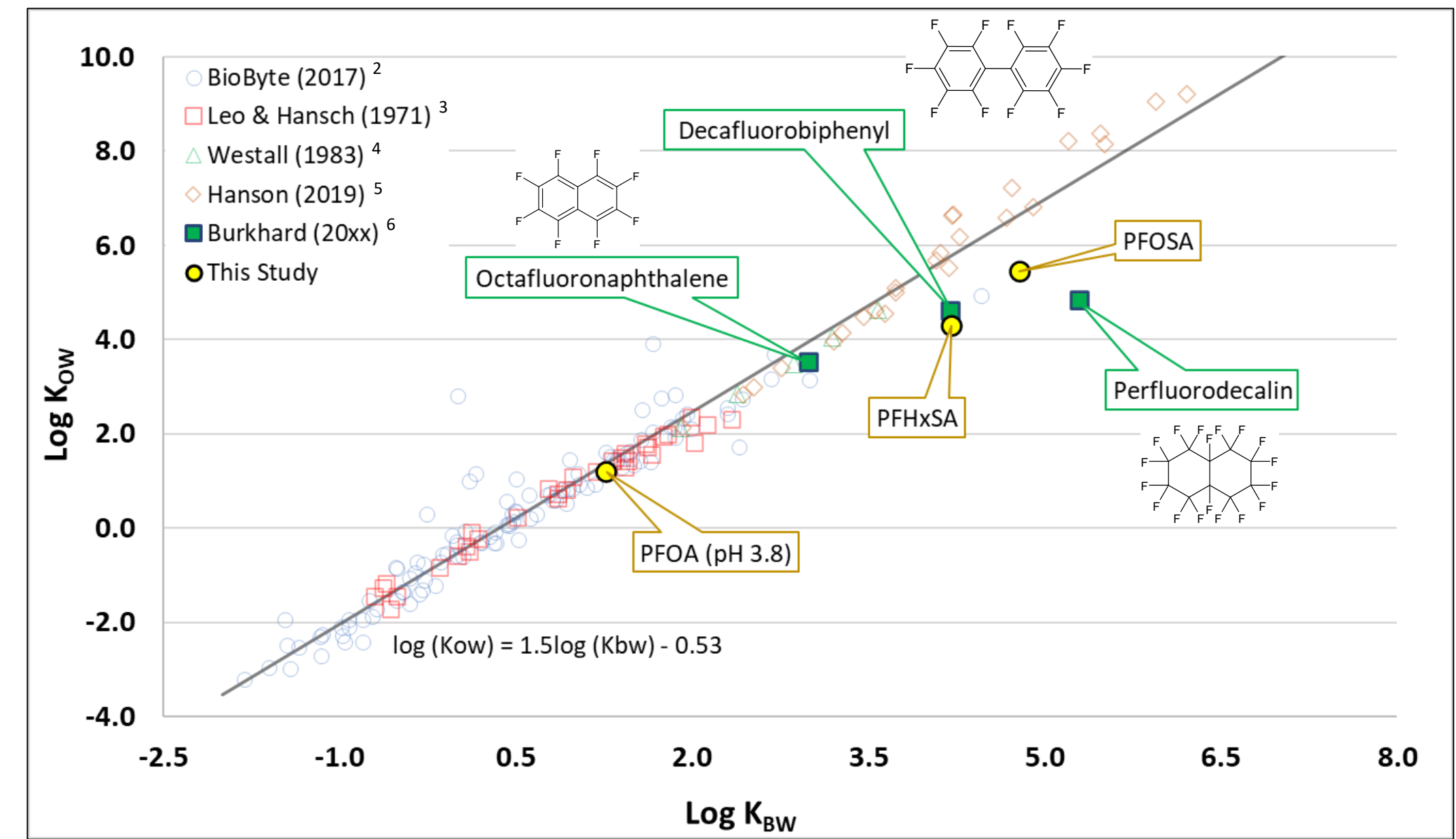
Previous studies on non-PFAS compounds show a strong relationship between butanol-water and octanol-water partitioning. Using this relationship, log $K_{BW}$ values can be used to estimate the values for high log $K_{OW}$ compounds for which aqueous measurements would be difficult to quantify otherwise. While data is currently sparse, PFAS with log $K_{OW}$ of < 4 agree well with the regression, while PFAS with log $K_{OW}$ of > 4 start to deviate. More experimentation will be need to determine to what extent PFAS fit this trend.

## Future Work

- Continue to evaluate the relationships between log $K_{OW}$, perfluorinated chain length, and other structural characteristics.
- Continue to evaluate relationship between log $K_{BW}$ and log $K_{OW}$ for PFAS
- Determine if, and to what extent, changes in pH effect the partitioning of carboxylates, sulfonates, telomer sulfonates and sulfonamides.
- Determine, if and to what extent, ionic strength plays a role in partitioning behavior.
- Compare the partitioning of different species of PFAS (e.g., PFOS-K and PFOS-H)

## Citations

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