Pesticides

-classes

-properties

-environmental fate

Pesticides

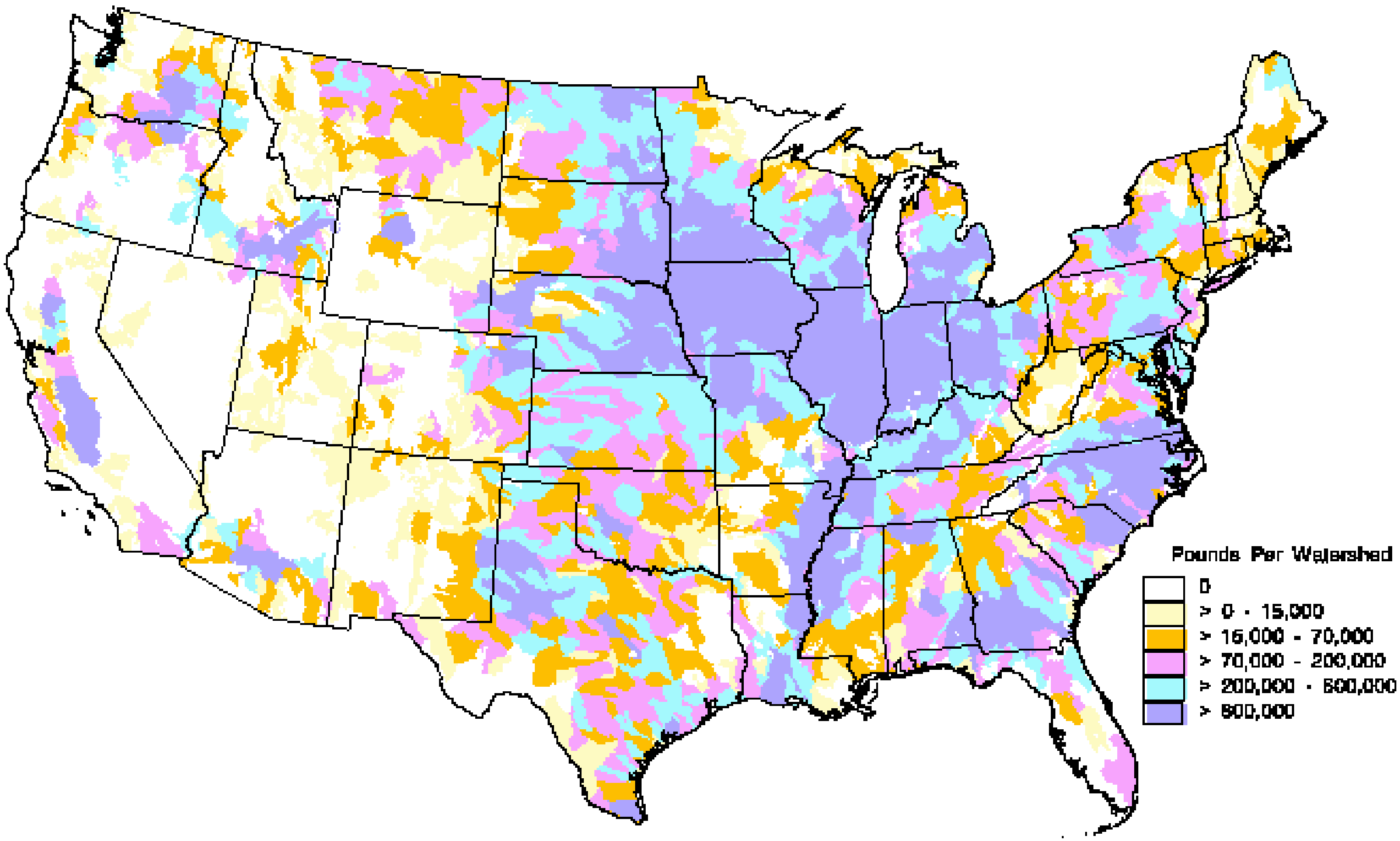
- FIFRA definition –
  - Any substance or mixture of substances intended for preventing, destroying, or mitigating any pest or intended for use as a plant regulator, defoliant, or desiccant.
- EPA definition –
  - Any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest. Pests can be insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms like bacteria and viruses. Though often misunderstood to refer only to *insecticides*, the term pesticide also applies to herbicides, fungicides, and various other substances used to control pests. Under United States law, a pesticide is also any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant.

