DEVELOPING A FREE ENERGY PARAMETER MODEL FOR THE PREDICTION AND MAPPING OF THE UPTAKE OF HAZARDOUS ORGANIC POLLUTANTS BY PLANT CUTICLE MEMBRANES

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PROBLEM

ONONDAGA LAKE

- Syracuse, New York
- Industrial Waste
- Municipal Sewage

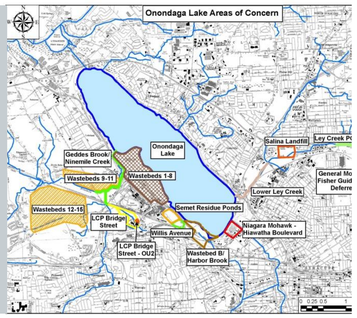


Figure 1: A map of Onondaga Lake, one of the word's most toxic waters as a result of high concentrations of hazardous chemical pollutants [1].

Stage 1
Pollution: Air, Water, Land

Stage 2
Contaminated soil, water, air

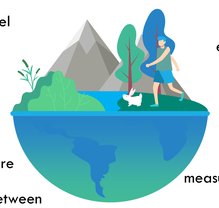
Stage 3
Absorbed into fruits and vegetables

Three-fold problem
Solve with most impact but too many factors in stage 1

Prevent the uptake into fruits and vegetables
Membrane diffusion mechanism

OBJECTIVES

GOAL
Devise predictive model producing quantifiable metrics

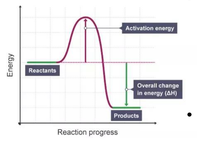


1. Understand mechanism behind the exchange of solute particles
2. Develop structure property relationships between cuticle membrane & organic contaminants
3. Extend the measured data to predict the solubility of additional plant species & pollutants

Solvent name	Safety	Health	Env	Ranking
1,4-Dioxane	7	6	3	Hazardous
Methyl acetate	5	3	5	Problematic
Acetonitrile	4	3	3	Problematic
Diethyl ether	10	3	7	Highly hazardous
Methyl tert-butyl ether	3	3	5	Hazardous
Chloroform	2	7	5	Highly hazardous
Methoxy-ethanol	3	6	3	Hazardous
Chlorobenzene	3	2	7	Problematic
Xylenes	4	2	5	Problematic
Hexane	8	7	7	Hazardous
DCE	4	10	3	Highly hazardous
Benzene	6	10	3	Highly hazardous
Formic acid	3	7	3	Problematic
Nitromethane	10	2	3	Highly hazardous

Table 1: List of few of the most hazardous organic solutes as released by the EPA.

Purpose: The ultimate goal of this study is to develop a computational method that can be used to quantify the chemical properties of various organic pollutants, determine the solute-solvent interactions that occur in the plant cuticle membrane, and develop a model that allows to predict, map and detect the absorption of these pollutants by various plant species



- Change in free energy of activation proportional to change in Gibbs free energy
- Stronger bonging = lower enthalpy

BACKGROUND

SOLVATION

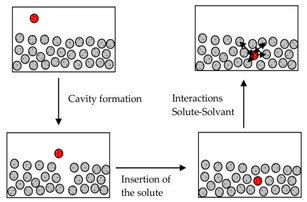


Figure 2: Above diagram depicts the process of solvation as the interactions between solute and solvent

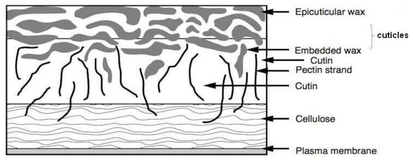
- Interactions that take place depend on various factors such as ionization energy, bond strength, charge, & acidic hydrogen bonds
- There is no tool that allows professionals to use experimental data to predict these properties though
- So how do we quantify this?

LINEAR FREE ENERGY

- Correlates the reaction constant *k* with the equilibrium constant *K*
- The change in free energy of activation is proportional to the change in Gibbs free energy
- Stronger binding between solute and solvent lowers enthalpy and vice versa
- This can be used to develop equations that can be used to correlate the logarithms of water-to-organic solvent transfer or gas-to-organic solvent transfer coefficients

PLANT CUTICLE MEMBRANE

PROTECTION | **REGULATION**

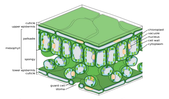


- Complex mixture of hydrophobic chemicals = Solvation
- Regulates the exchange of solutes between plant and atmosphere

METHODOLOGY

EXPERIMENTAL DATABASE

Diverse



Isolated Cuticular Membranes (CM)

Polymer Matrix Membrane (MX)

25 PLANT SPECIES

- 273 data points
- Capsicum pepper
- Lycopersicum esculentum Mill. (tomato fruit)
- Chenopodium album
- Cherry Laurel leaf
- Arabidopsis thaliana
- Juglans regia (English Walnut)
- Madagascar jasmine
- Malus domestica (apple)
- Pyrus Communis
- Spinacia oleracea (spinach)
- Vitus heyneana (grapefruit)
- Lolium multiflorum (annual rye grass)

