Removal of Persistent Organics from Reclaimed Waters in Aquatic Systems

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Water: A Sustainable Resource

- **Hydrologic cycle**
  - **Functioning & sustainable for centuries**
  - **We always seem to have water**
  - **Atmospheric GHG/CO_2 are increasing & weather patterns are projected to change**
- **Water for many cities is limited now**
  - **Population growth and intensity of water-use both increase water quality & quantity needs**
  - **Urban development: Water availability does not seem to be a primary driving factor.**

Water: A Sustainable Resource

- **Engineering impacts are:**
  - **Water supply & treatment have expanded focus on trace contaminants &**
  - **Wastewater reclamation requirements are expanding.**
    - **Secondary to Tertiary to Full reclamation/reuse**
    - **Water and energy**
      - **increasingly linked**
      - **climate-change and advanced treatment systems (MBR, UF, RO…) make it even more apparent**

Water & Natural Systems

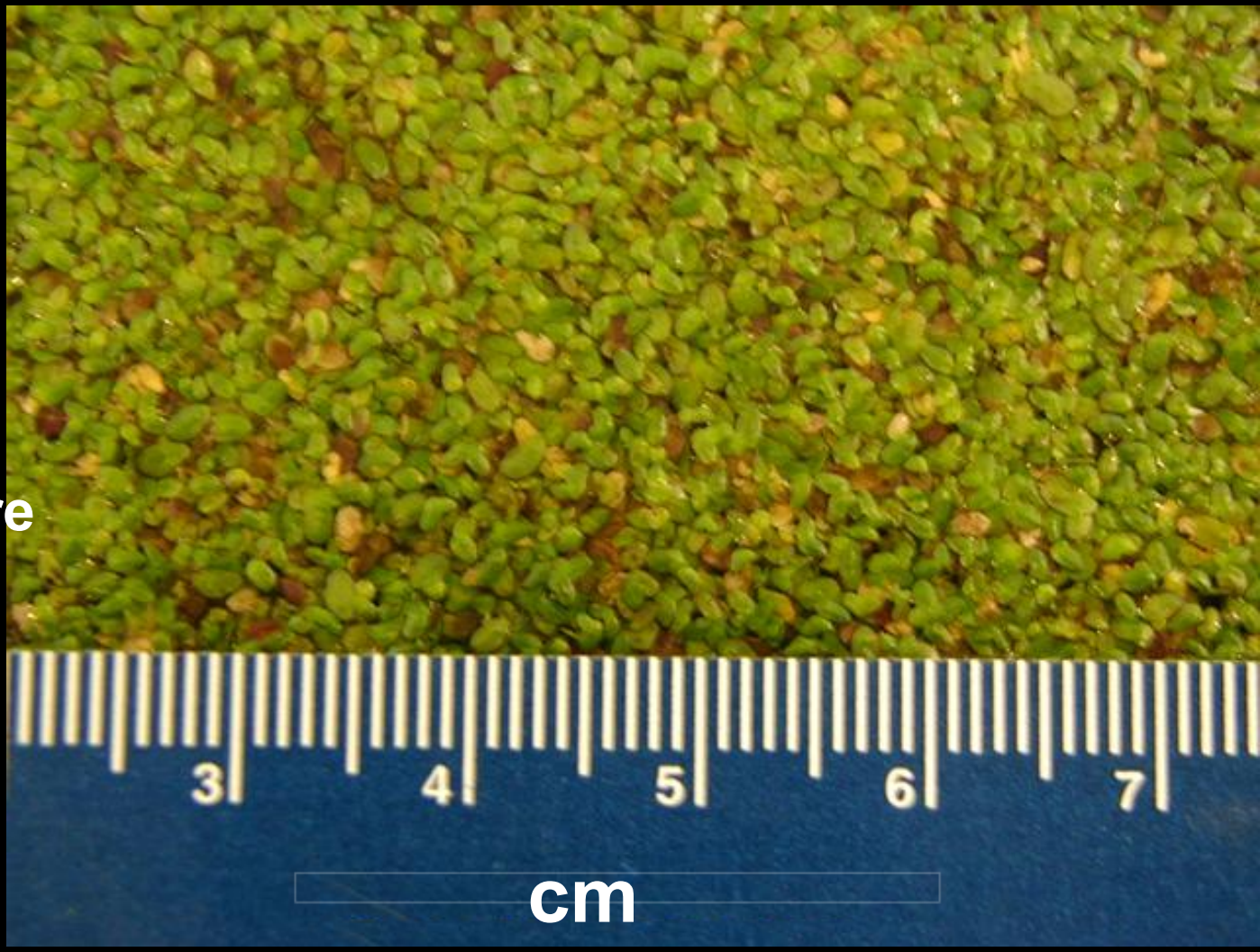
- Domestic water-supply and waste-disposal are both via natural streams, lakes & reservoirs.
- Industrial waters (wastewaters and storm waters) are similarly discharged to natural systems
- Our Inquiry

What are fates of trace & refractory wastewater contaminants in natural-system environments?

Constructed & Natural Wetlands

Experimental Study: Lemna minor

- **Monocot**
- **Angiosperm**
- **3-5 Fronds**
- **Single root**
- **Fast growth**
- **All Lemna were from natural-environment systems**

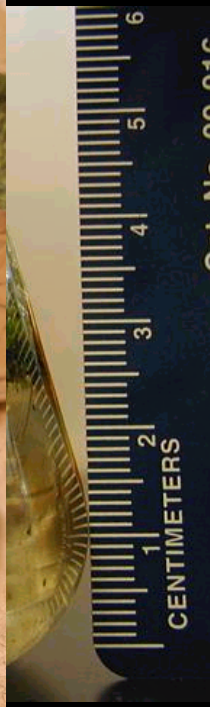


Duckweed: Lemnaceae / Araceae (Lemniodeae)

- **Duckweed - family of small freshwater plants**
  - **Food source for waterfowl & humans**
  - **Freshwater aquaria and ponds**
    - **NO_3^- removal; cover for fry; shelter by pond water species; reduce evaporation; clogging is a problem**
  - **Bioremediation via N & P removal**
  - **Toxicity assessments (WET) and food-chain assessments**
  - **Natural environment populations**
    - **naturally-occurring mixed populations driven by environmental selectors**
- ***Genus***
  - ***Lemna***
    - ***L. minor, L. gibba, L. trisulca***
  - ***Spirodela***
    - ***S. polyrhiza* - DOE-JGI sequencing for biomass & bio-energy**
  - ***Landoltia***
    - ***L. punctata***
  - **Wolffia**
  - **Wolffiella**

Serum-bottle systems with variable plant-density Incubation at 20C with 16-8hr illumination cycle

- **Experimental Unit:**
  - **250-mL flask**
  - **~3.5 g FW *L. minor***
  - **100 mL media**
- **Units run in parallel with data being avg. of 3 parallel reactors**
- ***Representative data includes DCP & TCP***



Overview

- *Lemna* (duckweed) used as model plant
- Assess fate of persistent organic compounds (POCs) in wetland and natural-environment systems
  - Natural-environment plants for bio-assays with multiple controls
  - O_2 production used to assess POC toxicity and plant activity
  - Halogenated-contaminant monitored in water column and inside plants
- Fate of POCs taken-up by plants & chemical metabolites
  - Experimental assessment
  - Modeling concept
  - Halogenated POC array & substituent position effects
- Ultimate fate of plant-sequestered POCs
- Callus and cell-culture approaches
- Field studies and reuse issues

Lemna (duckweed)