Pesticides

According to OPP PPI > 125,000 registered

- Agricultural benefits
- Household benefits
- Public/municipal benefits
- Active ingredient (a.i.) / inert ingredients
- Degradation products

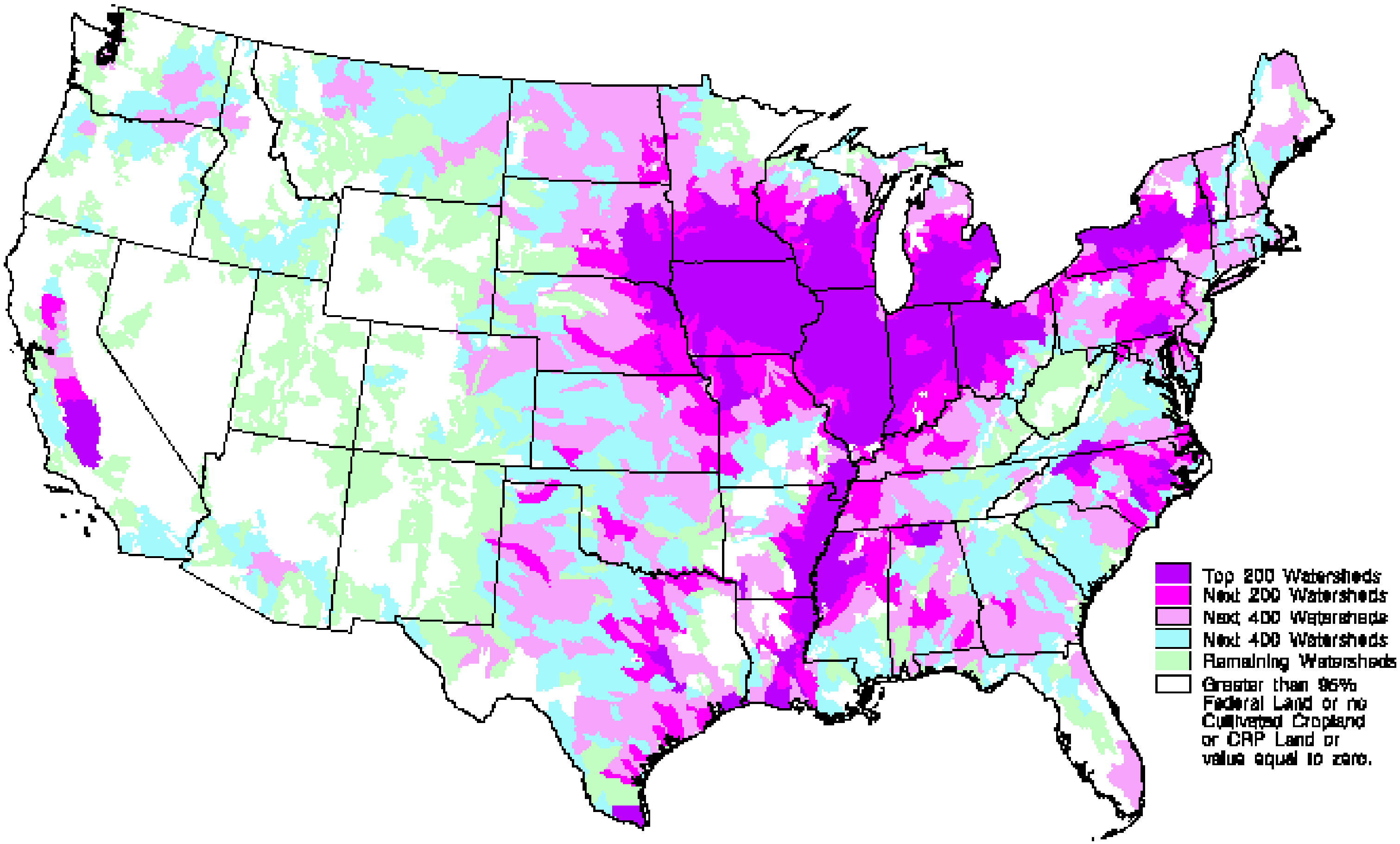
Pounds of Pesticides Applied to Field Crops



