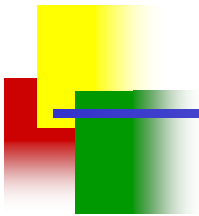


# Environmental Fate



## EPISuite™ Estimation Methods

# Why Evaluate Environmental Fate?

- ✚ How will the chemical behave in the environment?
- ✚ Once released, will the chemical go to air, water, soil, sediment?
- ✚ How long will it persist in the environment?
- ✚ How might humans and the environment be exposed to the chemical?

# Steps in Fate Assessment

- ✚ **Collect physical/chemical properties**
- ✚ **Collect environmental fate properties**
  - **Discussed in this presentation**
- ✚ **Perform environmental fate assessment**
  - **Distribution in the environment (transport)**
  - **Persistence (degradation)**
  - **Bioaccumulation (bioconcentration)**
  - **Modeling exercises**

# Experimental Data

- ✚ **Primary literature and reviews**
  - **Indexed in SRC's EFDB**
- ✚ **Books**
  - **Desk references**
  - **Handbooks**
  - **Encyclopedic sources**
- ✚ **EPA and other governmental publications**
- ✚ **Built-in database in EPI**
- ✚ **A list of sources by topic is provided in handouts**

# Transport

## Based on Chemical Properties

- **Physical/chemical properties**
  - Log  $K_{ow}$
  - Water solubility
  - Vapor pressure
  - Henry's Law constant
- **Fate properties**
  - Soil adsorption coefficient ( $K_{oc}$ )
  - Bioconcentration factor (BCF)

## Transport Assessment

- **Qualitative assessment using these properties**
- **Quantitative assessment using multi-media (fugacity model)**

# Persistence

## Removal in the Atmosphere

- Oxidation (AOP)
- Photolysis

## Removal in Soil and Water

- Hydrolysis ( $K_{\text{Hydro}}$ )
- Biodegradation (Biodeg)
- Photolysis
- Chemical decomposition

# Bioaccumulation

## Bioconcentration

- The increase in the concentration of a chemical over that in an organism's surroundings (e.g., water)

## Biomagnification

- The increase in the concentration of a chemical over that in an organism's diet

## Bioaccumulation

- The increase in the concentration of a chemical through all routes of exposure

**Bioaccumulation = Biomagnification & Bioconcentration**

# Soil Adsorption Coefficient (Koc)

## Provides

- A measure of a chemical's ability to sorb to the organic portion of soil and sediment

## Indicates to the assessor

- The potential for the chemical to leach through soil and be introduced into ground water
- The potential for partitioning of the chemical between water and suspended solids and sediment
- Strong adsorption will impact other fate properties

# $K_{oc}$

- +  $K_d$  = partitioning between the solid-phase (soil or sediment) and solution-phase (water) at equilibrium**
- + The soil adsorption coefficient,  $K_d$ , normalized with respect to the organic carbon content of the soil**

$$K_{oc} = K_d / \%OC \times 100$$

# **K<sub>oc</sub> Classifications**

<b>K<sub>oc</sub> Classifications</b>	<b>Predicted log K<sub>oc</sub> Values</b>
<b>Very Strong</b>	<b>≥ 4.5</b>
<b>Strong</b>	<b>3.5 – 4.4</b>
<b>Moderate</b>	<b>2.5 – 3.4</b>
<b>Low</b>	<b>1.5 – 2.4</b>
<b>Negligible</b>	<b>&lt; 1.5</b>

# Interpreting $K_{oc}$ Results

## Low $K_{oc}$ (not tightly bound to soil)

- Leaching into the soil
  - Reduces surface level concentration
  - Potential contamination of groundwater
- Contamination of surface water with storm runoff

## High $K_{oc}$ (tightly bound to soil)

- Removal from water column via sorption to sediment and particulate matter
- Reduces rate of degradation because the chemical is not available to microorganisms

# Interpreting $K_{oc}$ - Other Factors

## + pH

- Soil adsorption decrease as ionization increases

## + High clay content

- Some chemicals may absorb very strongly to high-clay content soils

## + Bond formation with humic matter

- Some chemicals, most notably aromatic amines, may form chemical bonds with organic matter, decreasing the potential for leaching

