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# Enhanced solubility of priority contaminants in high-biomass systems and associated impacts on biofilter operation

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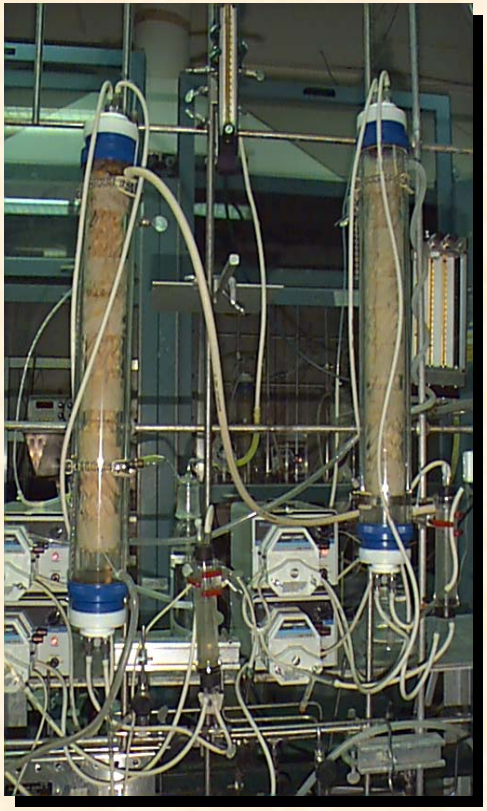
# Previous work on trickle bed bioreactors led to parameter measurement including actual VOC solubility in biofilm

**Two columnar trickle-bed biofilters used for removing sparingly soluble organic vapors from air**



- **Nutrient limitation & filter regeneration**
- **Alkanes & chloroorganics**
- **Mass transfer & kinetics**
- **Predictive model/program**

# Goal

- Understand and quantify how the presence of biomass affects solubilities of volatile organics
- Develop methods by which solubilities can be predicted given cell density (densities can be as high as 100 g dry weight $L^{-1}$)
- Utilize information to more accurately predict operation of trickle bed bioreactors used for VOC degradation
- Extend results to other systems where solubility limits and partitioning play key roles (groundwater)

# Henry's Law

- There are several ways to describe the solubility of a volatile organic in water. Usually, the Henry's law constant, H, is defined as

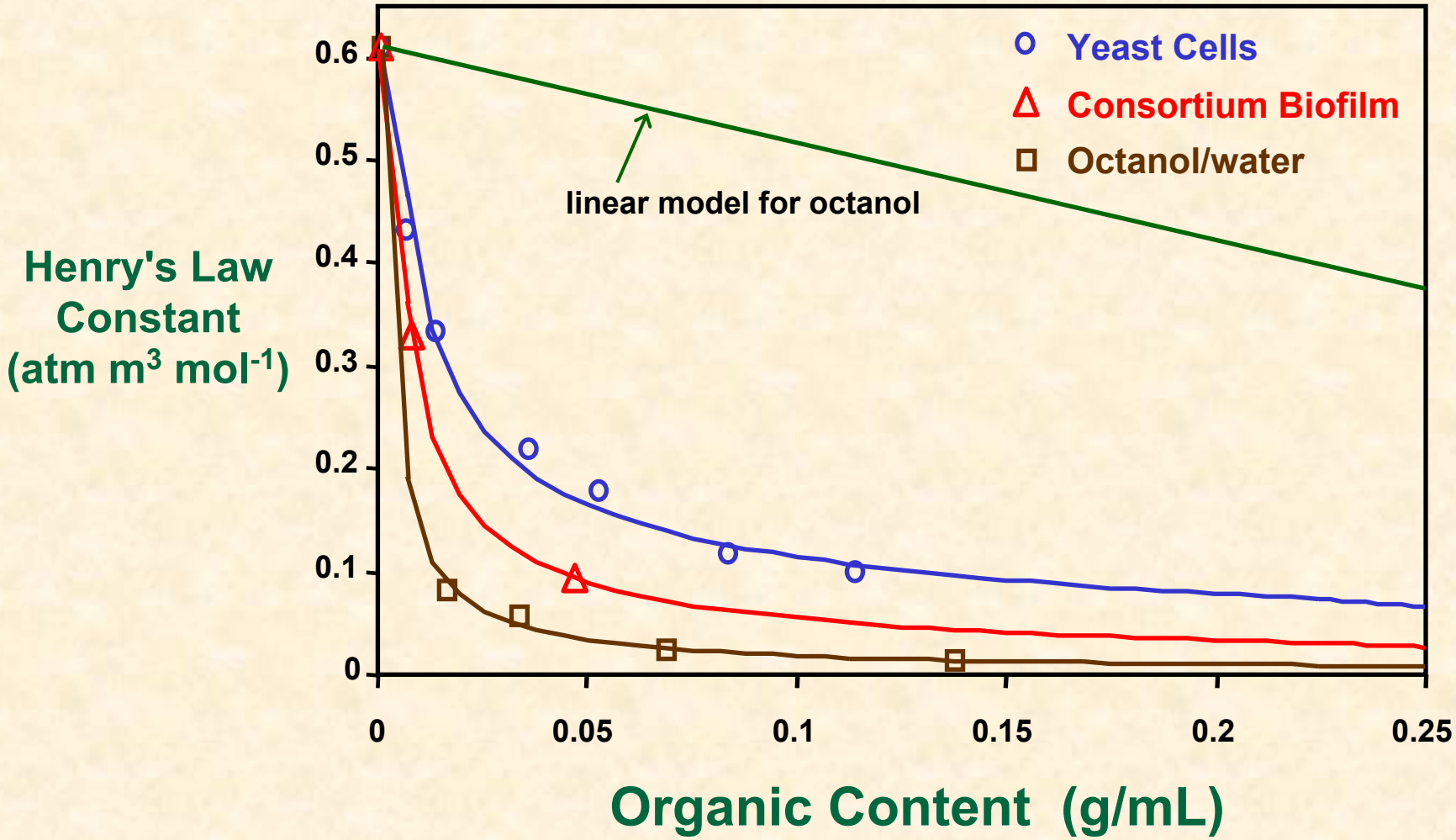
$$H = \frac{C_{headspace}}{C_{solvent}}$$