Corn, Wheat, Soybeans, Cotton, Barley, Sorghum, Rice, Oats, Peanuts, Potatoes, Beets, Sunflowers, and Tobacco

U.S. Department of Agriculture
Natural Resources Conservation Service
Resource Assessment and Strategic Planning Division
Map ID: [illegible] June 1998

Potential Pesticide Dissolved Runoff Loss from Farm Fields



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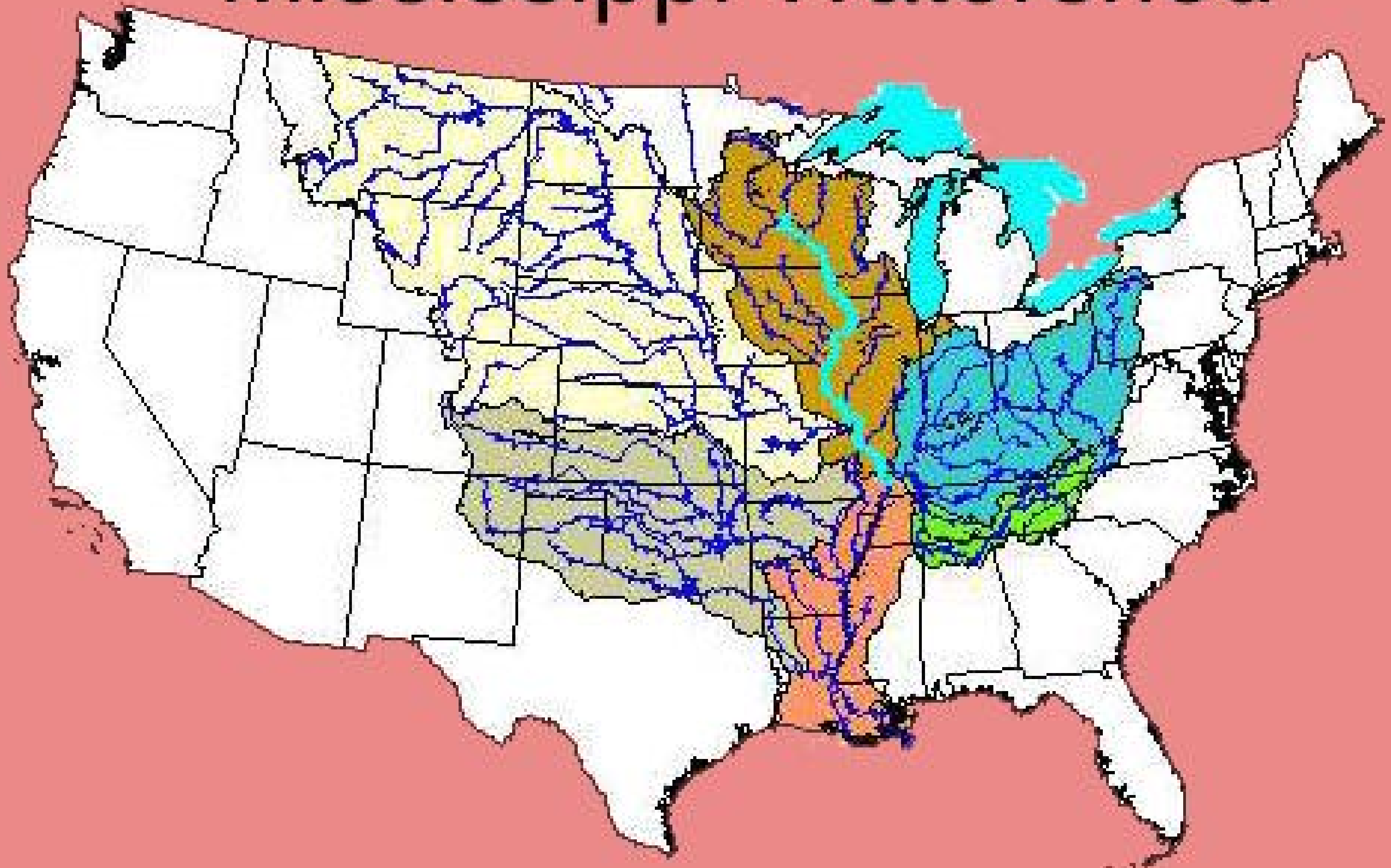
Map ID: SMW.2271 June 1998

