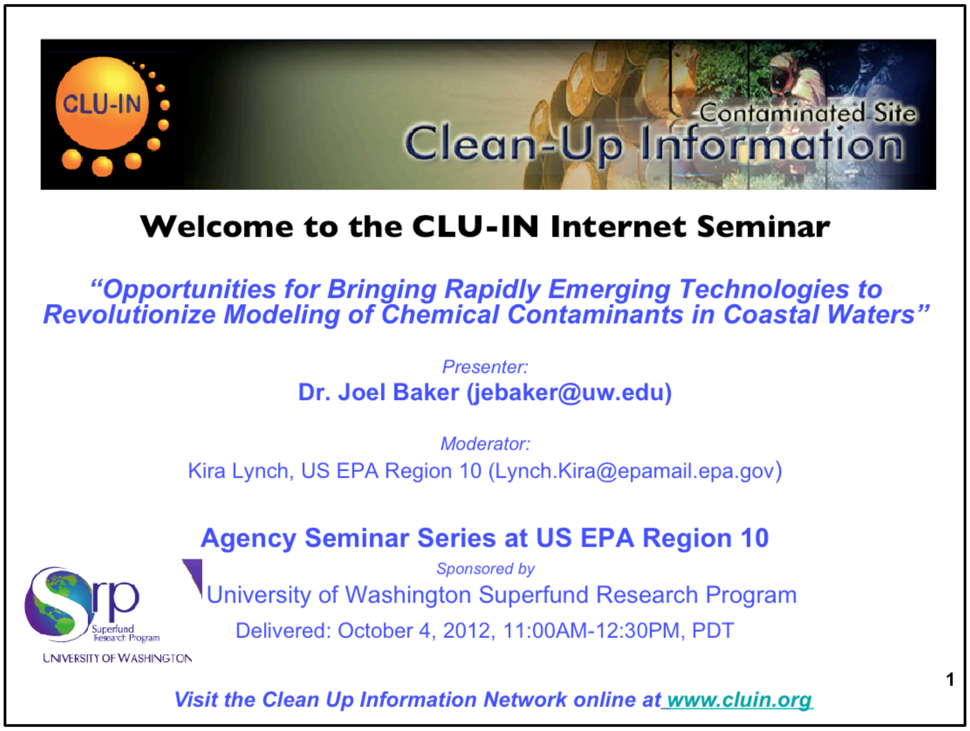

Welcome to the CLU-IN Internet Seminar

“Opportunities for Bringing Rapidly Emerging Technologies to Revolutionize Modeling of Chemical Contaminants in Coastal Waters”

Presenter:
Dr. Joel Baker (jebaker@uw.edu)

Moderator:
Kira Lynch, US EPA Region 10 (Lynch.Kira@epamail.epa.gov)

Agency Seminar Series at US EPA Region 10
Sponsored by
University of Washington Superfund Research Program
Delivered: October 4, 2012, 11:00AM-12:30PM, PDT