- A variety of H units are reported, the most common of which is atm/M
- Constants are strongly temperature dependent

# Related Work

- Mackay and Shiu (1981) and many others have reported values for dilute organics in pure water including many environmentally important compounds
- Octanol-air partition constants have been used as model systems to describe partitioning from a gaseous phase into a 'biomass' phase (Wania and Mackay, 1996)
- Chawla and McKay (2001) – measured effect of alcohol cosolvents on the aqueous solubility of TCE – for some mixures water solubility increased by two orders of magnitude

# Davison et al., 2000 – Partitioning of propane in yeast and consortium biomass

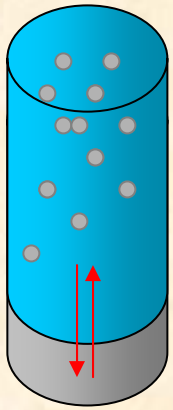


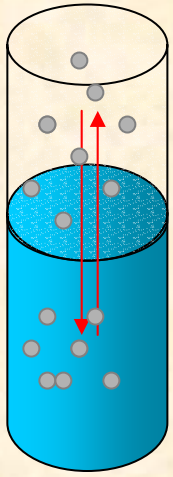
# Contaminants

- Benzene
- Toluene
- TCE (trichloroethylene)
- Chloromethane (a gas at room temperature, also known as methyl chloride)

These compounds are listed on DOE's priority contaminant list

# Two types of measurements





- Solubility limit (how much benzene or TCE can go into an aqueous phase when that aqueous phase is in direct contact with pure benzene or pure TCE?)
- Partitioning of benzene/TCE between headspace (air) and liquid when no pure phase is present
  - Partitioning of benzene/TCE between the aqueous medium and the cellular mass itself
  - Contribution of cellular fractions