Mississippi Watershed



http://whale.wheelock.edu/watersheds/mississippi/Mississippi.html

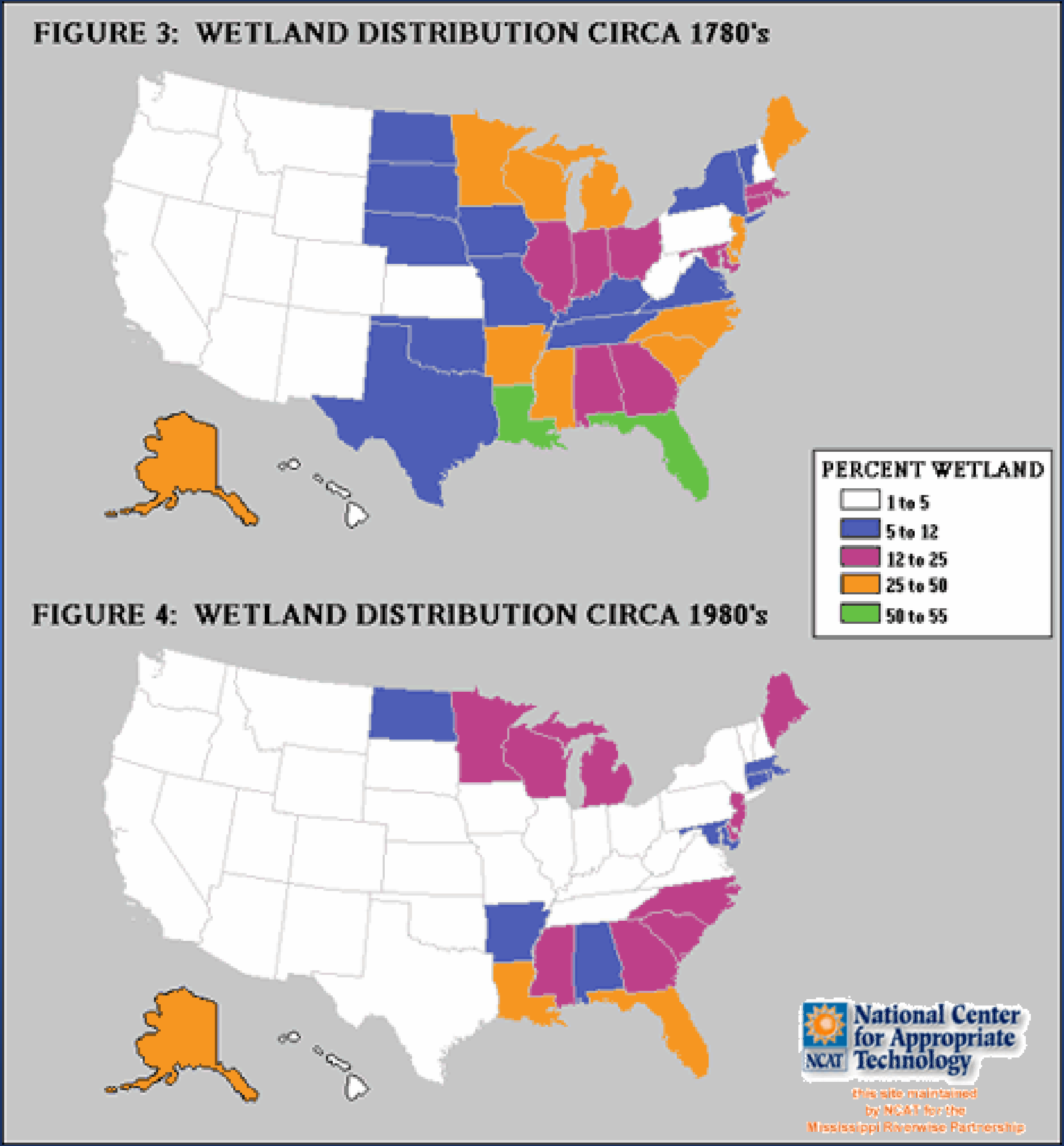


FIGURE 3: WETLAND DISTRIBUTION CIRCA 1780's
PERCENT WETLAND
1 to 5
5 to 12
12 to 25
25 to 50
50 to 55
FIGURE 4: WETLAND DISTRIBUTION CIRCA 1980's
National Center for Appropriate Technology
NCAT
this site maintained by NCAT for the Mississippi Riverwise Partnership