Key Collaborators

Dr. James Day, US DOD

Dr. Jacqueline Tront, US Dept. of State

Professor Dawn Reinhold, Michigan State

Professor Rosa Krajmalnik-Brown, Arizona State

Dr. Ben Amos, Geosyntech

Dr. Guangxuan Zhu, GA Tech

Professor Frank Löffler, Univ. of TENN

Professor Julia Kubanek, GA Tech

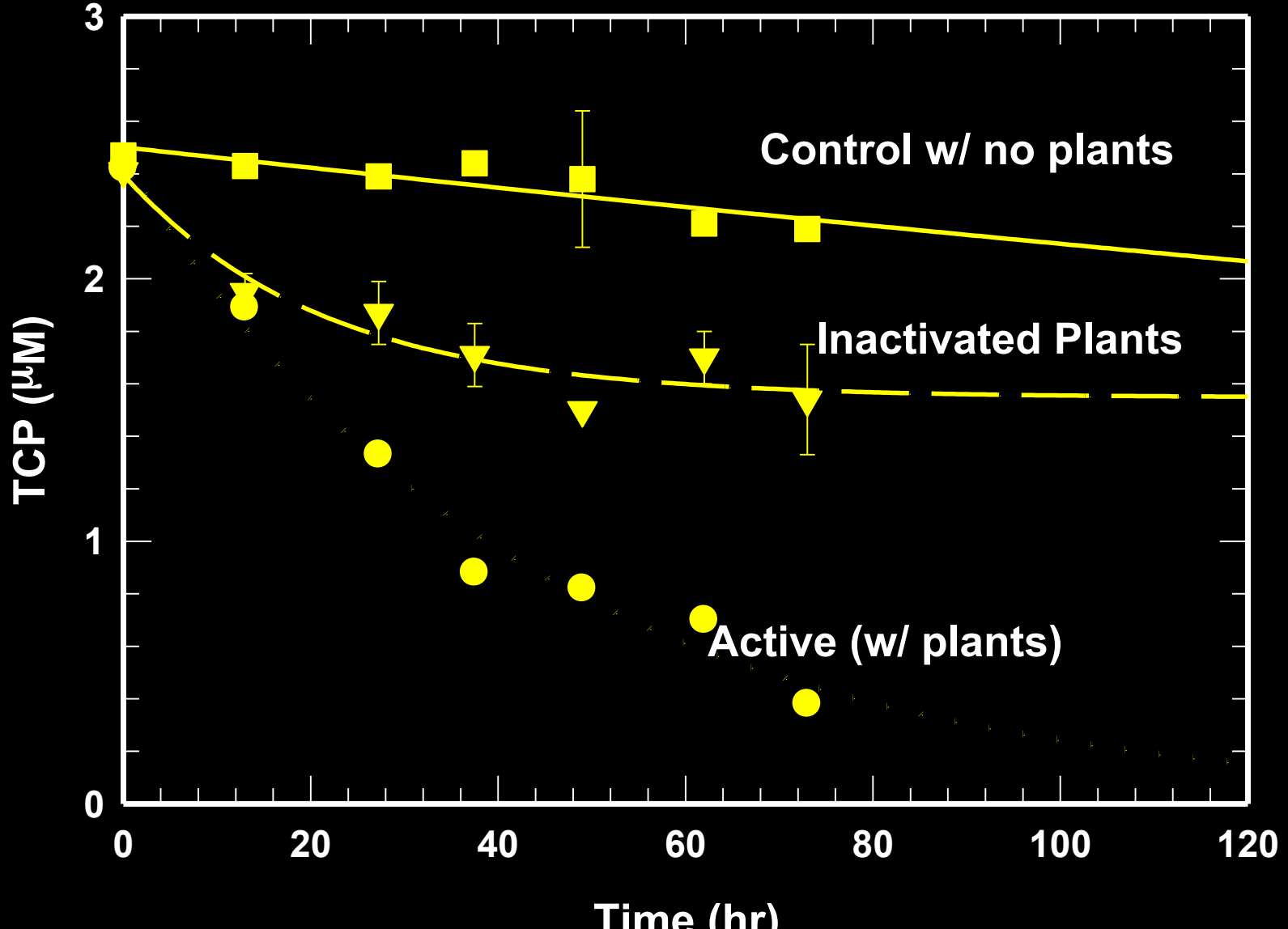
Dr. Robin Brigmon, SRNL

Contaminants of Interest

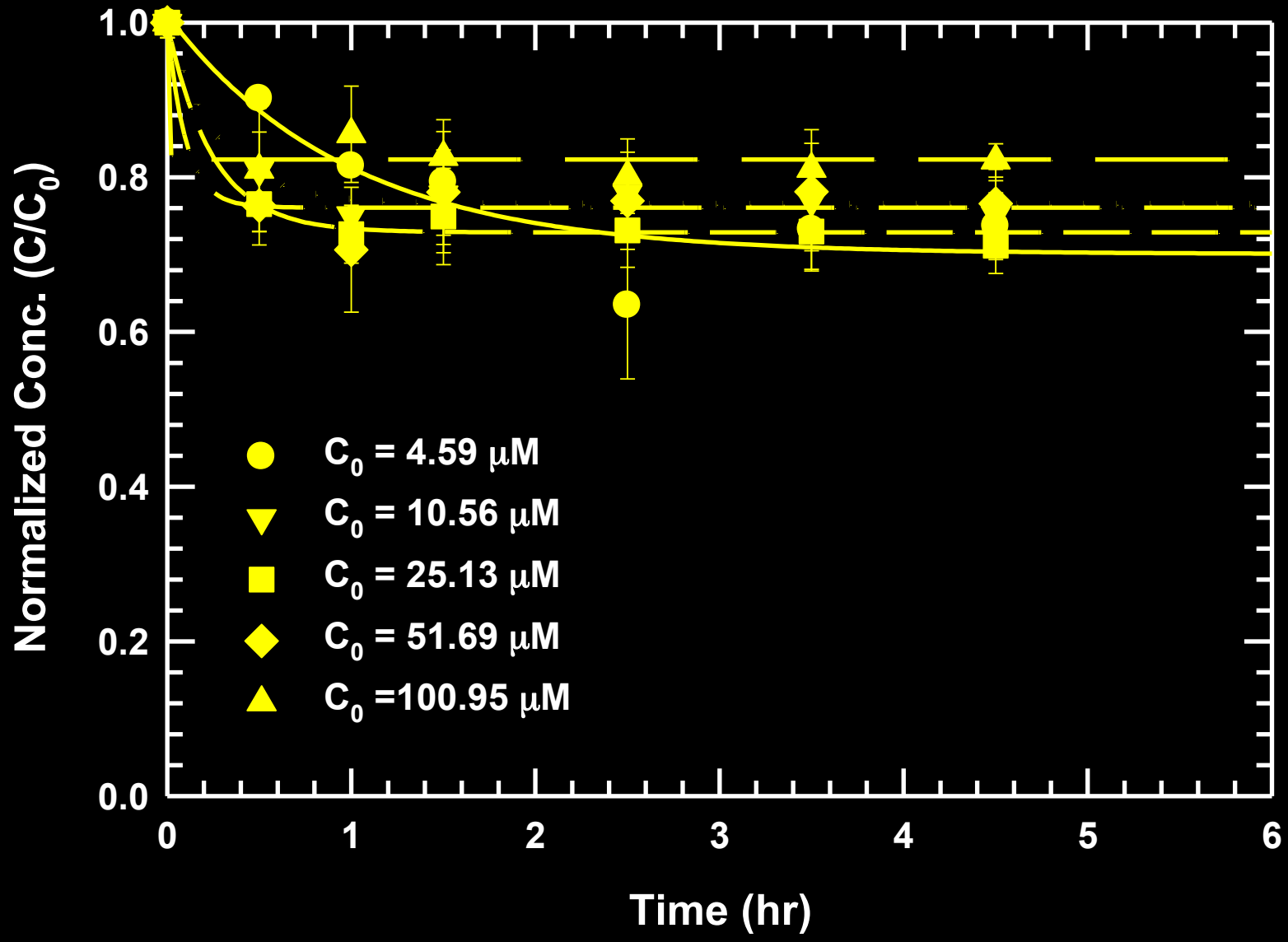
Chlorinated phenols
Fluorinated phenols
Chlorinated benzenes
Fluorinated benzenes

Ibuprofen
Fluoxetine
Clofibric acid
DEET
Triclosan
2,4-D
Prozac…

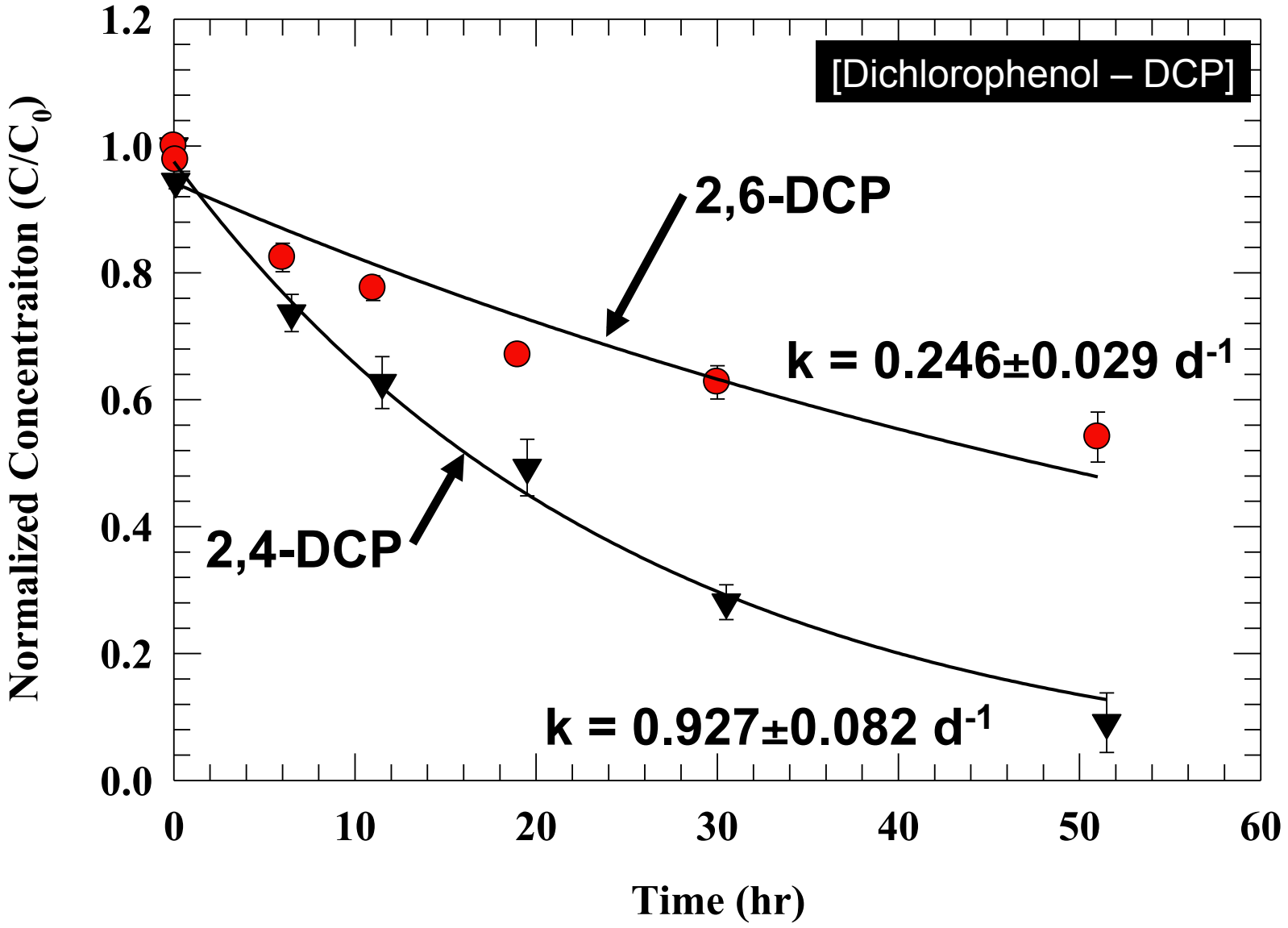
Example of Contaminant Uptake with Trichlorophenol (TCP)