# Measurement of Parameters

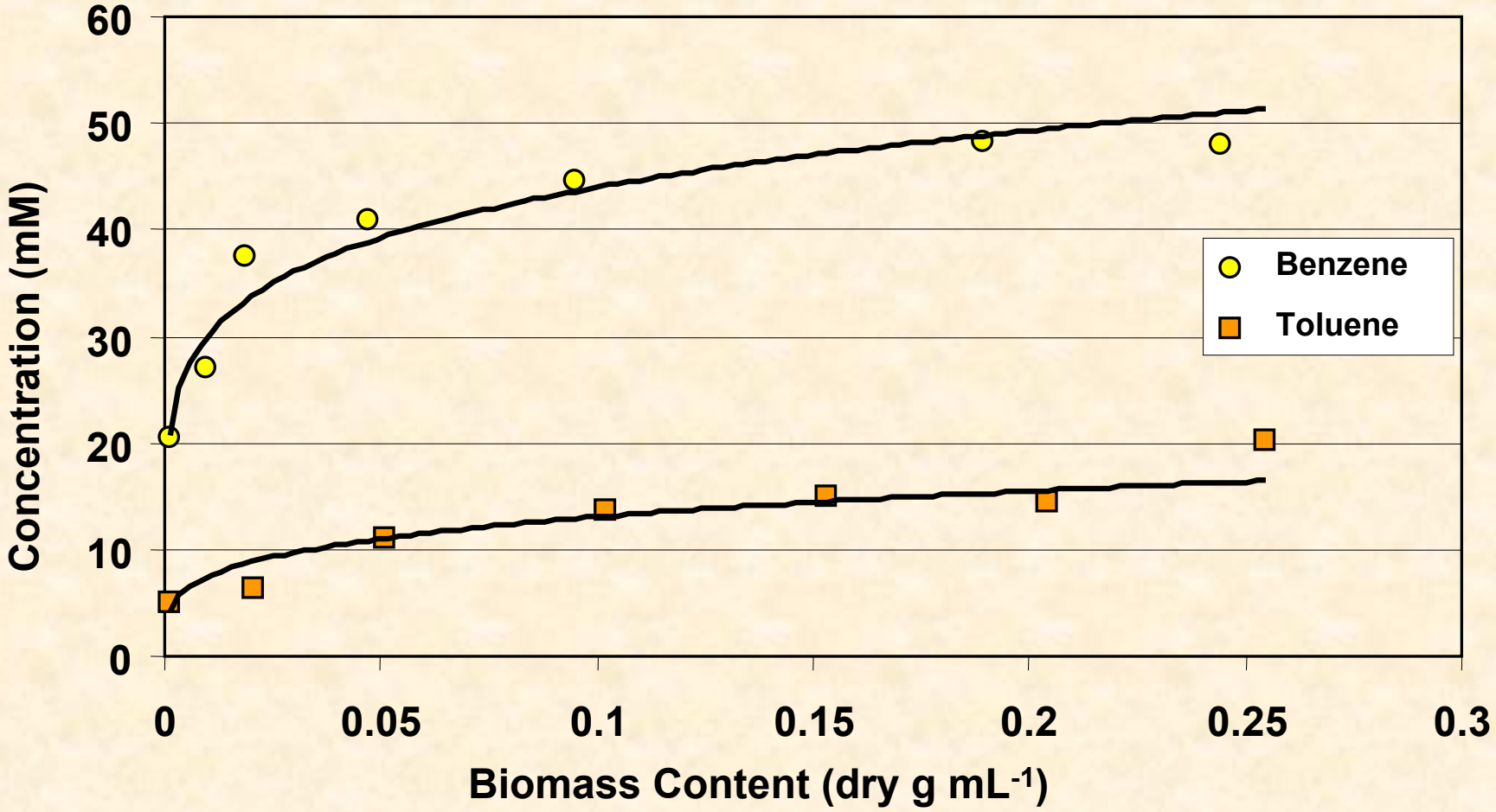
- Serum-cap Test Tubes
- 27 mL Volume
- Biomass: whole cell yeast, lipids, proteins, polysaccharides, etc
- Benzene, toluene, TCE, chloromethane
- Solubility limit and Henry's partitioning constant