Types of pesticides

- Grouped according to target organism:
  - Insecticides
  - Herbicides
  - Fungicides
  - Rodenticides
  - Acaracides (miticides)
  - Molluscicides
  - Antimicrobials / biocides
  - Microbial pesticides

Pesticides

- Grouped according to:
  - Narrow-spectrum vs. broad-spectrum
    - Targeted organisms – no harm to non-target
    - Kills a variety of organisms in addition to pest
  - Pesticide generation
    - 1st generation
    - 2nd generation
    - 3rd generation

Pesticides

- First generation pesticides
    - Historically-used pesticides
  - Inorganic compounds (minerals)
      - Lead
      - Mercury
      - Arsenic
    - Accumulation potential
  - Botanicals
      - Nicotene
      - Pyrethrum
      - Rotenone

Pesticides

- Second generation pesticides
  - Synthetic
    - Dichloro-diphenyl-trichloroethane (DDT)
      - Synthesized in 1873
      - Insecticidal properties – Paul Müller 1939 (Nobel Prize)
        - » WWII used to control body lice
      - Widespread use 1940-1960; banned in US in 1972
    - Currently there are thousands of synthetic pesticide products
      - Made up of more than 1,000 different chemicals and combinations
      - Not as environmentally persistent as DDT

Pesticides

- Third generation pesticides
  - Insect pheromones
  - Insect growth regulators
    - Disrupt the normal activity of the endocrine or hormone system of insects, affecting the development, reproduction, or metamorphosis of the target insect
  - Chitin synthesis inhibitors
    - Target exoskeleton
  - Juvenile hormones
    - Mimic hormones / insect remains in juvenile stage
  - *Bacillus thuringiensis*
    - Toxins produced following ingestion

Insecticide classification

1. Organochlorines
   - DDT, aldrin, dieldrin, endrin, chlordane
2. Organophosphates
   - Malathion, parathion, diazinon, methylparathion
3. Carbamates
   - Carbaryl, carbofuran, methylcarbamate
4. Biological / botanical / pyrethroids
   - Fenvalerate, permethrin, lambda-cyhalothrin, rotenone, nicotene, Bt

Herbicides

Constitutes approximately 70% of pesticides applied

1. Bipyridyls (Quats) - paraquat / diquat
   - nonselective
2. Triazine - atrazine*
   - used on monocot crops
3. Acetamides – propanil
   - barnyard grass
4. Chlorophenoxy – 2,4-D
   - dicot selective

Herbicides

Modes of action

1. Bipyridyls (Quats) – chlorophyll inhibitor
   - diquot registered for aquatic use
   - also used as cotton defoliant

2. Triazine - atrazine – interrupt electron flow in photosynthetic pathway

3. Acetamides – propanil – lack of acylamidase enzymes in target plants (e.g. barnyard grass) causes plant death

4. Chlorophenoxy – 2,4-D – plant growth regulator – results in production of ethylene

Herbicides

Environmental fate

Typically characterized by

- water solubility → low bioaccumulation
- transported in surface runoff
- $t_{1/2}$ 60 to >100 days in soil / sediments
- slow degradation in neutral waters and soils
- low toxicity to non-targets (invertebrates & vertebrates)
- cotton defoliants (lung irritant – childhood asthma)

Atrazine found in surface waters of the MS drainage

Also detected in well water in the Midwest (corn belt)

Atrazine

- Registered for use in the US in 1959
- Minimum contaminant level for drinking water = 3 μg/L
- Exceedance in 27% of raw water from 12 Midwestern states (USGS)
- Rarely exceed 20 μg/L; NOEL at 15-20 μg/L mesocosm studies (Solomon et al. 1996, ET&C)
  - Shift in primary producers in some studies
- Amphibian studies
  - Abnormalities / deformities
  - Demasculinization
  - Feminization
  - Controversial effect level