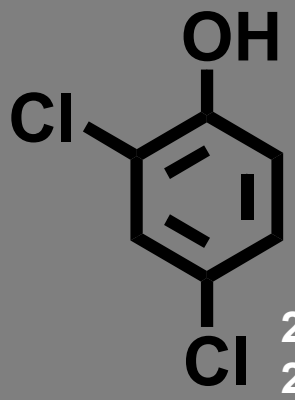
DCP Partitioning w/ Inactivated Plant Mass



Uptake of persistent organics - monitored with aqueous-phase conc. & pseudo-first order reaction kinetics

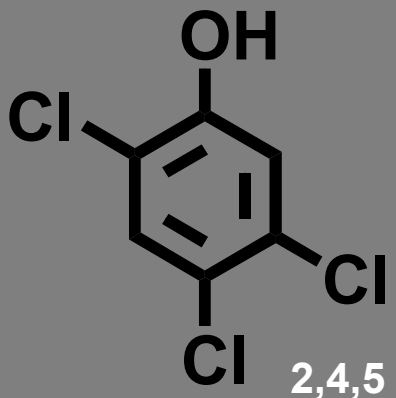


Chloro-phenols



2,4 dichloro-phenol
2,4 DCP

- 2,4 DCP (DCP)
  - MW=163, IM=161, pKa=7.8



2,4,5 trichloro-phenol
2,4,5 TCP

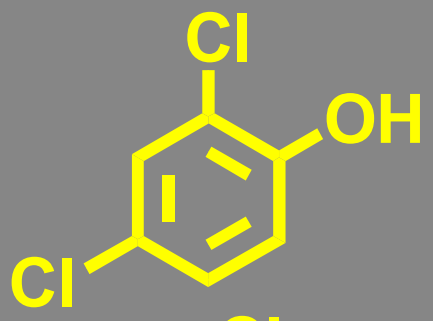
- 2,4,5 TCP (TCP)
  - MW=197.5, IM=195, pKa=7.0

Metabolite Identification

- **LC-Electrospray Ionization (ESI)-MS**
  - Direct analysis of liquid samples
  - Soft Ionization, little fragmentation
  - Adapt chromatography to preparative scale
- **^{1}H-NMR [& ^{19}F-NMR]**
  - Shift
  - Number of unique protons
  - Information on adjacent atoms
- **Carbohydrate analysis & synthesis**
  - Chemical Synthesis
    - Glycosides: Koenigs-Knorr (Sinnot & Souchard 1971)
    - Esterified Glycosides: (Roscher *et al.* 1996)
  - Monosaccharide Composition
    - Compare chromatographic distribution of perbenzoyl derivatives
  - Linkage Analysis
    - Compare retention and EI-MS of partially methylated alditol acetate derivatives

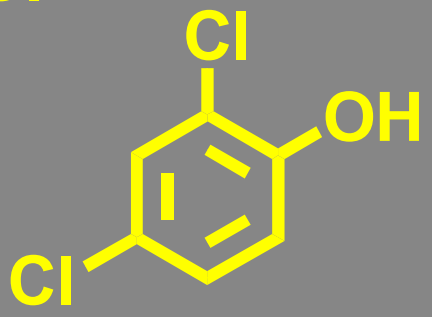
System Components

Aqueous DCP



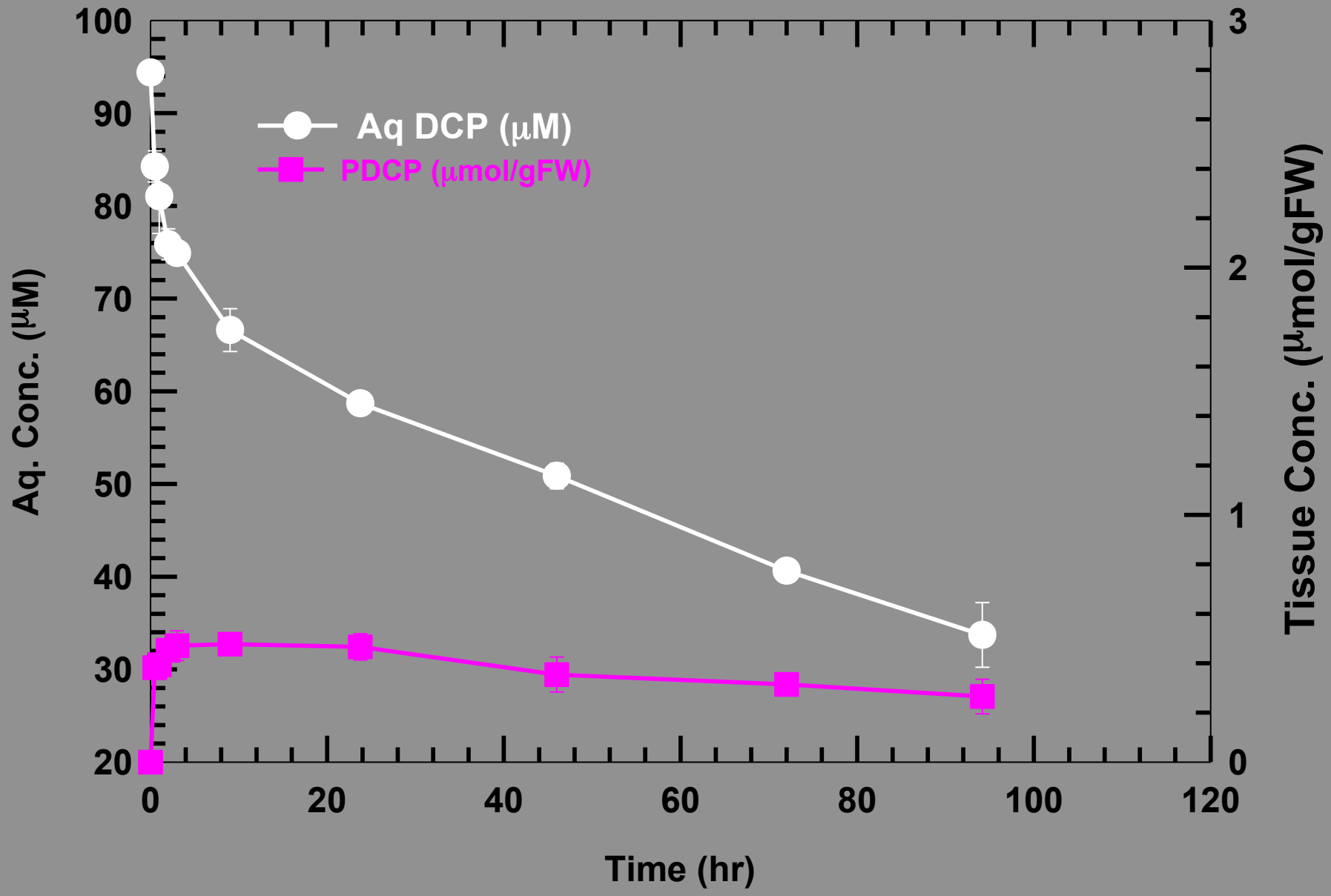
Aq DCP

DCP (Plant Tissue)



PDCP

DCP Partitioning

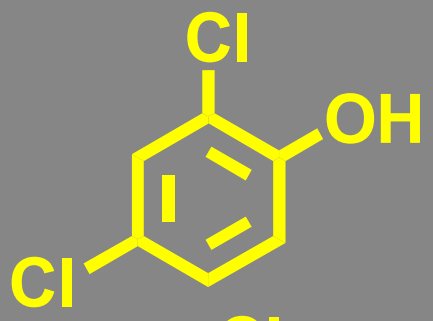


System Components

J. Day

Structure

Aqueous DCP



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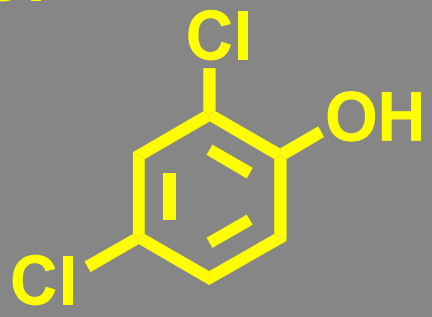
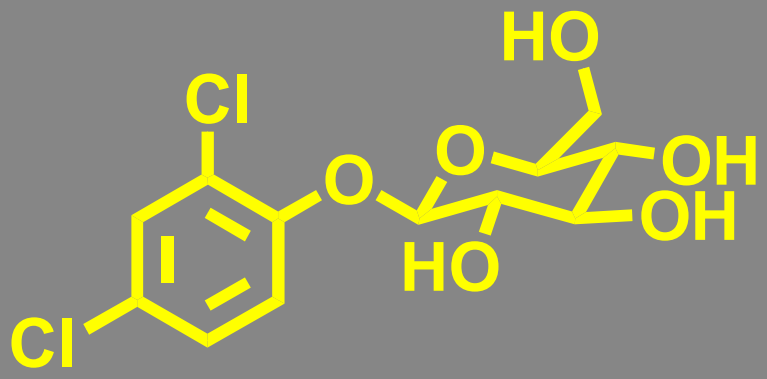