# Analytical – GC/FID

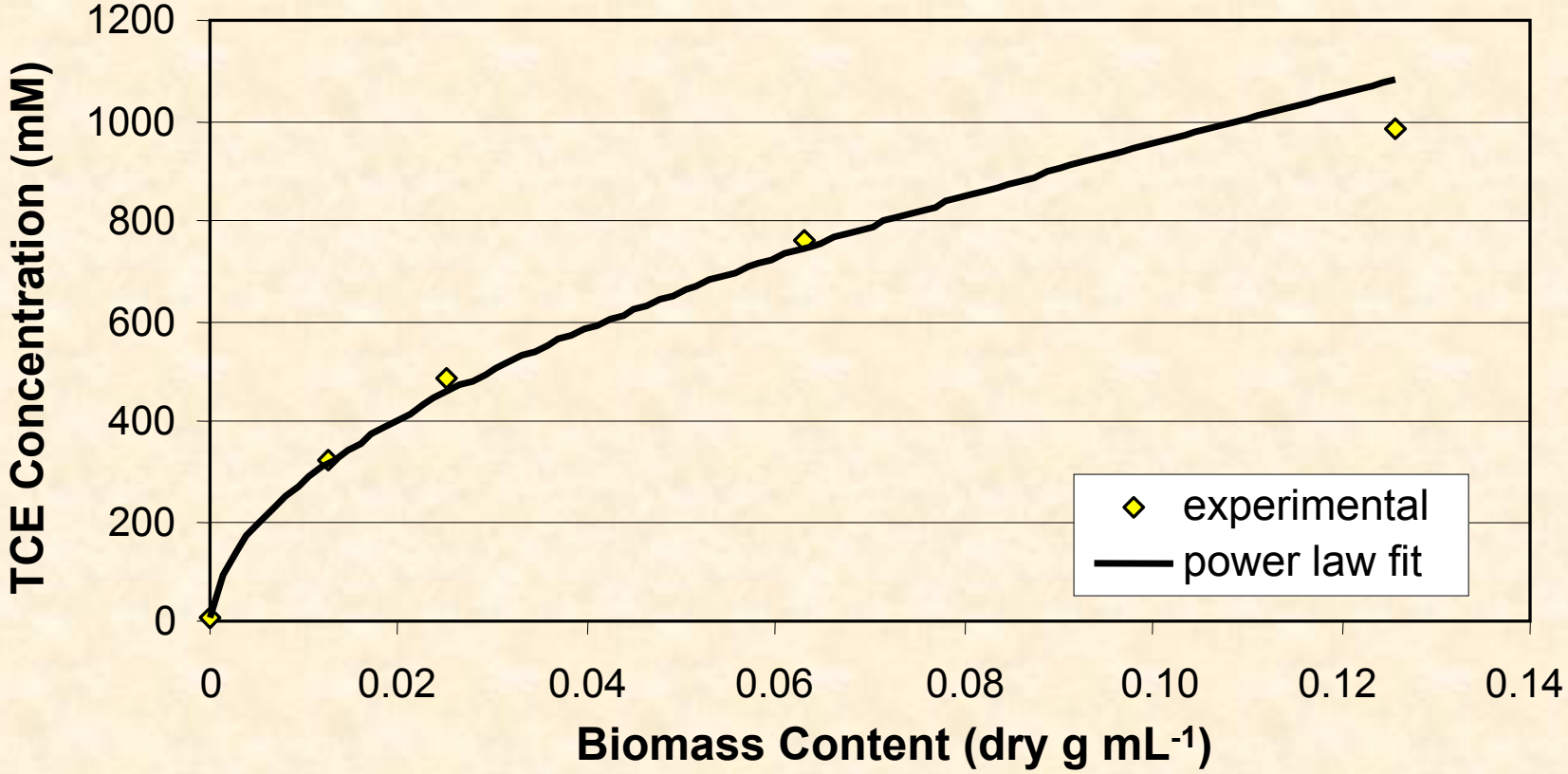
# Biomass Production

- **Model Biomass: *Saccharomyces cerevisae***
- **Grown and frozen prior to use**

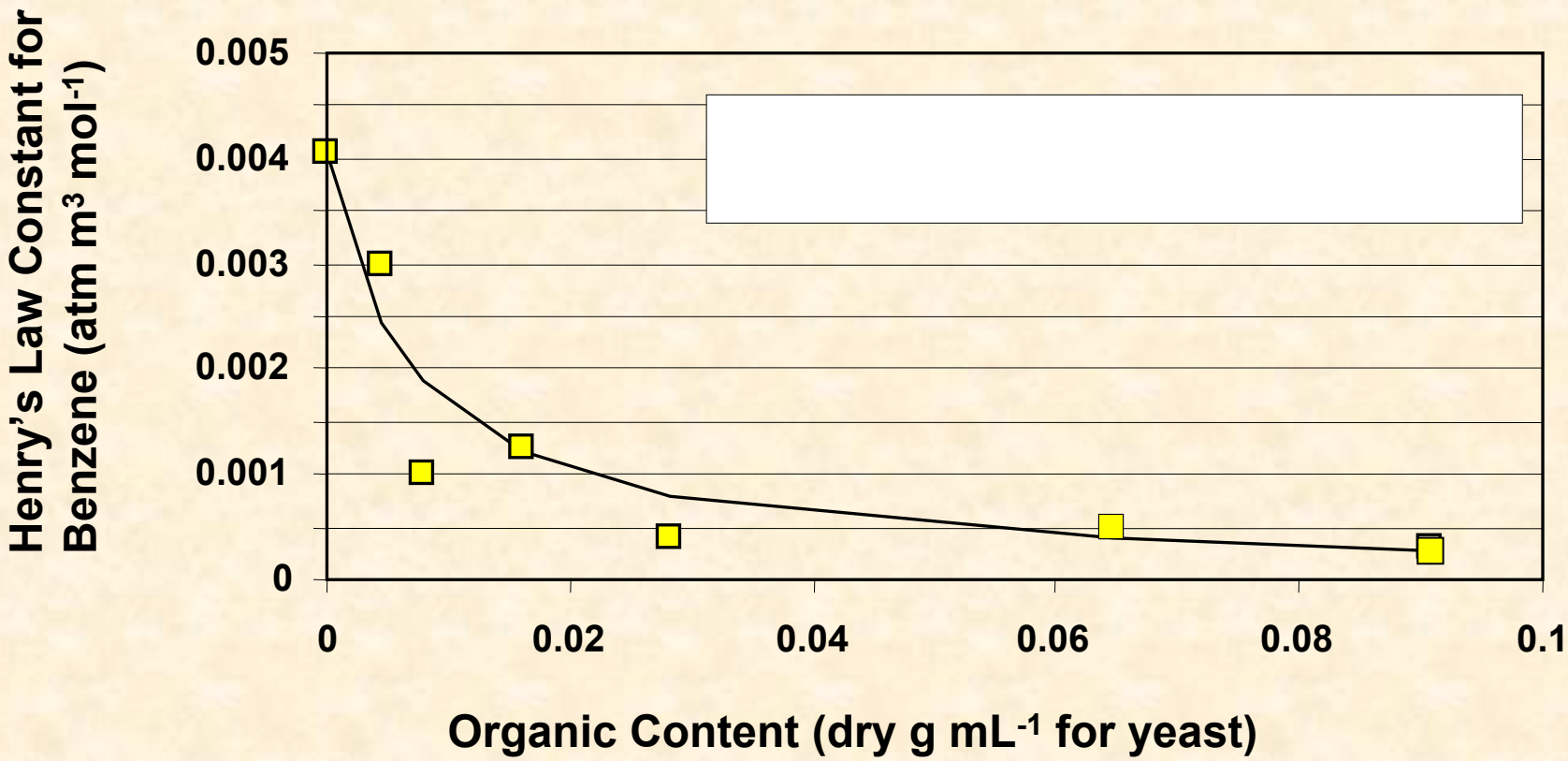
# Solubility Limits of Toluene and Benzene in Water Containing Biomass