Insecticides

Modes of action

- Organochlorines & Pyrethroids
  - Retards closure of ion channel in CNS
    - Results in repetitive spontaneous nervous discharges
- Organophosphates & Carbomates
  - Binds to hydroxyl group to inhibit formation of acetylcholinesterase
    - May require liver MFOs to elicit full ChE inhibition (hepatic metabolism)
    - Results in excess acetylcholine, repetitive synapses stimulation
    - OPs produced as nerve gases during WWII
- Biological
  - Targets production hormones
  - Pheromones to attract and trap
- Botanical
  - Incorporation of genes (e.g. Bt) in plant crops
    - Results in death to pest

Insecticides

Environmental fate

- **Organochlorines (DDT)**
  - Highly lipophilic – stored in fatty tissue
    - Environmental persistence ($t_{1/2}$ > 30yrs)
      - DDE – primary breakdown product
      - Currently detected in sediments / water in MS Delta
    - High bioaccumulation potential
      - Biomagnification (30-100X birds of prey)
      - Bioconcentration (oysters >700,000X)
    - Dutch Elm disease
      - Soil → earthworms → Robins

Insecticides

Environmental fate

- **Pyrethroids**
  - Highly lipophilic
    - Short environmental persistence ($t_{1/2}$ soil ~15-90 d; water ~21 d)
    - Little bioaccumulation potential
  - Often pesticide of choice
    - Highly toxic but short-lived
    - Little residual
  - Isomers of parent compound

Insecticides

Environmental fate

- **Organophosphates / carbomates**
  - Relatively short-lived / labile compounds
    - $t_{1/2}$ soil ~15 - 41 d; water ~ up to 140 d
  - Water solubility varies
  - No bioaccumulation / readily excreted
  - May require liver MFOs to elicit full ChE inhibition (hepatic metabolism)
  - Sensitivity – fish > birds > mammals
  - Subacute antiChE effects not well known

Insecticides

Environmental fate

- Biological / botanical
  - GMO crops
    - Bt cotton
    - Roundup ready
      - Environmental fate of these proteins not known
      - Degradation
  - Nicotene
    - Used over 200 yrs ago
    - Retards closure of ion channel in CNS
      - Results in repetitive spontaneous nervous discharges
  - Rotenone
    - Derived from plant roots
    - Insecticide in 1930s
    - Mitrochondrial poison – interferes with ATP synthesis
    - Highly toxic to fish

Factors aFFecting Fugacity

Chemical properties

- K_{ow}
- K_{oc}
- pK_a
- Solubility
- Volatilization
- Henry's Law constant
- $t_{1/2}$
- Photolysis

Environmental factors

- Climate
- Geomorphology
- Temp
- Light quality/quantity
- pH
- Water cycle
- Rainfall
- Infiltration rate
- Vegetation
- Dissolved salts
- Suspended solids

Ecological Risk Assessment

Fugacity **<u>model</u>** – tendency of a chemical to reach equilibrium within environmental compartments (Mackay, 2004)

- Modeling environmental partitioning and fate
  - Think of the simple model of osmosis
    - Movement from high gradient to low gradient (concentration) until in equilibrium
    - Simplest model
  - Fugacity model includes ‘tendency’ or ‘fugacity’ to move to another compartment

Developing the model

- Define **‘unit world’**
  - Air
  - Water
  - Soil
  - Sediment
- These are the ‘worlds’ MacKay (2004) defines
- Environmental factors affect these ‘worlds’
- Models = mathematical equations used to estimate or predict outcomes

Simplify & Estimate

- C (concentration) = Z (mol/m^3 Pa) x f (fugacity Pa)
- Pascal = unit of partial pressure (T^o + chem concentration)
- f = C / Z
- Fugacity is dependent upon the chemical concentration and the partition coefficient
- Chemicals will migrate into ‘unit worlds’ in which Z is large
- e.g. Z is large in fish lipid tissue for DDT
  - DDT is lipophilic / high K_{ow}
- e.g. Z is large in air for many aromatic compounds
  - Benzene has high volatility constant

Transport & transformation

- D = transport & transformation values

  D = rate constant in fugacity format

Chemical reactions are governed by:

VCk

V = volume
C = concentration
k = rate constant

Fugacity transport & transformation is governed by:

Df

D = fugacity rate constant
f = fugacity (C/Z)
C = concentration
Z = capacity of phase (world) to absorb the chemical

Simplicity is best

- Keeping the model simple (KISS)
- Best accurate prediction of outcome

<u>Temporal predictions</u>

Prediction of long-range transport of chemicals

<u>Spatial predictions</u>

Apply to multiple connected words

Back to basics

- Environmental fate controlled by chemical properties
- Rely on accurate physiochemical data
- Garbage in = garbage out
- Reliable data in = reliable predictions out

Ability to predict:

- Sink vs. source
- Bioaccumulation
- Bioconcentration
- Biomagnification
  - Not just a lack of ability to excrete

Chemical properties

- K_{ow}
- K_{oc}
- pK_a
- Solubility
- Volatilization
- Henry's Law constant
- $t_{1/2}$
- Photolysis

Applications

- Breathalyzer
  - Fugacity of alcohol in terms of blood alcohol
- IBI
  - Biota for water quality indices
  - High concentrations in lipids relative to those in water

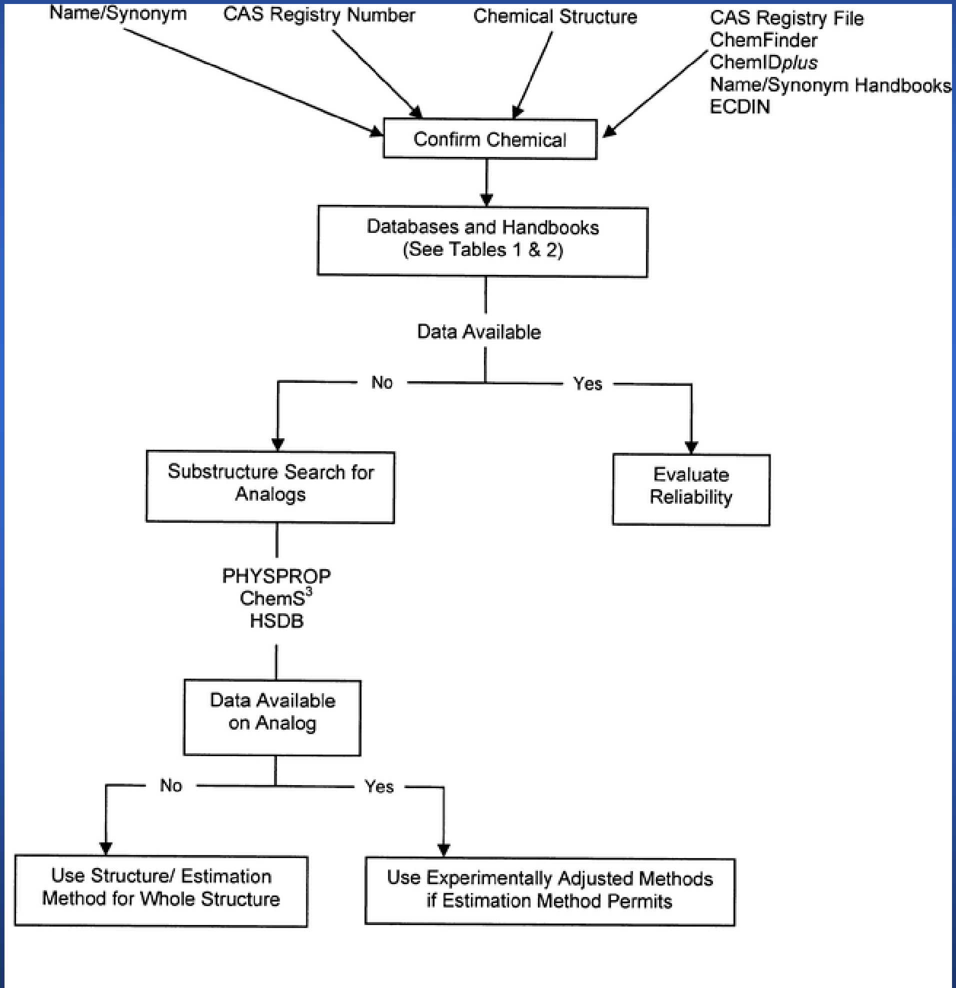
Boethling et al. (2004)