PDCP



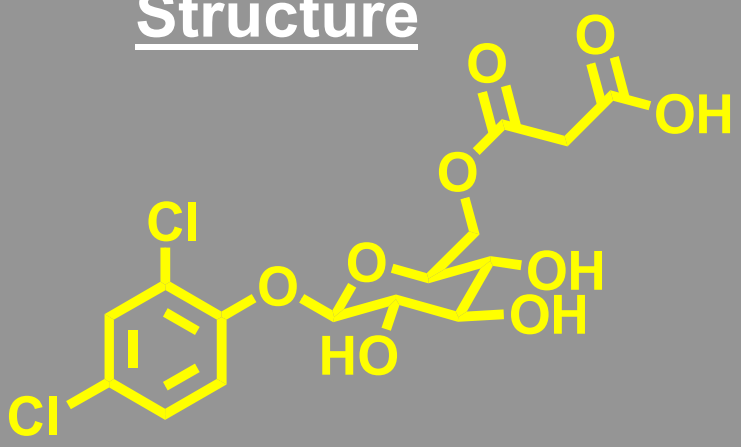
DCPG

2,4-Dichlorophenyl-β-D-Glucopyranoside = DCP-Glycoside

System Components

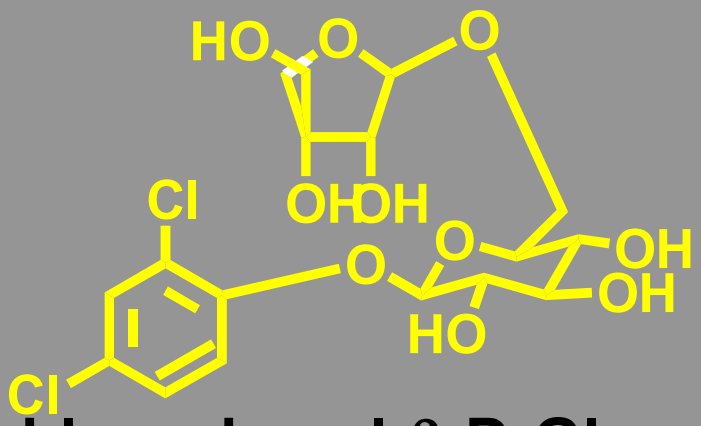
J. Day

Structure



Malonyl-glycoside
DCPMG

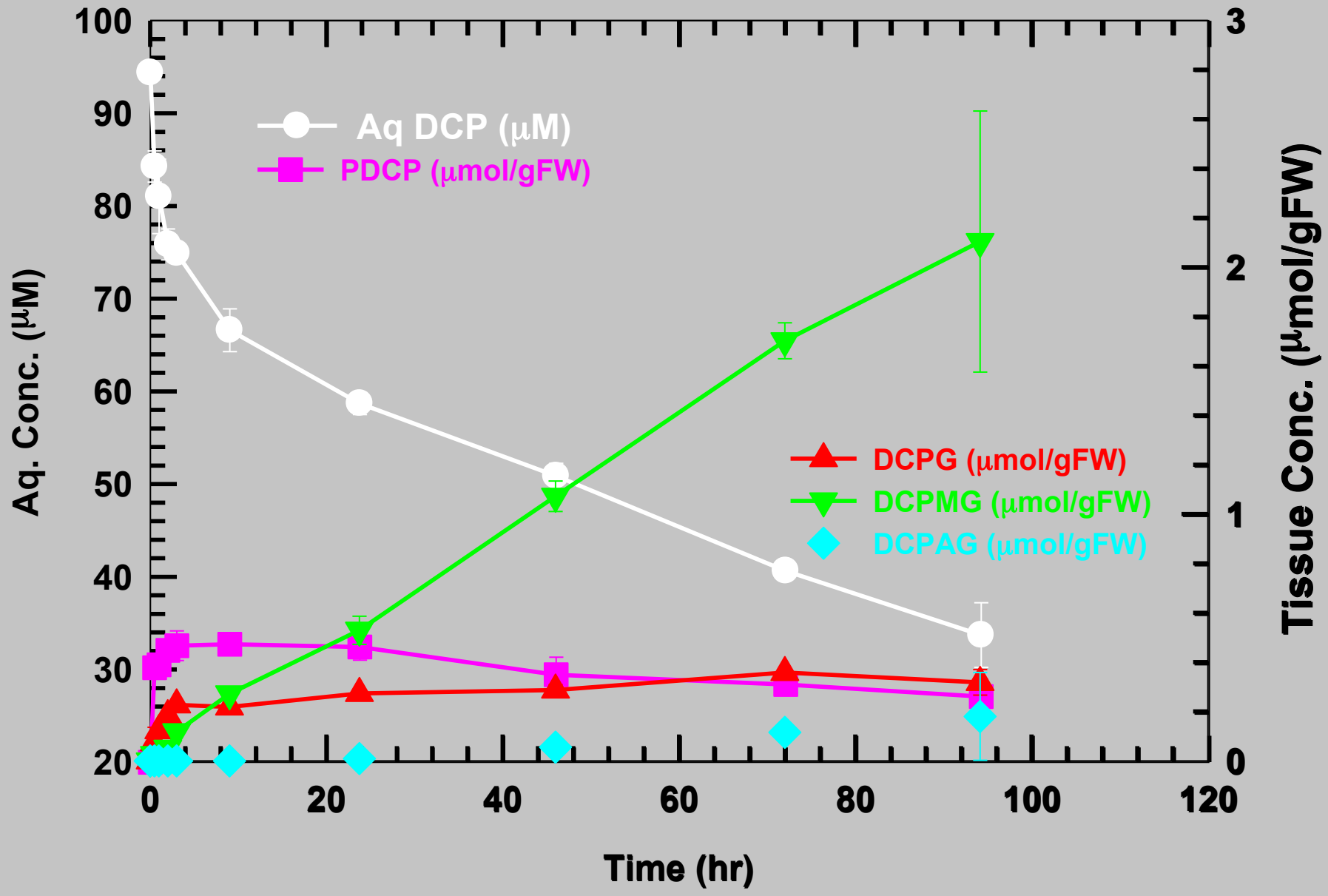
2,4-Dichlorophenyl-(6-O-Malonyl)-β-D-Glucopyranoside →→→ DCPMG



Di-glycoside DCP
(apiose + glucose)
DCPAG

2,4-Dichlorophenyl-β-D-Glucopyranosyl-β-D-Apiofuranoside →→→ DCPAG

DCP Metabolite Formation



Kinetic Examination using “Conversion”

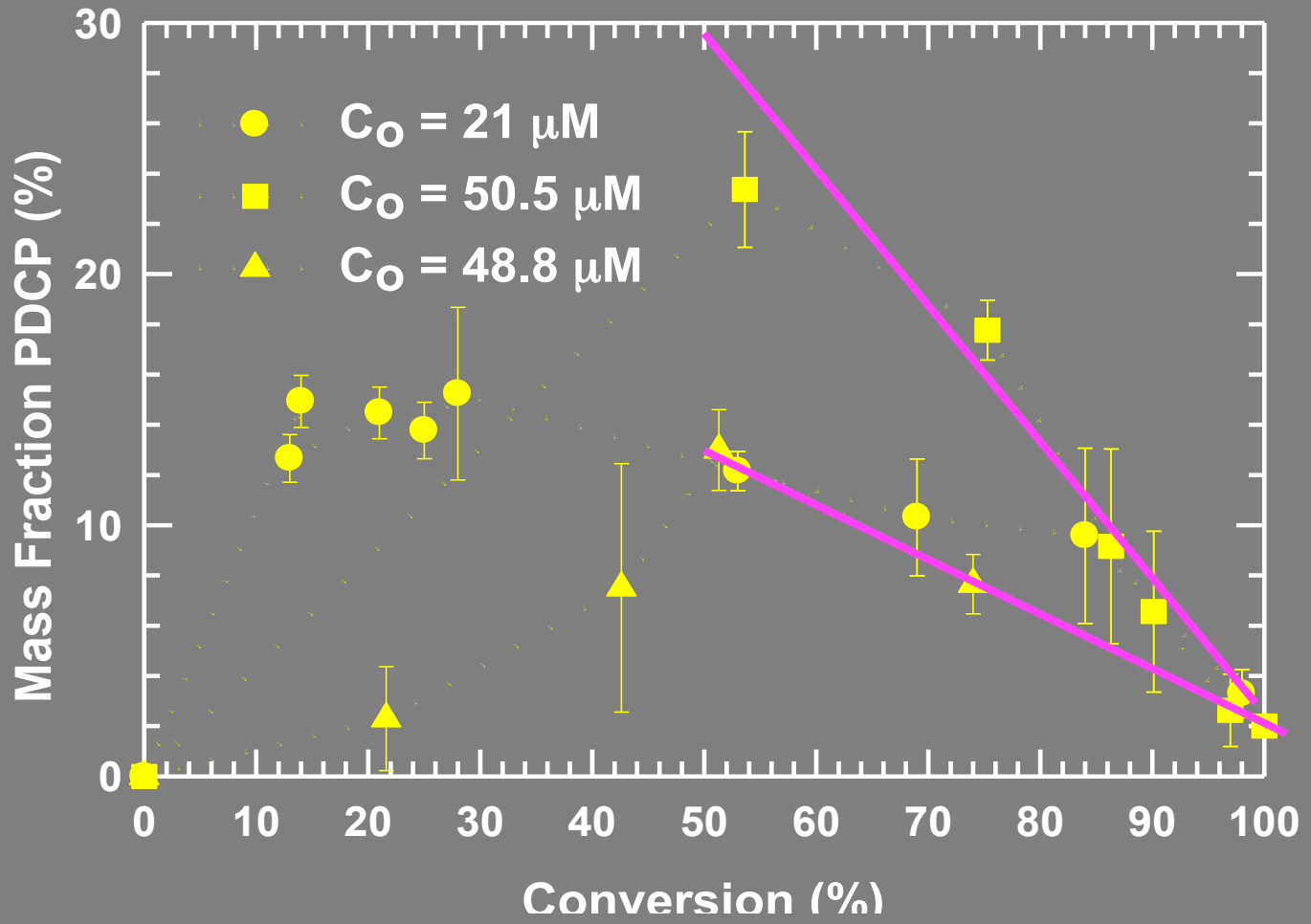
- **Normalize factors with “conversion”**
  - **amount removed from aqueous phase**

