Modern Models for Predicting Partitioning, Bioconcentration, and Toxicity of Organic Chemicals
The End of the Age of Octanol

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2015 HDC SETAC Fall Workshop
Porewater: The Interactions between Sediment, Biota and Water
D&R Greenway Land Trust
Johnson Education Center
Princeton, NJ 08540
Environmental Engineering
Model Parameters

Difficulty
(1)
(2)
(3)
Environmental Engineering Model Parameters

- Water
  - K_{OW}
  - H
  - Solubility
- Octanol
- Gas
- Organic Lipid
- Pure Phase
- Plant Cuticle
- Aquatic Terrestrial Organisms
- Soil Drinking Water
- Humans Toxicity

Difficulty
(1)
(2)
(3)
The Age of Octanol

$K_{OC} - K_{OW}$ - Discovered 1979

$K_{OC} = K_P / f_{OC}$

Log $K_{OC} = a_0 + a_1 \text{ Log } K_{OW}$

Fig. 4. Methoxychlor $K_P$ as a function of sediment organic carbon.

The Age of Octanol - $K_{OC}$ - 2000’s

- **Monoaromatic hydrocarbons**
  - Linear Regression
  - $\log K_{OC} = 0.84 \log K_{ow} - 0.28$
  - $R^2 = 0.96$
  - $a_1 = 0.84$

- **Halogenated hydrocarbons**
  - Linear Regression
  - $\log K_{OC} = 0.94 \log K_{ow} - 0.43$
  - $R^2 = 0.98$
  - $a_1 = 0.94$

- **PAHs**
  - Linear Regression
  - $\log K_{OC} = 1.14 \log K_{ow} + 1.02$
  - $R^2 = 0.97$
  - $a_1 = 1.14$

- **Polar chemicals**
  - Linear Regression
  - $\log K_{OC} = 0.73 \log K_{ow} + 0.52$
  - $R^2 = 0.83$
  - $a_1 = 0.73$

The End of the Age of Octanol
The Age of the Polyparameter LFER Model

Octanol-Water Model

$$\log K_{OC} = a_0 + a_1 \log K_{OW}$$

$\log K_{OW}$  Chemical Parameter
$a_0, a_1$  Solvent-water Parameters

Abraham Parameter Model

$$\log K_{OC} = c + eE + sS + aA + bB + vV$$

$E, S, A, B, V$  Chemical Parameters
$c, e, a, s, a, b, v$  Solvent-water Parameters
Abraham Parameters Quantify Chemical Interactions

- $eE$ – excess molar refractivity
- $sS$ – (di)polarizability
- $aA$ – hydrogen-bond acidity
- $bB$ – hydrogen-bond basicity
- $vV$ – molar volume

http://www.science.uwaterloo.ca/~chleh/cact/c123/intemol.html

Particulate Organic Carbon


\[ n = 317 \quad \text{and} \quad n = 440 \]

\[ \text{RMSE} = 0.582 \quad \text{and} \quad \text{RMSE} = 0.477 \]

<table>
<thead>
<tr>
<th>RMSE</th>
<th>Factor</th>
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<tbody>
<tr>
<td>0.3</td>
<td>2.0</td>
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<tr>
<td>0.5</td>
<td>3.2</td>
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<tr>
<td>0.7</td>
<td>5.0</td>
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</table>
Dissolved Organic Carbon  \( n = 263 \)

\[ K_{\text{OW}} \]

\[ \text{ppLFER} \]

\[ \text{RMSE} = 0.869 \]

\[ \text{RMSE} = 0.697 \]

RMSE  Factor
0.3    2.0
0.5    3.2
0.7    5.0
1      10.0

Comparison Kow and ppLFER Models

Burkhard, L. P., ES&T 2000, 34, (22), 4663

Predictions using ppLFER Model

Predictions using EPI Suite Model
Predictions using ppLFER Model

Earthworm BCF

Predicted log K Worm–Water

Observed log K Worm–Water

RMSE = 0.425
N = 81

Barley Shoots BCF

Predicted log K Plant–Water

Observed log K Plant–Water

RMSE = 0.329
N = 67

Kuo, D. T. F., & Di Toro, D. M.
In preparation 2015

Torralba-Sanchez, T.L. & Di Toro, D. M.
PhD Thesis University of Delaware 2015
Why Use the Abraham Model?

Many Useful Models Exist

<table>
<thead>
<tr>
<th>Partitioning</th>
<th>Biological Phases/Blood</th>
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<tbody>
<tr>
<td><strong>Environmental Phase/Water</strong></td>
<td>Lung</td>
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<tr>
<td>Particulate Organic Carbon</td>
<td>Fat</td>
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<td>Dissolved Organic Carbon</td>
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<td><strong>Environmental Phase/Air</strong></td>
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<td>Diesel Soot</td>
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<td>Mineral Surfaces</td>
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<td><strong>Biological Phases/Water</strong></td>
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<td>Storage Lipid</td>
<td>Resp. Irritation Mice</td>
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<td>Phospholipid Membrane</td>
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<td>Serum Albumin</td>
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<td>Muscle Protein</td>
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Applications of Polyparameter Linear Free Energy Relationships in Environmental Chemistry

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Supporting Information

ABSTRACT: Partitioning behavior of organic chemicals has tremendous influences on their environmental distribution, reaction rates, bioaccumulation, and toxic effects. Polyparameter linear free energy relationships (PP-LFERS) have been proven to be useful to characterize the equilibrium partitioning of organic chemicals in various environmental and technical partitioning systems and predict the respective partition coefficients. Over the past decade, PP-LFER solute descriptors for numerous environmentally relevant organic chemicals and system parameters for environmentally important partitioning systems have been determined, extending substantially the applicability of the PP-LFER approaches. However, the information needed for the use of PP-LFERS including descriptors and parameters is scattered over a large number of publications. In this work, we review the state of the art of the PP-LFER approaches in environmental chemical applications. The solute descriptors and system parameters reported in the literature and the availability of their database are summarized, and their calibration and prediction methods are overviewed. We also describe tips and pitfalls associated with the use of the PP-LFER approaches and identify research needs to improve further the usefulness of PP-LFERS for environmental chemistry.

Abraham Parameters Estimates Using Absolv

http://www.acdlabs.com/products/percepta/predictors/absolv/
Solvent-Water Partition Coefficients

Absolv and COSMO-SAC Based Abraham Parameters

Yuzhen Eva Liang
University of Delaware
Acknowledgements

ER-1688 Improving Understanding of the Fate and Transport of Munitions Constituents to Enhance Sustainability of Operational Ranges

ER-1734 Developing Quantum Chemical and Polyparameter Models for Predicting Environmentally Significant Parameters for New Munitions Compounds

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