- Accurate predictions of physicochemical properties
  - E.g. isomers of same chemical structure
- “Data mining”
  - Data bases available for use in models
  - CAS numbers
  - Chemical name
  - Chemical structures
- More complex model
  - More ‘unit worlds’
  - More physicochemical properties

Boethling et al. (2004)

- Unavailable data
- QSARs
- Isomers
- Analogs
- Chiral chemicals

***Accuracy enhanced with measured values**



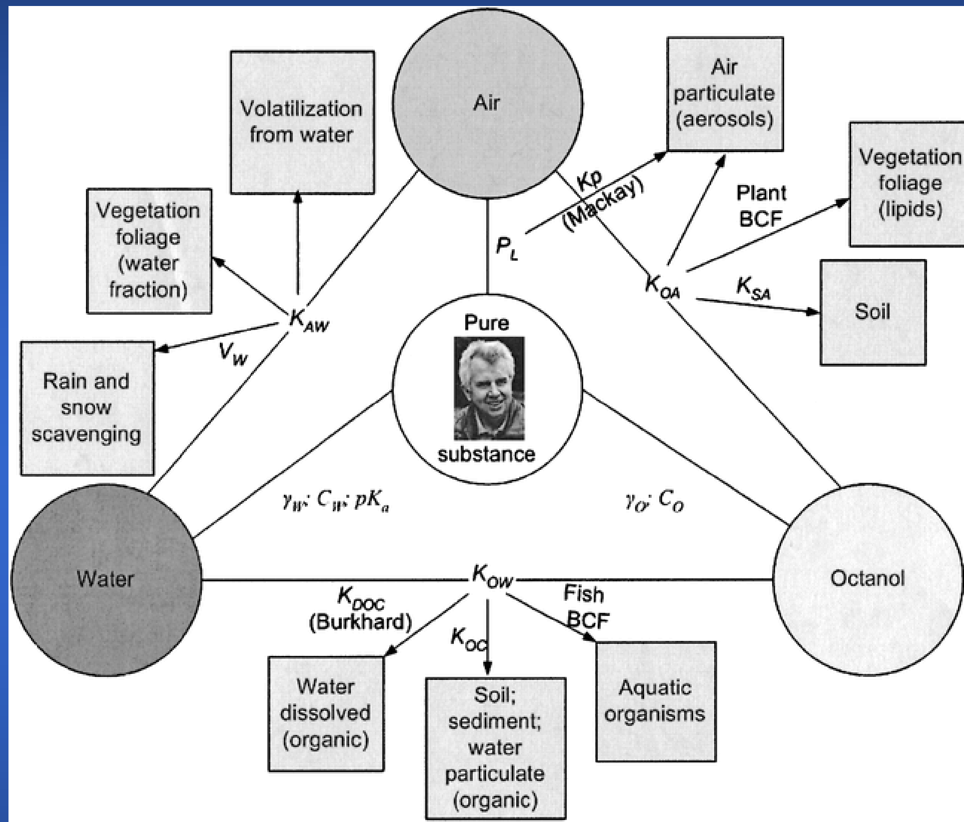
CAS = Chemical Abstract Service; ECDIN = Environmental Chemicals Data and Information Network; HSDB = Hazardous Substances Databank; ID = Identification; PHYSPROP = Physical Properties Database (contains ChemS[3], available online at: http://esc.syrres.com/ChemS3/default.htm)

Boethling et al. (2004)

Warning!

- Accuracy enhanced with measured values
- Substitutions can be risky
  - Hydrophobic is not analogous to lipophilic

Boethling et al. (2004)



Key to symbols

K_{AW} = air/water partition coefficient
K_{OW} = n-octanol/water partition coefficient
K_{OA} = n-octanol/air partition coefficient
P_L = liquid vapor pressure (supercooled liquid for solids)
C_W = saturation solubility in water
C_O = saturation solubility in n-octanol
g_W = activity coefficient in water
g_O = activity coefficient in n-octanol
pK_a = acid dissociation constant
BCF = bioconcentration factor
K_p = air/aerosol partition coefficient
K_{SA} = air/soil partition coefficient
Koc = soil/sediment sorption coefficient normalized to organic carbon
K_{DOC} = water/dissolved organic carbon (DOC) sorption coefficient
V_W = effective transport coefficient for air to rain and snow