$$Conversion = \frac{C_o - C_i}{C_o} \times 100\%$$

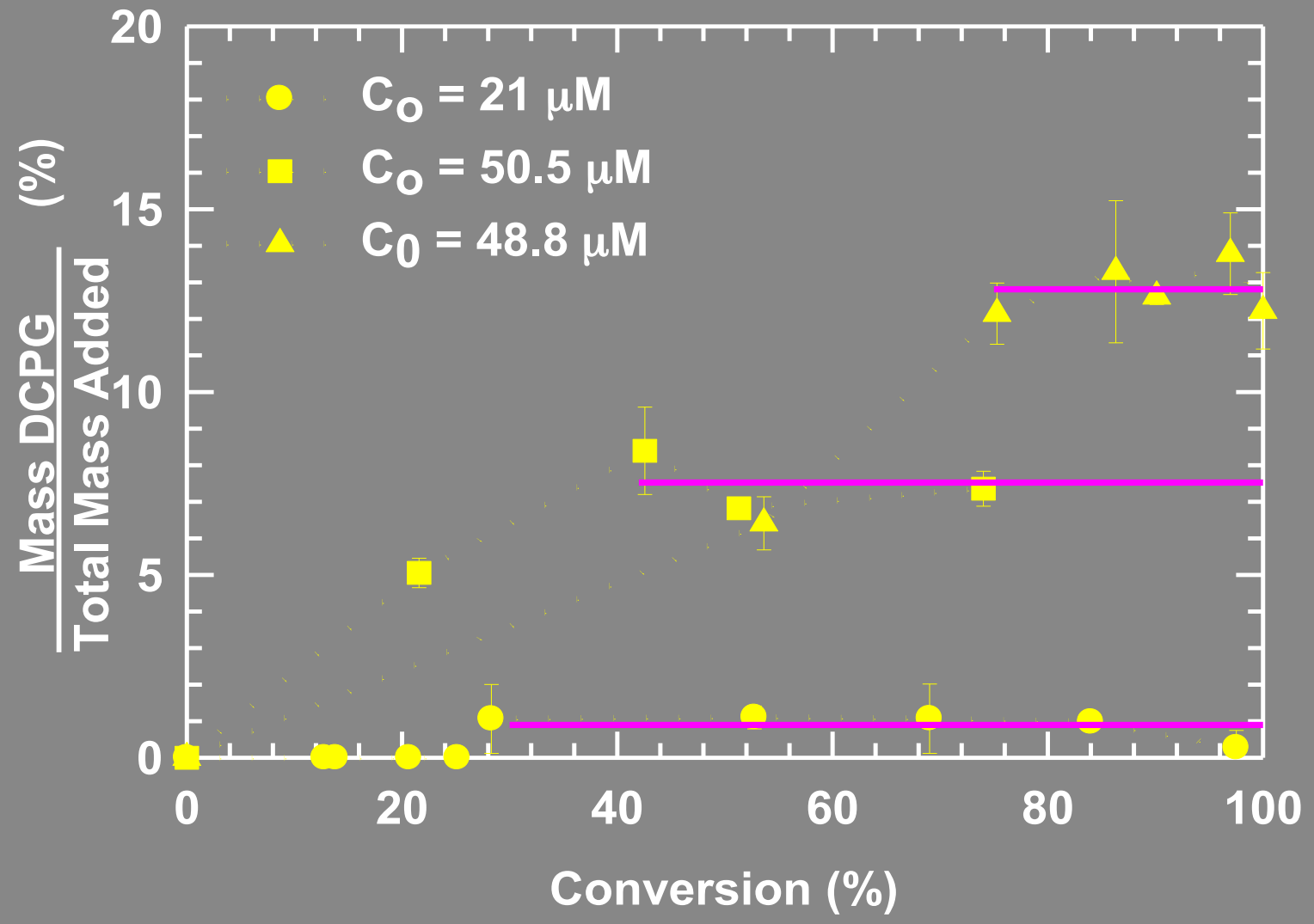
C_o = Initial Aqueous Concentration
C_i = Aqueous Concentration at time t_i

Internal Plant DCP - PDCP

- Transitory maxima
- Not Correlated to C_0 or X_p
- Approaching Zero at 100% Conversion

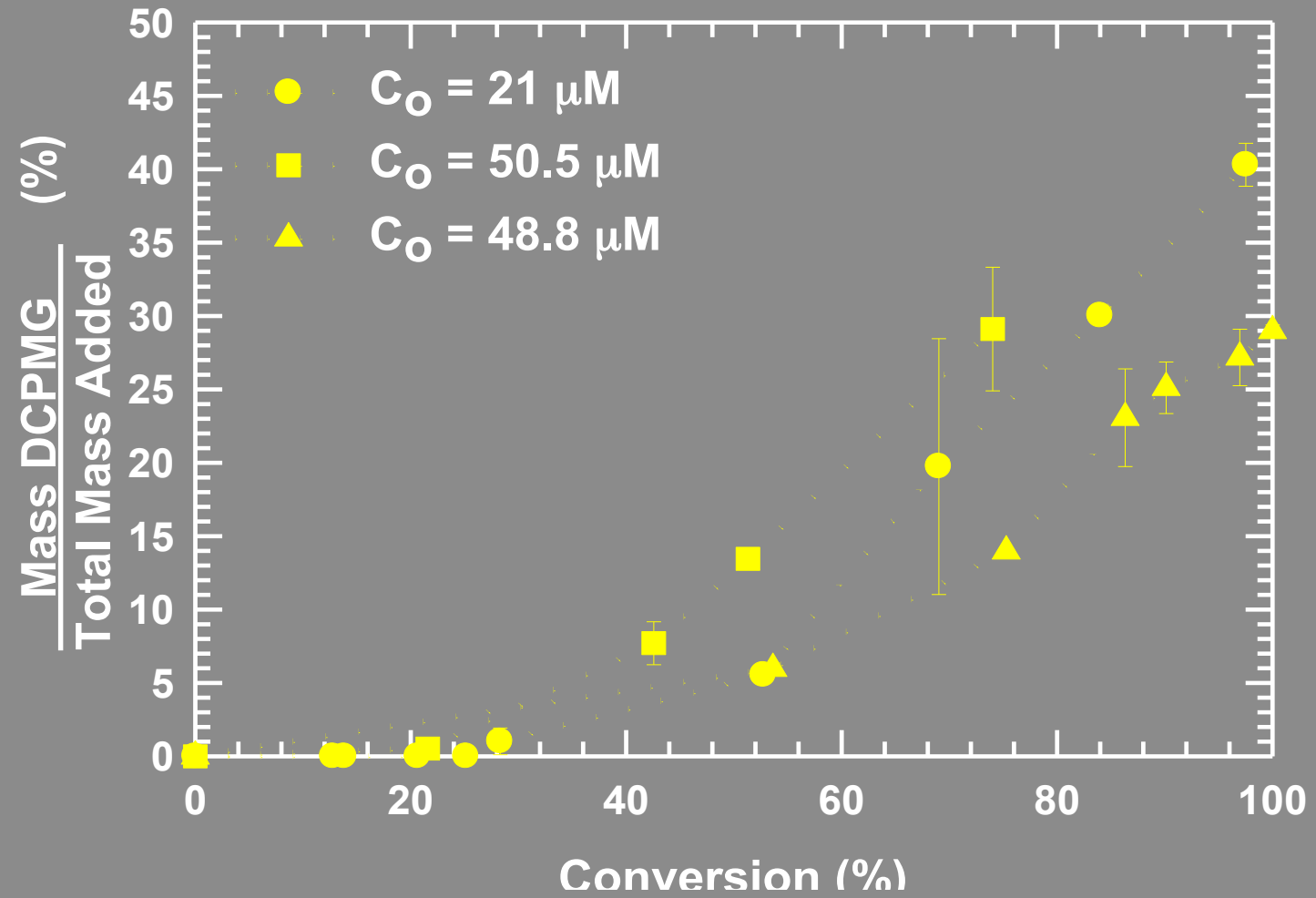


Formation of DCP-glycoside, DCPG



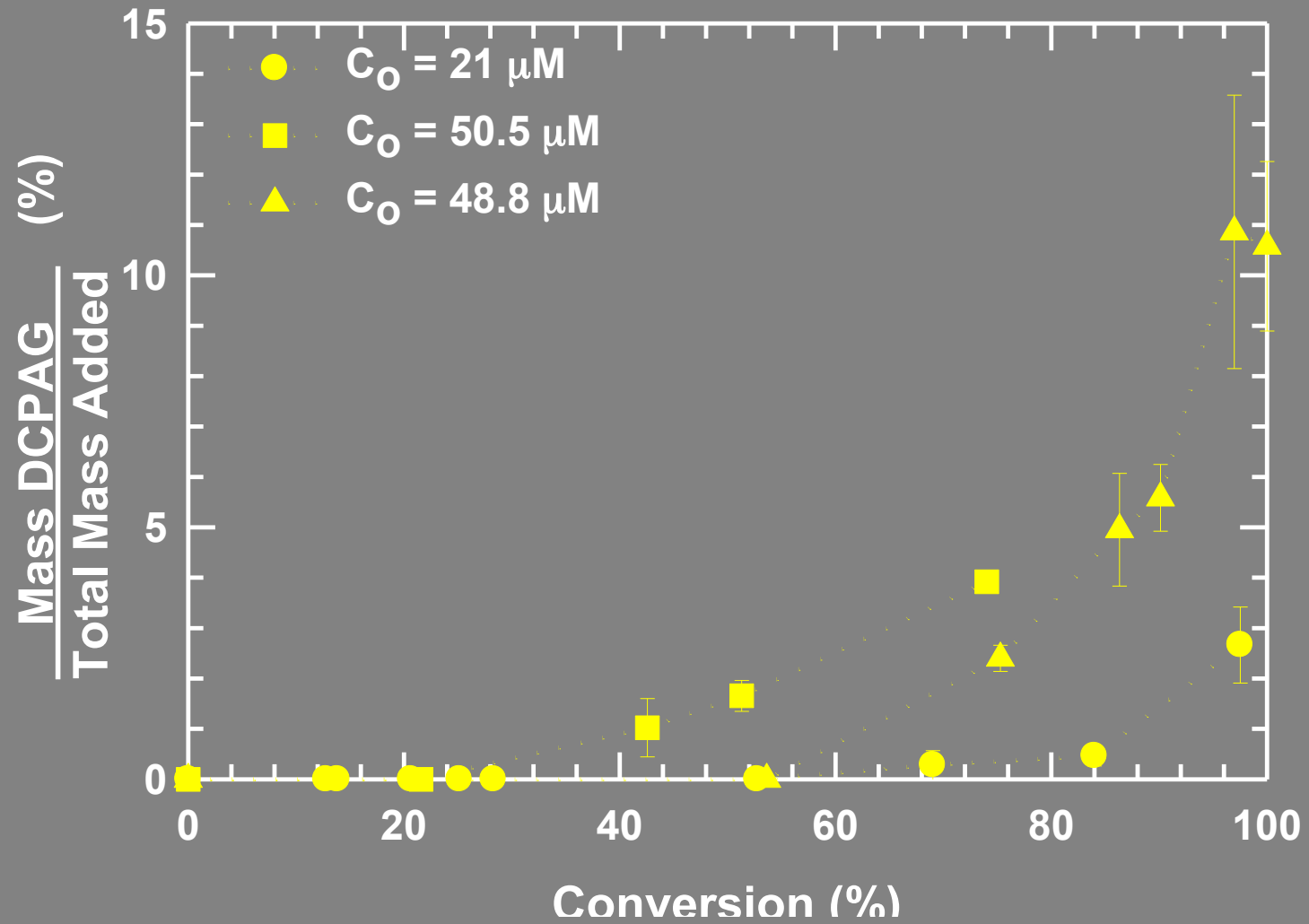
- Approaches Plateau [DCPG] at ~30- ~80% conversion