# Atmospheric Oxidation

## Provides

- The atmospheric persistence of a compound

## Indicates to the assessor

- How long the chemical may reside in the atmosphere
- Potential to travel long distances from the original point of release

# Atmospheric Oxidation Processes

## Hydroxyl radicals (OH• radicals)

- The dominant atmospheric oxidant
- Produced by UV radiation in sunlight

## Ozone (O<sub>3</sub>)

- Selective oxidant

## Nitrate radicals (NO<sub>3</sub>)

- Only important at night
- Limited primarily to urban areas

# Interpreting Results

Classification	Half-life
Rapid	$\leq 2$ hrs
Moderate	2 hrs - $\leq 1$ day
Slow	$> 1$ day - $\leq 10$ days
Negligible	$> 10$ days

- **Half-life  $> 2$  days**
  - Persistence criteria for New Chemicals
- **May be used to determine the potential for long-range transport**
  - Traveling large distances in air from the original point of release; crossing international boundaries

# Hydrolysis

## Provides

- Reaction of a compound with water

## Indicates to the assessor

- Persistence of a chemical substance
- When hydrolysis products also need to be considered in the assessment

# Hydrolysis Process

## pH sensitive

- Typical environmental pHs range from 5 to 9

## Acid or base catalyzed

- Half-life can be calculated from the rate constant and the pH

# HYDROWIN v1.67

- ✚ **Converts acid, neutral, and base rate constants to half-lives at pH 7 & 8**
- ✚ **Limited set of chemical classes**
  - **Esters**
  - **Carbamates**
  - **Epoxides**
  - **Halomethanes**
  - **Alkyl halides**

# Hydrolysis Rules of Thumb

- ✚ **Some classes of chemicals hydrolyze extremely rapidly (i.e., in hours)**
  - Knowledge of rate constant not important
    - Acid chlorides, epoxides, and siloxanes
- ✚ **Changes in temperature can dramatically change the rate of the reaction**
  - 10 degree change = 250% change in rate
- ✚ **Besides natural bodies of water, it may also occur in clouds, fog, or moist soil, and effluent**

# Assessment for Hydrolysis

<b>Hydrolysis Half-Life</b>	<b>Assessment</b>
<b>&lt;1 hour</b>	<b>Hydrolysis product</b>
<b>1 hour – 14 days</b>	<b>Parent compound &amp; hydrolysis product</b>
<b>&gt;14 days</b>	<b>Parent compound</b>

# Biodegradation

## Provides

- **The degradation of a chemical substance by the action of microorganisms**

## Indicates to the assessor

- **Persistence in soil, water, and sediment**
- **The amount of a chemical that may be removed in sewage treatment plants**

# Biodegradation Introduction

## Aerobic

- Occurs in oxygenated environments
  - Surface water and soil

## Anaerobic

- Occurs in oxygen-free systems
  - Sediment and groundwater
  - Generally much slower than aerobic degradation

## Primary

- Initial step in degradation process – forms a new compound

## Ultimate

- Complete mineralization to CO<sub>2</sub> and water

# BIOWIN v4.00

- ✚ **Uses 6 fragment-based models**
  - **Probability of Rapid Biodegradation**
    - **Linear and non-linear models**
      - >0.5 – likely to biodegrade fast
      - <0.5 – *not* likely to biodegrade fast
  - **Expert Survey**
    - **Ultimate and primary degradation**
  - **Readily Biodegradable Probability (MITI Model)**
    - **Linear non-linear model**

# Survey Models

- ✚ **Fragment-based QSAR based on the results of an expert survey on the biodegradability of 200 substances**
- ✚ **Ultimate biodegradation model**
  - **Semi-quantitative estimate of rate of aerobic ultimate biodegradation**
- ✚ **Primary Biodegradation Survey Model**
  - **Semi-quantitative estimate of rate of aerobic primary biodegradation**
- ✚ **Result can be converted to a relative time frame**