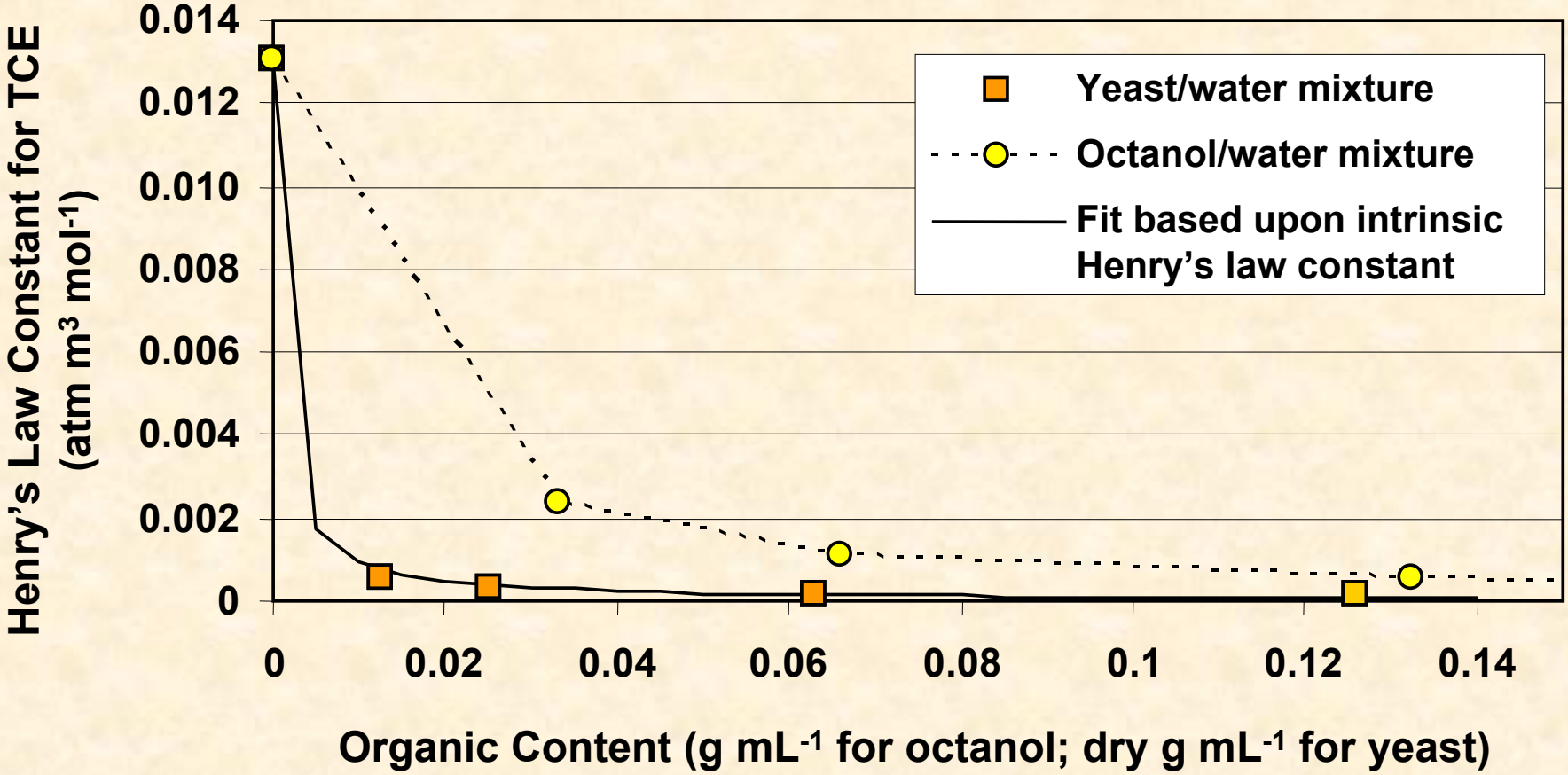
# Solubility Limits of TCE in Water Containing Biomass