Formation of malonyl DCP-glycoside, DCPMG



Pseudo-exponential accumulation as conversion approaches 100%

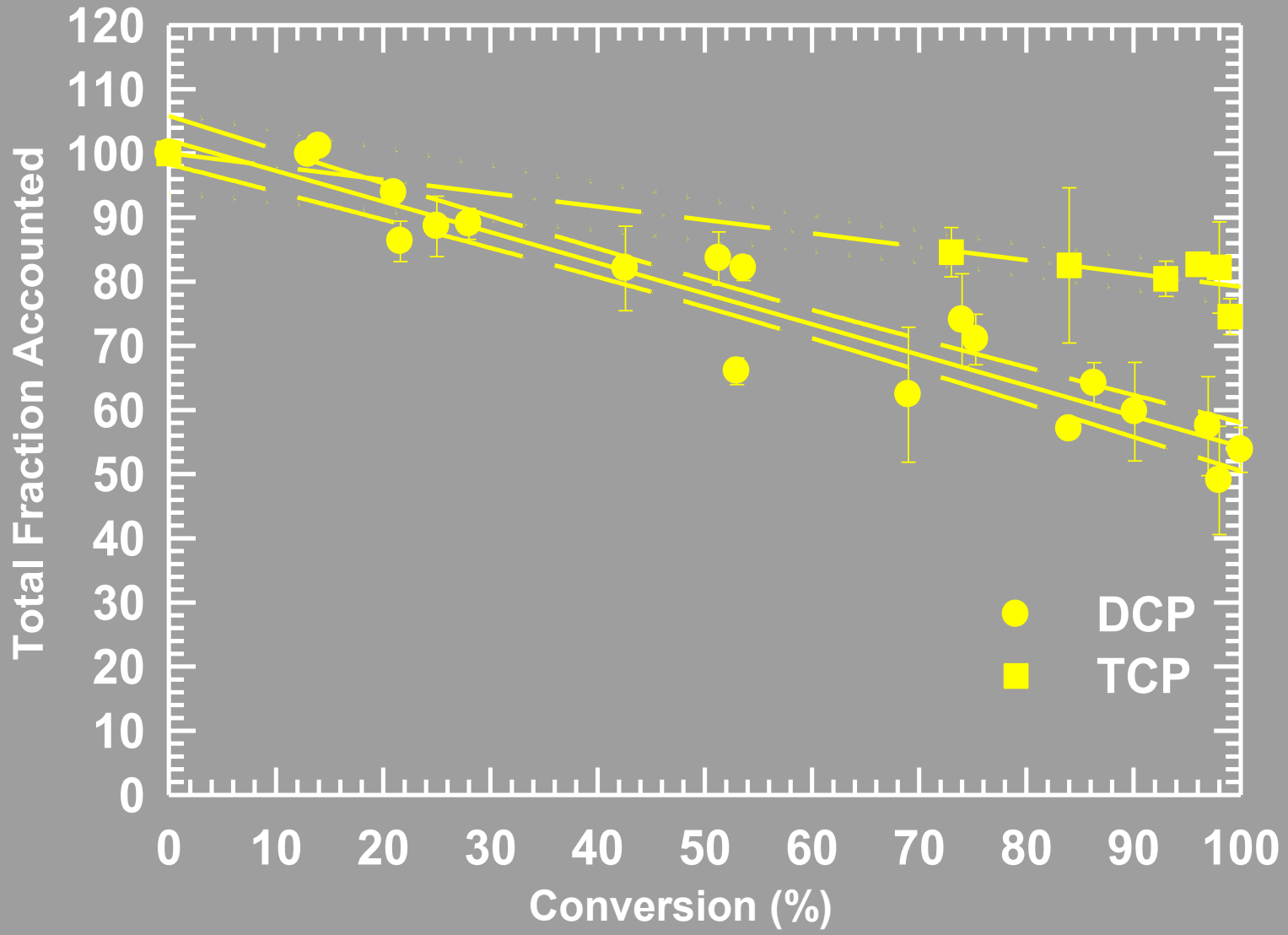
Formation of apiose-glycoside from DCP-glycoside, DCPAG



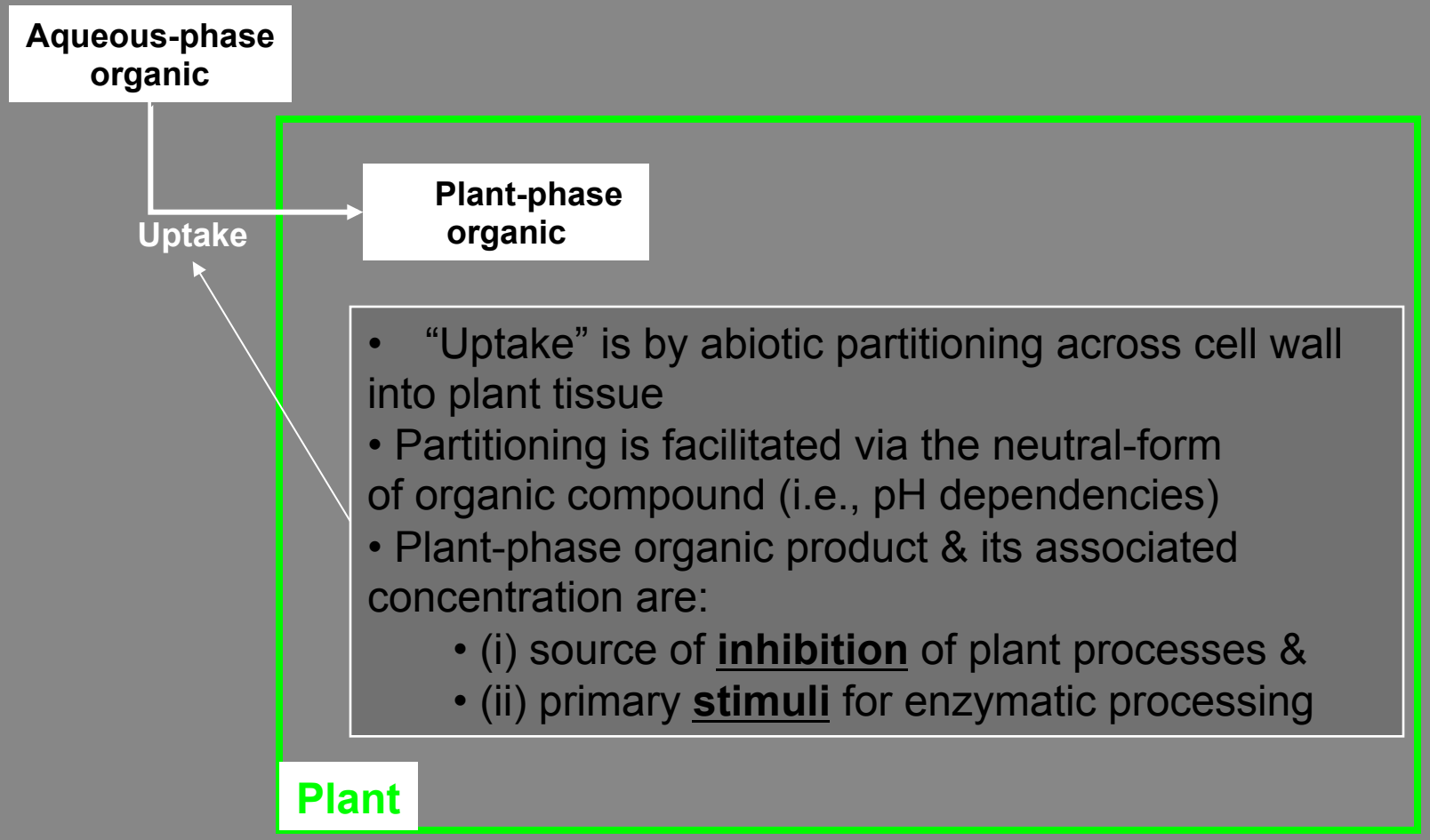
Comparison of Identified Metabolites to "Conversion"

- All internal contaminant & metabolites identified =
  - PDCP + DCPG + DCPMG + DCPAG
- Sum of internal contaminant and metabolites (DCP & TCP) vs "percent conversion"
- Note: % conversion analogous to the term $(1-e^{-kt})$ for a psuedo-1^{st}-order reaction