<u>Result</u>	<u>Time</u>	<u>Result</u>	<u>Time</u>
5.0	hours	3.0	weeks
4.5	hours – days	2.5	weeks – months
4.0	days	2.0	months
3.5	days – weeks	1.0	longer

# Biodegradation Results to Half-life

<b>BIOWIN Output</b>	<b>Half-Life (days)</b>
<b>Hours</b>	<b>0.17</b>
<b>Hours to Days</b>	<b>1.25</b>
<b>Days</b>	<b>2.33</b>
<b>Days to Weeks</b>	<b>8.67</b>
<b>Weeks</b>	<b>15</b>
<b>Weeks to Months</b>	<b>37.5</b>
<b>Months</b>	<b>60</b>
<b>Recalcitrant</b>	<b>180</b>

# Ready Biodegradability Model

- ✚ Fragment method developed using data on 884 chemicals from the Japanese MITI protocol

- ✚ Provides pass/no pass results

$>0.50$       Ready biodegradable

$<0.50$       Not Ready biodegradable

- ✚ Stringent test – a chemical giving a positive response is expected to biodegrade in the environment

# Persistence Assessment

## Criteria

	Low Persistence	Persistent Concern	
Water, soil, sediment	< 60 d	≥ 60 d	> 180 d
Air	≤ 2 d	> 2 d	

## Other considerations

- If the half-life is not known precisely, but it is known to be rapid ( $\ll 60$  days), then chemical is of low persistence concern
  - Includes hydrolysis and chemical degradation
  - May include photolysis

# Bioconcentration Factor (BCF)

## Provides

- The ratio of a chemical's concentration in the tissue of an aquatic organism to the concentration in the ambient water

## Indicates to the assessor

- The potential for a chemical to bioconcentrate in lipids (fatty tissue) of aquatic organisms
- The potential to bioaccumulate in higher trophic levels

# BCFWIN v 2.14

- ✚ **SAR based on  $K_{ow}$** 
  - **Neutral (non-ionic)**
    - Estimation equations based on  $\log K_{ow}$  value
  - **Ionic**
    - BCF assigned based on  $\log K_{ow}$  range
  
- ✚ **The BCFWIN method does not account for metabolism under field conditions**
  - **Compounds that metabolize would have a lower BCF than predicted**

# BCF Criteria

<b>Bioaccumulation</b>	<b>Low Bioaccumulation Concern</b>	<b>Bioaccumulation Concern</b>	
<b>Fish BCF</b>	<b>&lt;1000</b>	<b>≥1000</b>	<b>≥5000</b>
<b>Fish Log BCF</b>	<b>&lt;3</b>	<b>≥3</b>	<b>≥3.7</b>

# Volatilization From Water Model

## + Provides

- The results from a simple model indicating how fast a chemical will volatilize from moving and still bodies of water

## + Indicates

- Partitioning in the environment

Volatilization from Water:

Henry LC: 0.0012 atm-m<sup>3</sup>/mole (estimated by Group SAR Method)

Half-Life from Model River: 2.198 hours

Half-Life from Model Lake : 146.2 hours (6.09 days)

# Removal in Wastewater Treatment

## Provides

- **Information on the amount of a compound removed in a model sewage treatment plant**

## Indicates to the assessor

- **How much of the chemical is discharged to surface water**
  - **May affect aquatic life**
  - **May affect amount of subsequent human ingestion from drinking water**

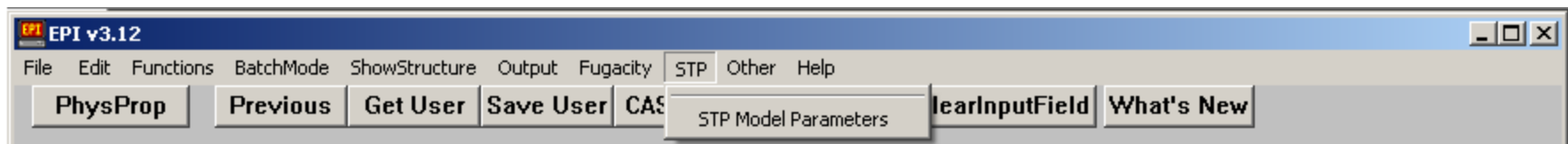
# STP Model

- ✚ **Determines losses from physical processes**
  - **Sludge adsorption**
  - **Air stripping**
- ✚ **Uses default values for residence time in primary, aeration, and settling tanks**