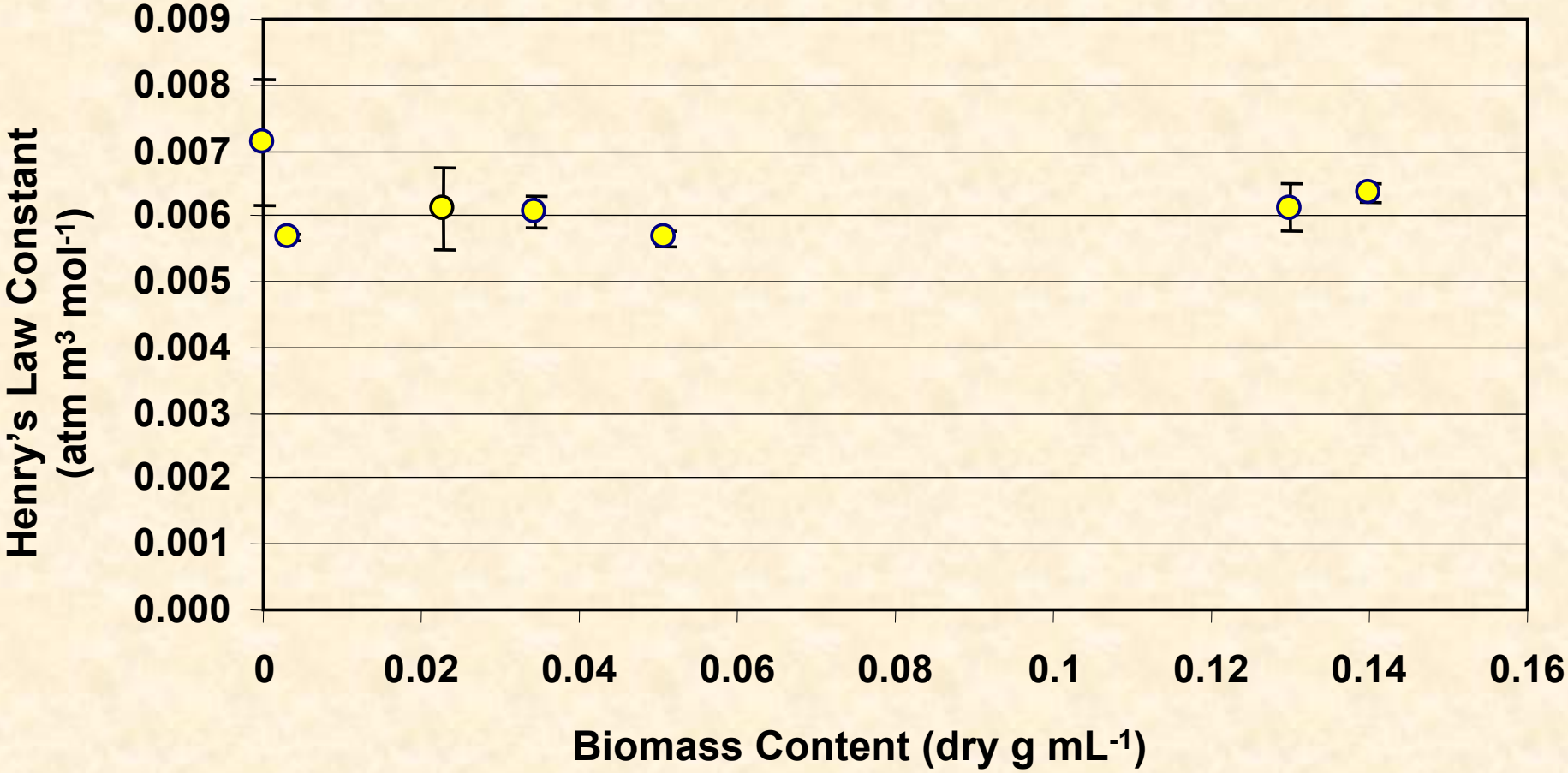
# Henry's law constants for benzene in yeast/water mixtures