Metabolites vs Conversion



Conceptual Model for Processing of Plant-active Persistent Organic Compounds



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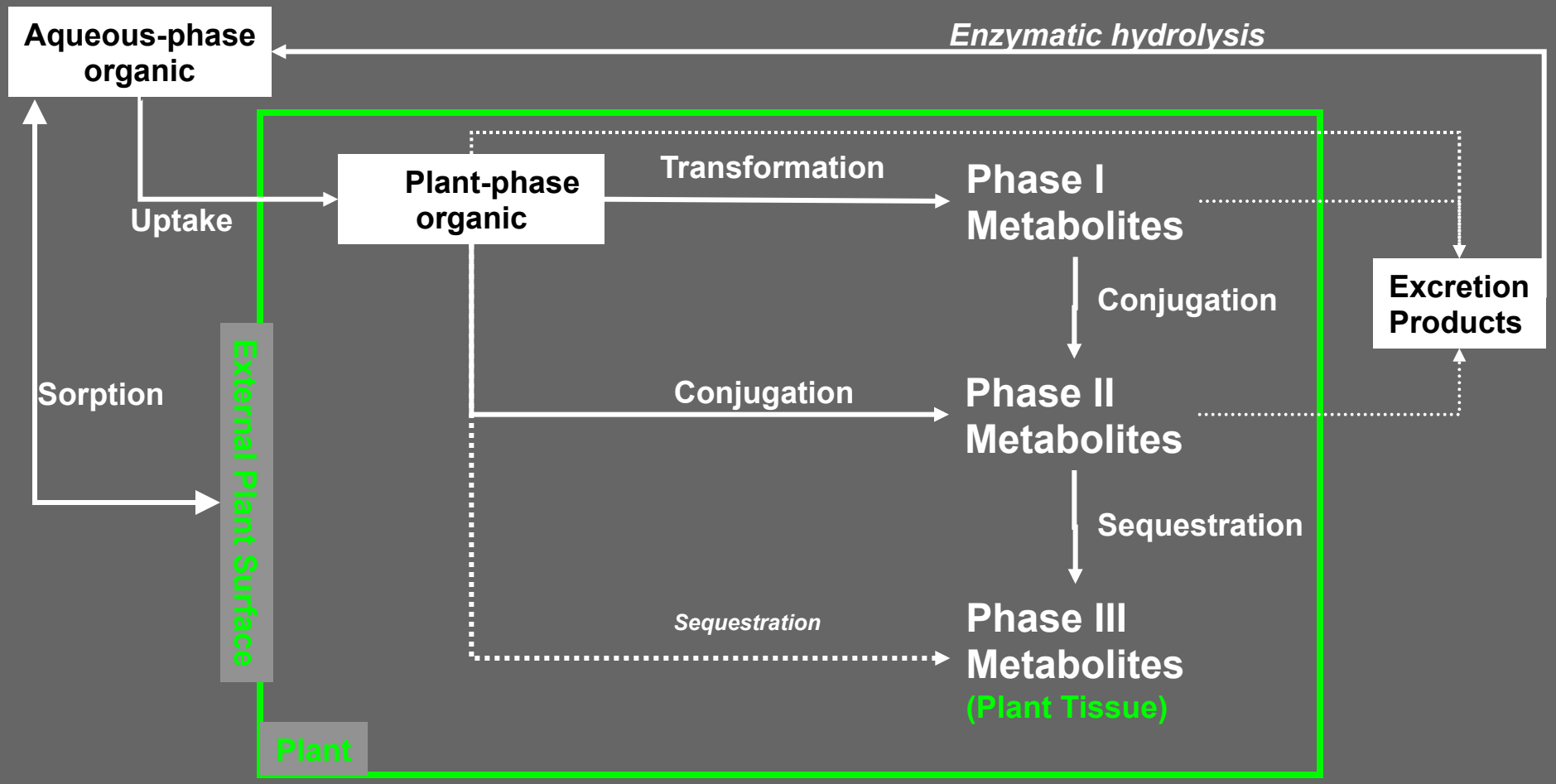
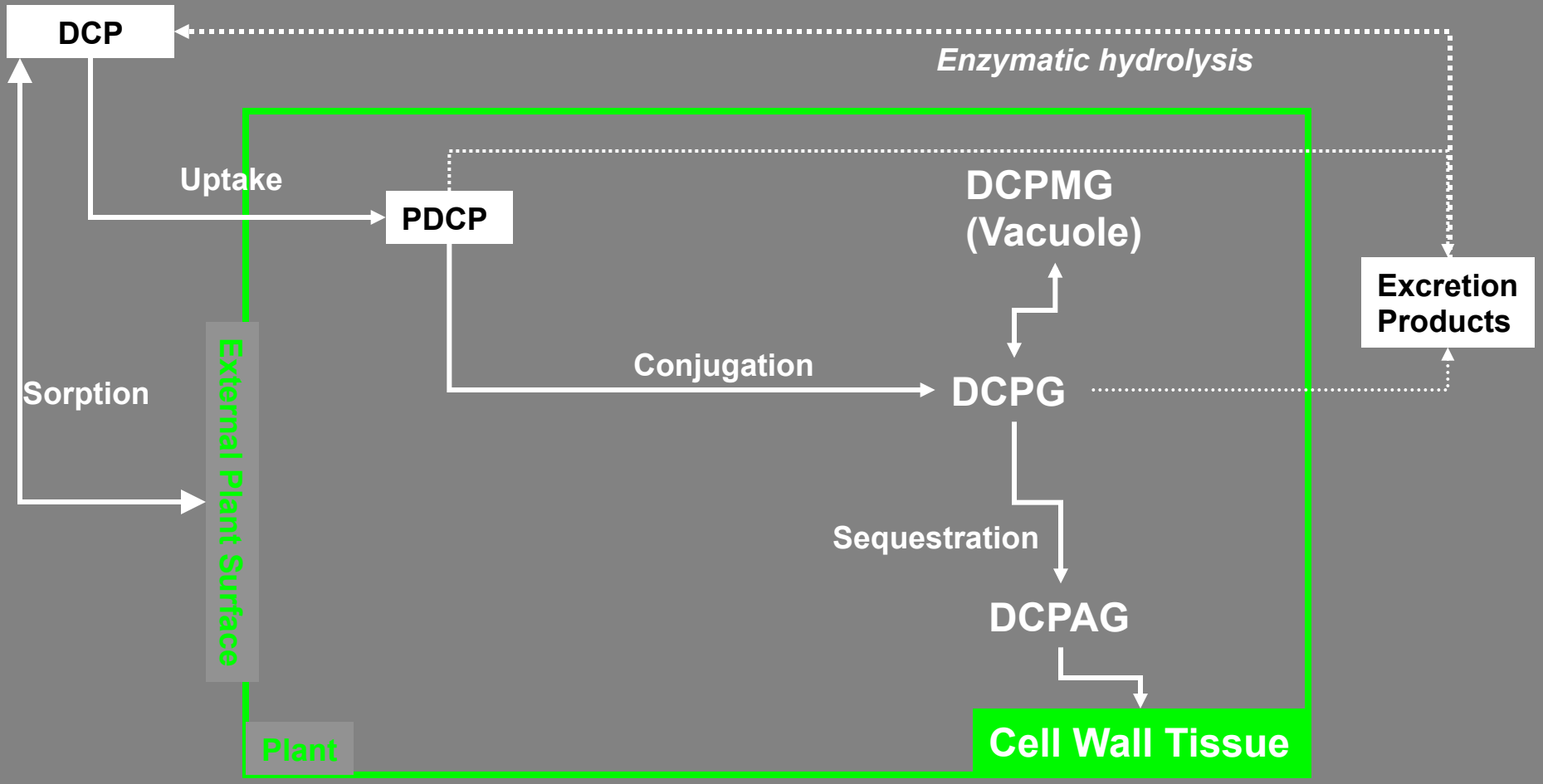
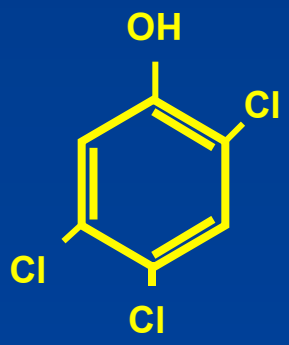