## Removal In Wastewater Treatment:

<b>Total removal:</b>	<b>82.34</b>	<b>percent</b>
<b>Total biodegradation:</b>	<b>0.62</b>	<b>percent</b>
<b>Total sludge adsorption:</b>	<b>75.28</b>	<b>percent</b>
<b>Total to Air:</b>	<b>6.44</b>	<b>percent</b>

# STP Model Options



### STP Half-Life Parameters

Use 10000 hr default values

Use BIOWIN output and EPA draft method for assigning half-lives

Use Half-lives entered below (in hours):

Bio P (primary clarifier):

Bio A (aeration vessel):

Bio S (settling tank):

Guidance for selecting Bio A half-lives:

- 1 hr = rapid biodegradation
- 3 hr = moderate biodegradation
- 10 hr = moderate-to-slow biodegradation
- 30 hr = slow biodegradation
- 100 hr = very slow biodegradation

#### BIOWIN Half-Life Relationships

	Bio P	Bio A	Bio S
Biowin3 <= weeks + Biowin5 > 0.5	<input type="text" value="10"/>	<input type="text" value="1"/>	<input type="text" value="1"/>
Biowin3 <= weeks	<input type="text" value="30"/>	<input type="text" value="3"/>	<input type="text" value="3"/>
Biowin5 > 0.5	<input type="text" value="100"/>	<input type="text" value="10"/>	<input type="text" value="10"/>
Biowin3 = wk-mo	<input type="text" value="300"/>	<input type="text" value="30"/>	<input type="text" value="30"/>
Biowin3 = months	<input type="text" value="1000"/>	<input type="text" value="100"/>	<input type="text" value="100"/>
Biowin3 = recalcit	<input type="text" value="10000"/>	<input type="text" value="10000"/>	<input type="text" value="10000"/>