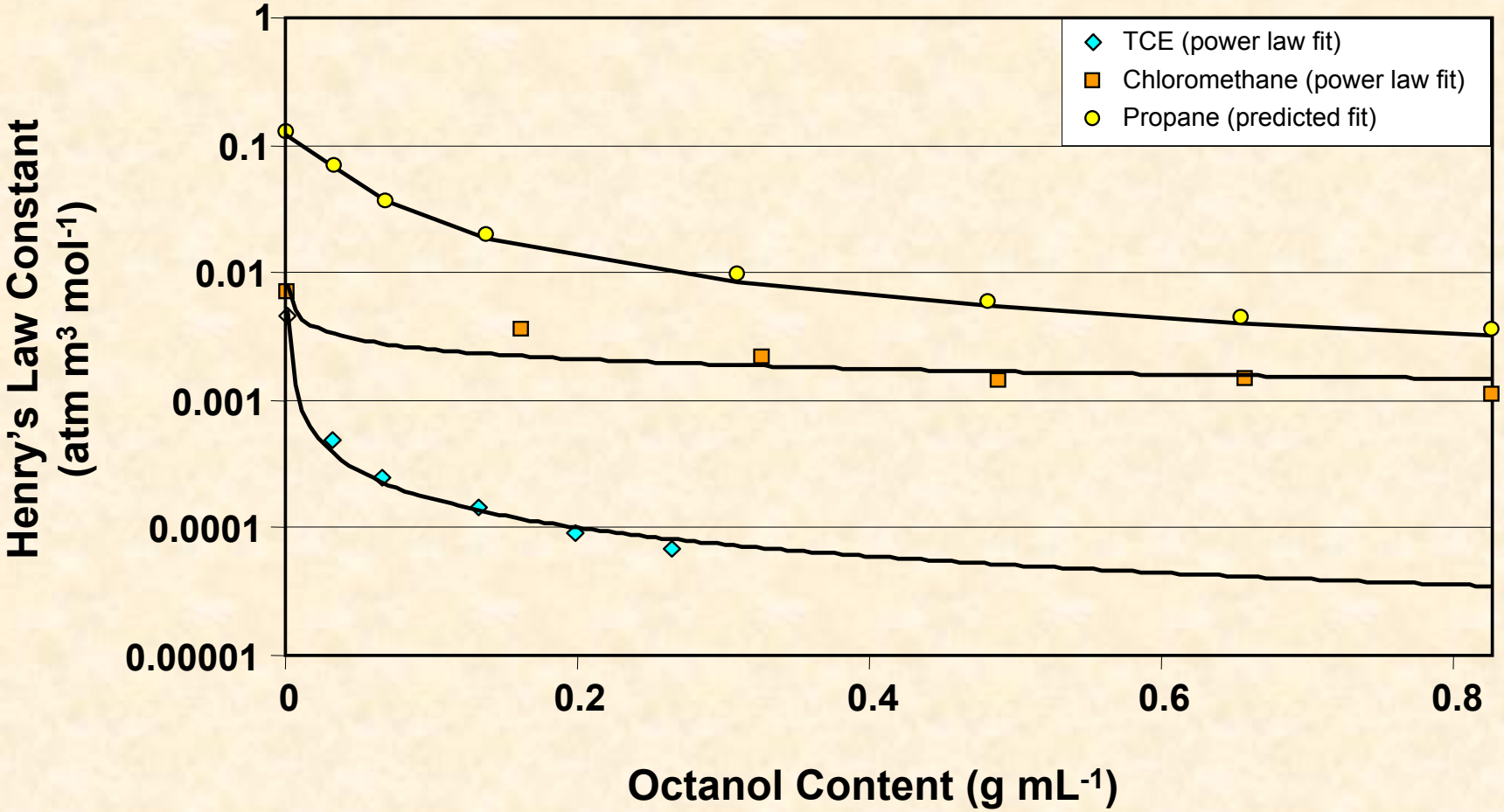
# Henry's law constants for TCE in yeast/water mixtures