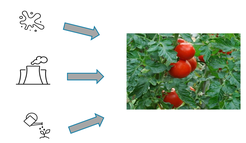
TRAINING MODEL

$$\log(P \text{ or } \frac{Cs,\,organic}{Cs,\,water}) = c_{p-} e_p \cdot E + s_p \cdot S + a_p \cdot A + b_p \cdot B + v_p \cdot V$$

$$\log(K \text{ or } \frac{Cs,\,organic}{Cs,\,gas}) = c_{k-} e_k \cdot E + s_k \cdot S + a_k \cdot A + b_k \cdot B + l_k \cdot L$$

Programmed on IBM SPSS Software

- Each solute-plant membrane pair is a unique interaction
- Separate for each phase
  - Log P = Log Kcw = soil & water
  - Log K = Log Kca = air
- Roughly 600 simultaneous linear equations



$$\log Kcw = -0.153(.040) + 0.928(.031)\mathbf{E} - 0.768(.056)\mathbf{S} - 0.084(.0049)\mathbf{A} - 3.601(.055)\mathbf{B} + 3.451(.038)\mathbf{V}$$

$$\log Kca = -0.453(.040) + 0.302(.041)\mathbf{E} + 1.159(.062)\mathbf{S} + 3.313(.058)\mathbf{A} + 1.038(.073)\mathbf{B} + 0.778(.011)\mathbf{L}$$

MODEL DEVELOPMENT

- Not much numerical data that quantifies the chemical solubilizing properties of various chemicals
- The properties that were most important in understanding the solvation process were chosen
- Using the principles of LFER, these properties were given a variable and developed into 2 equations

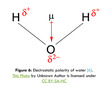
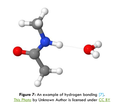
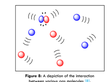
Two Condensed Phases $\log(P \text{ or } \frac{Cs,\,organic}{Cs,\,water}) = c_{p-} e_p \cdot E + s_p \cdot S + a_p \cdot A + b_p \cdot B + v_p \cdot V$

Gas and Condensed Phases $\log(K \text{ or } \frac{Cs,\,organic}{Cs,\,gas}) = c_{k-} e_k \cdot E + s_k \cdot S + a_k \cdot A + b_k \cdot B + l_k \cdot L$

Dependent Variable

Capital Letters: Independent Variable Solute Descriptors

- The model takes form in two equations
- Left Hand Side
  - Log P and Log K: Independent Variables. This will be experimentally calculated with the below methodology
  - The Log P equation represents the transfer of solute between two condensed phases
  - The Log K equations represents transfer of solute between a gas and condensed phase
- Right Hand Side
  - Capital Letters: Independent Variables: solvent descriptors. We will ultimately determine a set of unique descriptors for both the compounds

E	S	A & B	V	L
➢ Molar refraction of given solute ➢ Calculated using Index of refraction ➢ Interactions with light	 ➢ Electrostatic polarity ➢ Polarizability ➢ Ability to form dipoles ➢ Electric field	 ➢ Hydrogen bond donating ➢ Hydron bond accepting	 ➢ McGowan Volume ➢ Atomic Sizes and Chemical Bond Numbers ➢ Quantifies 3D size	 ➢ Logarithm of gas to hexadecane partition coefficient ➢ 298.15 K ➢ Dispersion

COMPOUNDS

- Solvent: 25 Plant Species
- Solutes: wide array of chemical diversity
- Allows for us to train model to be predictive
- Total of 50 solutes

DATA ANALYSIS

TESTS FOR ACCURACY & PRECISION

Because the partition coefficients and solubility data cover chemicals from inorganic gases to liquid and crystalline organic compounds, the solutes were able to cover a wide range of experimental values. After obtaining the values of Log P and Log K, we calculated the solvent descriptors using the IBM SPSS Statistical 22 software. To do this, 50 simultaneous linear equations were generated and were then solved as a traditional system of equations.

- N: number of experimental data points for determining the correlations
- SD: standard deviation
- R^2 : squared correlation coefficient
- F: Fischer F-statistic

Accuracy	Precision	Smaller Training Set
• Within 0.21 and 0.23 log units	• R squared: 0.987 and 0.995	• No bias observed

In order to combine the data dataset, we applied an indicator variable approach in which we assigned a dummy variable to each plant species. This allowed us to create a single expression to represent multiple different plant species.

To test for accuracy and precision, we performed a regression analysis between the solubility ratios that the model determined and the values that were experimentally determined.

The model was incredibly accurate with a RMSEs of 0.21 and 0.23 log units, as well as precise with R2values of 0.987 and 0.995. In order to further test the predictive capability of the mode, I divided the dataset into small training sets to test for bias and found a very small average error of 0.035 log units. Overall, despite my having used a relatively small dataset, these results suggest that the proposed mathematical expressions accurately and precisely model the absorption of organic pollutants by various plant species.

CONCLUSION

- Understood plant absorption mechanism and developed structure property relationships
- More accurate, less tedious, and faster than current methods
- Predictive and quantitative, can be used in wide range of plants and pollutants

A thorough analysis of the results reveals that experimental measures can be used to determine the chemical properties (molar refractivity, electrostatic polarity, hydrogen bond accepting and donating abilities, and gas partition coefficient) of a given environmentally green organic solvent and be used to generate Abraham model correlation expression and coefficients. Not only do the results support the initial research question, but they also show a high level of accuracy and precision that is crucial in the detection of pollutants.

In sum, this project presents a novel solution to quantifying and predicting the behavior of any given organic solvent. My work has been reported in a recent publication [7].

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