# Multi-Media (Fugacity) Model

## ✚ Provides

- Quantitative estimates for a model system the size of Ohio

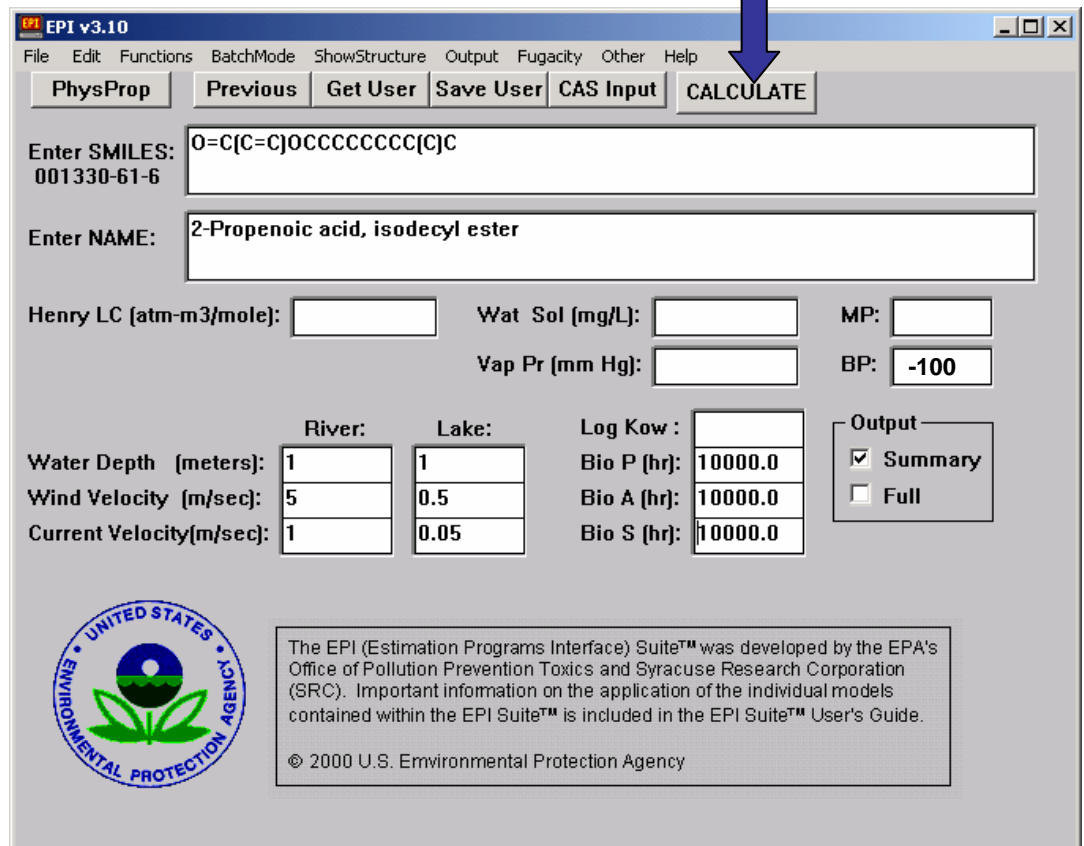
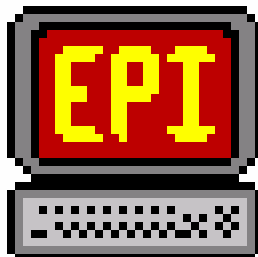
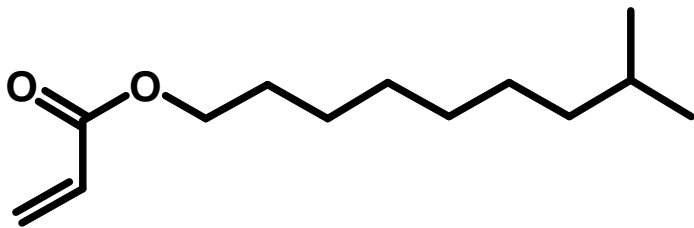
## ✚ Indicates to the assessor

- The estimated amount of a chemical that is expected to be in air, water, soil, and sediment based on a default release scenario

Level III Fugacity Model:			
	Mass Amount (percent)	Half-Life (hr)	Emissions (kg/hr)
Air	2.92		1000
Water	22.4	15.6	1000
Soil	60.1	360	1000
Sediment	14.6	360	0

# Sample Chemical Assessment

CAS # 1330-61-6 2-Propenoic acid, isodecyl ester



The screenshot shows the EPI v3.10 software interface. A blue arrow points to the 'CALCULATE' button. The interface includes a menu bar (File, Edit, Functions, BatchMode, ShowStructure, Output, Fugacity, Other, Help), a toolbar with buttons for PhysProp, Previous, Get User, Save User, CAS Input, and CALCULATE, and input fields for SMILES and NAME. Below these are various property input fields and a table for environmental parameters.

Henry LC (atm-m3/mole):		Wat Sol (mg/L):		MP:	
Vap Pr (mm Hg):		BP:		Output	
			-100	<input checked="" type="checkbox"/> Summary <input type="checkbox"/> Full	
River:		Lake:		Log Kow :	
Water Depth (meters):		Bio P (hr):		Bio A (hr):	
1		1	10000.0	10000.0	
Wind Velocity (m/sec):		Bio S (hr):			
5		0.5	10000.0		
Current Velocity(m/sec):					
1		0.05			

The EPI (Estimation Programs Interface) Suite™ was developed by the EPA's Office of Pollution Prevention Toxics and Syracuse Research Corporation (SRC). Important information on the application of the individual models contained within the EPI Suite™ is included in the EPI Suite™ User's Guide.