# Henry's law constants for Chloromethane in yeast/water mixtures



# Henry's law constants for TCE, Chloromethane, and propane in octanol/water mixtures



**Intrinsic Constant for Biomass**

$$H_{headspace/biomass} = \frac{C_{headspace}}{C_{biomass}}$$

**Definition of Henry's constant for a mixture**

$$H_{headspace/mixture} = \frac{C_{headspace}}{C_{mixture}}$$

## Solvent-mass-based units (atm kg mol$^{-1}$)

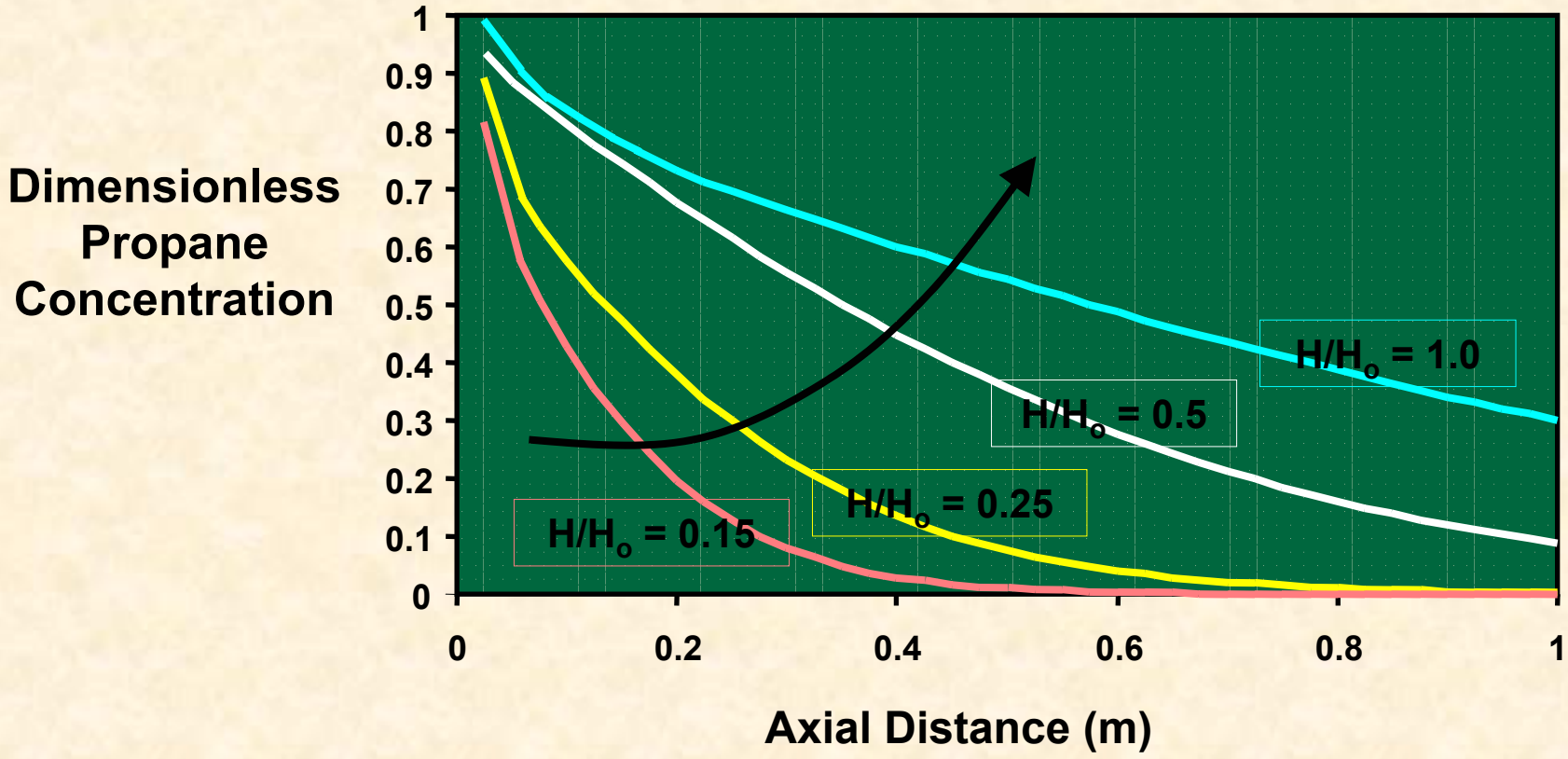
$$\frac{1}{H_{mixture}} = \frac{1}{H_{biomass}} \frac{m_{biomass}}{m_{biomass} + m_{water}} + \frac{1}{H_{water}} \frac{m_{water}}{m_{biomass} + m_{water}}$$

# Implications for biofiltration

- Questions have been raised regarding high rates of removal for some biofiltration systems -- rates reported are higher than solubilities of substrate in pure water would allow
- Existing predictive models usually use pure-water partition values, or, at best, octanol-water relationships to estimate solubilities

# Example of Model Profile Effects

## Using ORNL predictive model for trickle-bed biofilter



# Summary

- **Solubility limit**
  - limit of benzene in ‘aqueous’ phase increased by >2X
  - limit of toluene increased by 4X
  - limit of TCE increased by >100X
- **Partitioning constant**
  - Benzene and toluene partitioning constant increased up to 33X
  - TCE partitioning constant increased more than 100X
- **Contribution due mainly to the ‘insoluble’ biomass, and not extracellular material**
- **Have seen negligible effect on partitioning of chloromethane**

# Ongoing Work

- Pure-substance effects:  starch, protein, lipid, etc.
- Contribution of cellular fractions; no additive relationship apparent
- Determine impact on various models
  - Biofilter
  - Groundwater

# Acknowledgments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