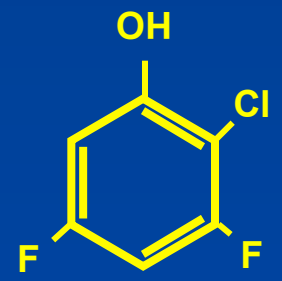
After Trapp & McFarlane 1995

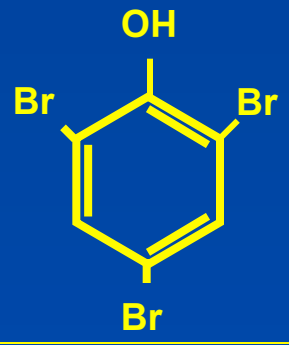
Conceptual Model for DCP Fate

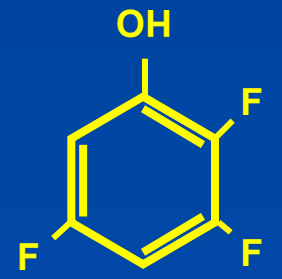


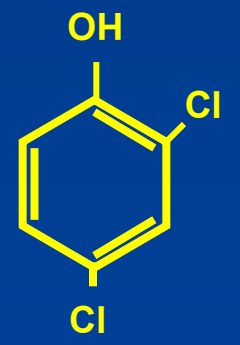
Halogenated Phenols Examined

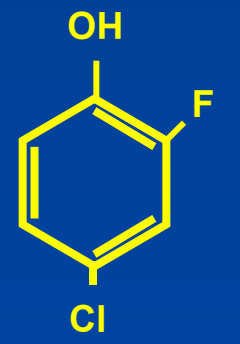


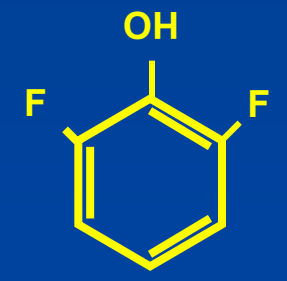


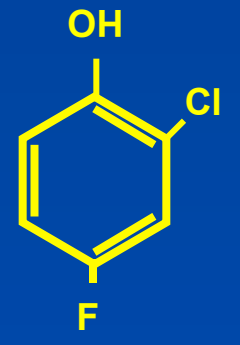


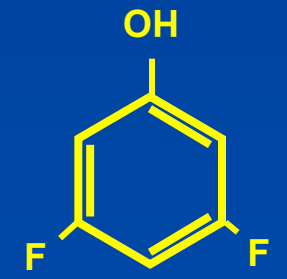


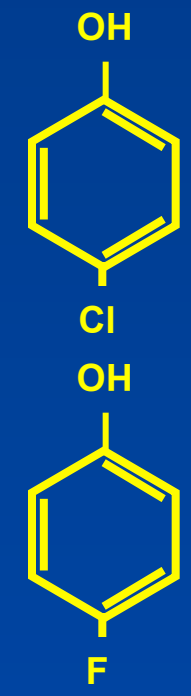






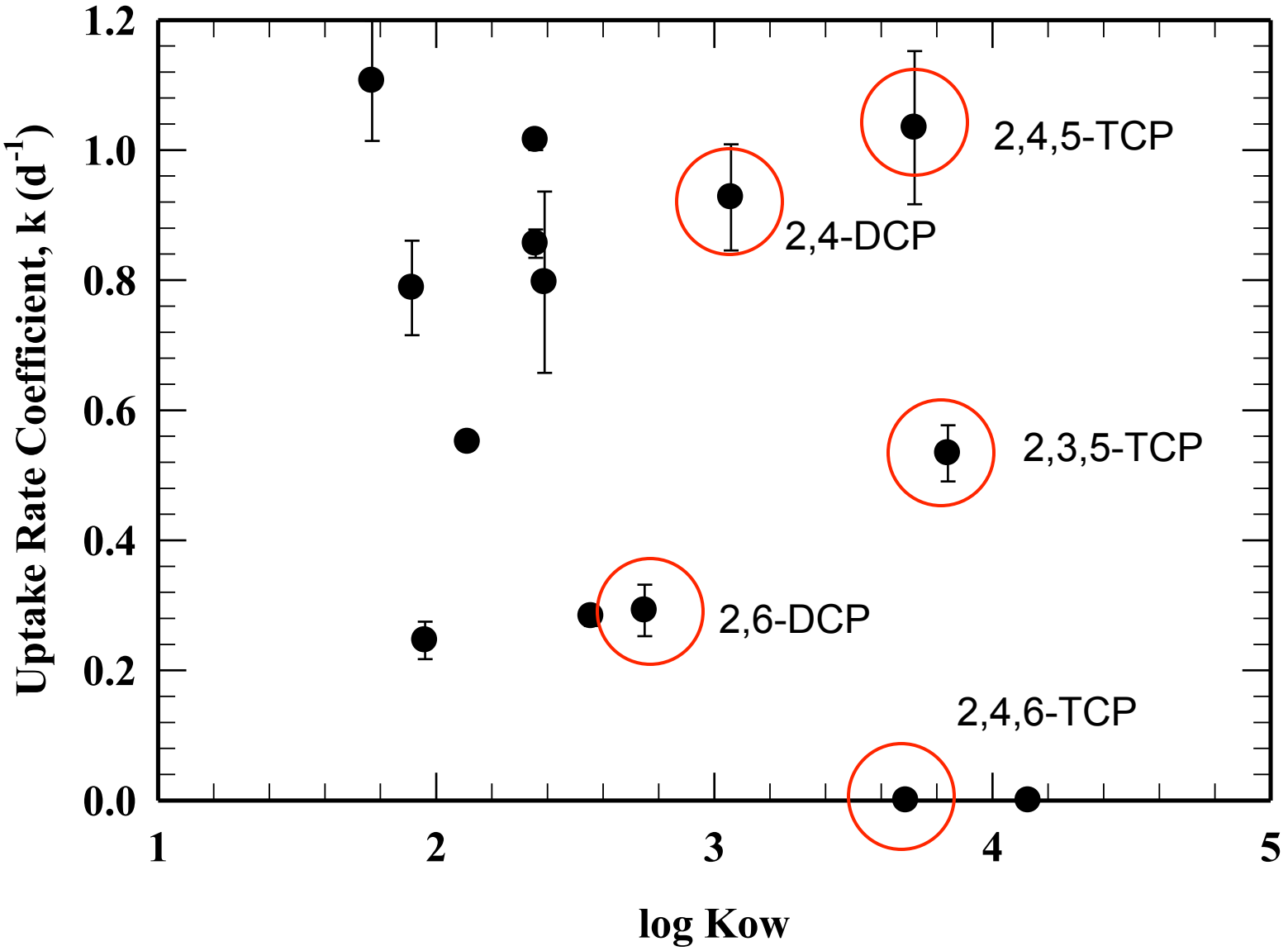




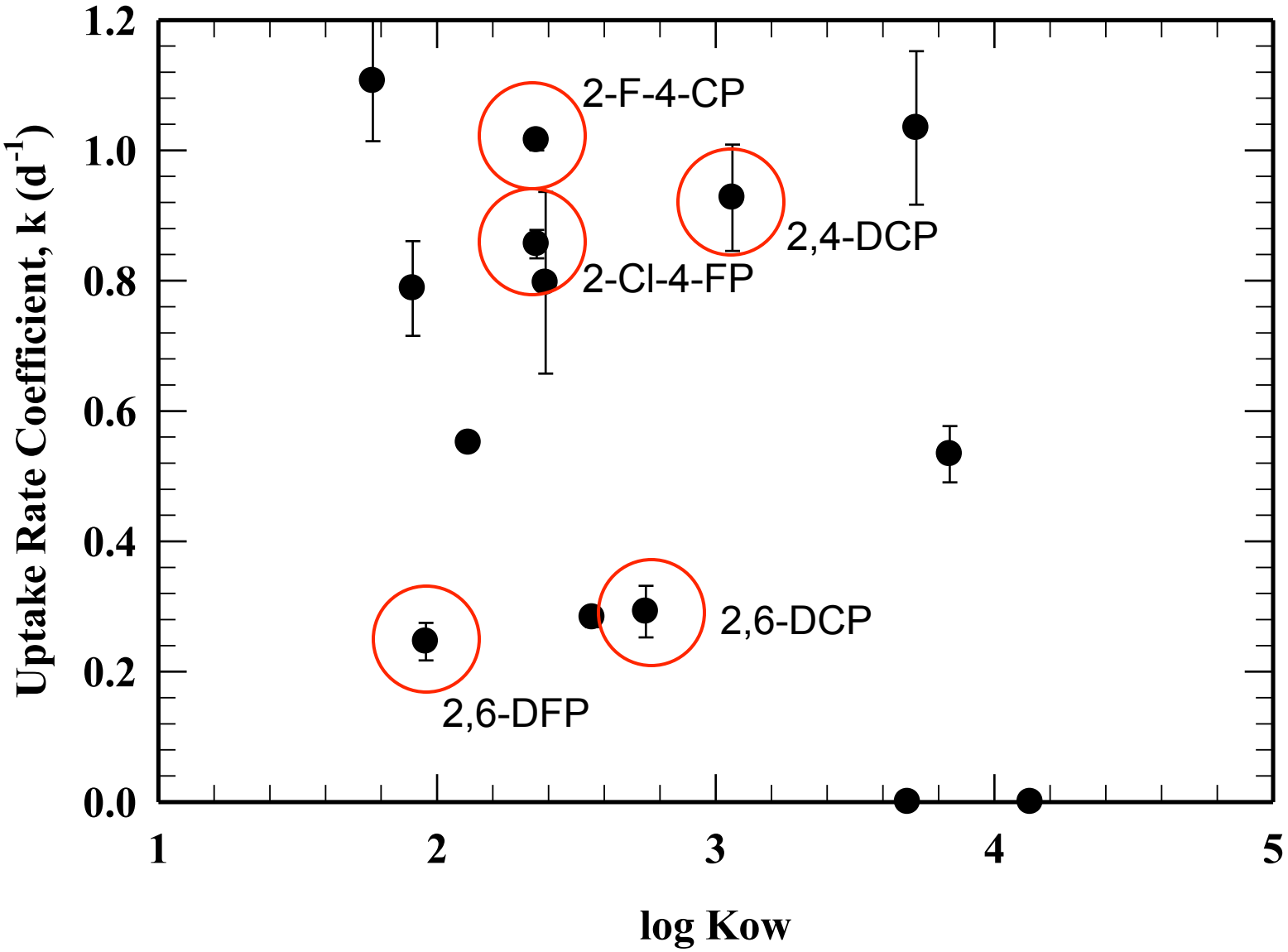


14 Halogenated Phenols: k vs. log Kow

Examine Substituent Number



Chlorine vs. Fluorine Substituents



Outcomes

- Aquatic plants
  - sequester persistent organics & “package” within tissue
  - do not mineralize persistent organics
- Opportunities & Concerns
  - use natural systems to remove trace organics from waters
  - use CO_2-derived plant tissues for sustainable mineralization of persistent organic contaminants
  - sequestered contaminant may enter food chain
  - release of contaminants into natural systems
- Natural plant systems remove toxins and can be a used as a sustainable “treatment” system
- Update role of wetlands and oxidation ponds in overall water-quality management system

Water Reuse & Persistent Organics

- *Removal of POCs via aquatic plants is established*
- *Plant-microbe mineralization is possible*
- *Use of natural-systems processes provides another key aspect for human-health protection*
- *Engineering use of aquatic plant systems can have a role in system design*

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- Assess fate of persistent organic compounds (POCs) in wetland and natural-environment systems
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- *Field studies and reuse issues*

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