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# Fate Summary for Sample

- + Slightly water soluble liquid**
- + Low bioaccumulation concern**
- + Expected to partition primarily to soil**
  - Moderately volatile from water
  - Limited transport to groundwater
- + Low persistent in the environment**
  - Biodegrades in soil and water (no hydrolysis)
  - Oxidizes rapidly in the atmosphere
- + 82 - 99.9% removal in sewage treatment plant**

# Hand's On Session

- ✚ **Run the example chemicals through EPI**
  - **Example 1**
  - **Example 2**
  - **Example 3**
- ✚ **Identify the fate property estimates**
- ✚ **Enter results into the Sustainable Futures Summary Assessments for each chemical**

# Physical/Chemical Properties

<b>Physical State</b>	<b>MP = -100 °C</b> <b>BP = 253 °C</b>	<ul style="list-style-type: none"><li>• <b>Liquid</b></li><li>• <b>Potential exposure by dermal contact</b></li></ul>
<b>Vapor Pressure</b>	<b>VP = <math>2.3 \times 10^{-2}</math> mm Hg</b>	<ul style="list-style-type: none"><li>• <b>Vapor in atmosphere</b></li><li>• <b>Won't rapidly volatilize from dry surfaces</b></li></ul>
<b>Henry's Law Constant</b>	<b>HLC = <math>1.2 \times 10^{-3}</math> atm/m<sup>3</sup>-mole</b>	<ul style="list-style-type: none"><li>• <b>Volatilizes from water</b></li><li>• <b>Potential inhalation exposure</b></li></ul>
<b>Ionization</b>		<ul style="list-style-type: none"><li>• <b>No functional groups that will ionize</b></li></ul>

# Physical/Chemical Properties II

<b>Water Solubility</b>	<b>WS = 3 mg/L</b>	<ul style="list-style-type: none"><li>• Slightly soluble</li><li>• Not expected to partition primarily to water – rain washout or runoff with water not expected to be significant</li><li>• Water solubility sufficiently high to indicate potential ingestion exposure</li><li>• Rate of absorption in tissue relatively low</li></ul>
<b>Octanol-Water Partition Coefficient</b>	<b>Log <math>K_{ow}</math> = 5.1</b>	

# Fate Properties

<b>Soil Adsorption</b>	$K_{oc} = 1330$ ( $\log K_{oc} = 3.1$ )	<ul style="list-style-type: none"><li>• Moderately bound to soil</li><li>• Moderate potential to migrate to ground water</li><li>• Moderate potential to adsorb to sediment in surface water</li></ul>
<b>Atmospheric lifetime</b>	OH radical half-life = 5.8 hr	<ul style="list-style-type: none"><li>• Rapidly degrades by gas-phase reaction in the atmosphere</li><li>• Limited potential for long-range transport</li></ul>

# Persistence

<b>Hydrolysis</b>	<b>Half-life = 10.6 yr at pH 7; 1.1 yr at pH 8</b>	<ul style="list-style-type: none"><li>• <b>Resistant to hydrolysis</b></li></ul>
<b>Biotic</b>	<b>Ultimate = weeks Primary = days Rapid biodeg = Probable (&gt; 0.5) Ready biodeg = probable (&gt;0.5)</b>	<ul style="list-style-type: none"><li>• <b>Low persistence in environment</b></li></ul>

# Model Results

<b>Water volatilization</b>	<b>Half-life from model river = 2 hrs; model lake = 6 days</b>	<ul style="list-style-type: none"><li>• <b>Rapidly volatilizes from surface waters</b></li></ul>
<b>Multi-media (fugacity) model</b>	<b>Air = 1.2% Water = 12.9 % Soil = 68.8% Sediment = 17.1%</b>	<ul style="list-style-type: none"><li>• <b>Partitions predominately to soil</b></li><li>• <b>Model results consistent with assessment based on P/Chem properties</b></li></ul>

# Bioaccumulation

<b>BCF</b>	<b>161</b>	<ul style="list-style-type: none"><li>• <b>Low potential for bioconcentration</b></li><li>• <b>Low concern for bioaccumulation</b></li></ul>
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