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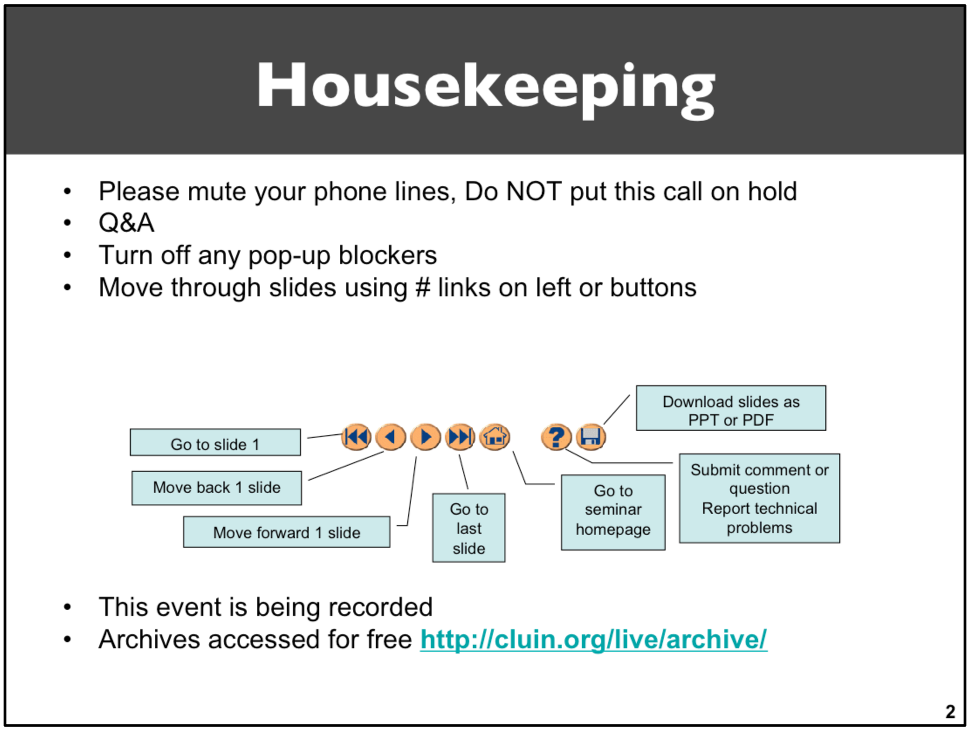

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2

Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/ backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

Opportunities for Bringing Rapidly Emerging Technologies to Revolutionize Modeling of Chemical Contaminants of Coastal Waters

Dr. Joel Baker
Director, UW Puget Sound Institute
University of Washington Tacoma

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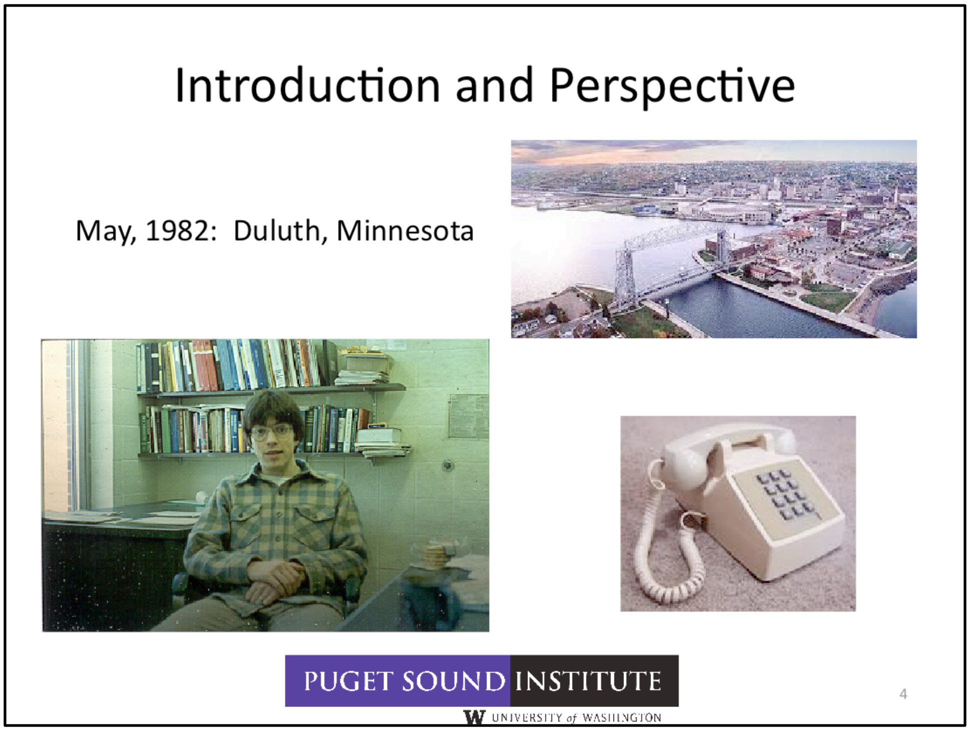

Introduction and Perspective

May, 1982: Duluth, Minnesota

Introduction and Perspective

October, 2012: Tacoma, WA

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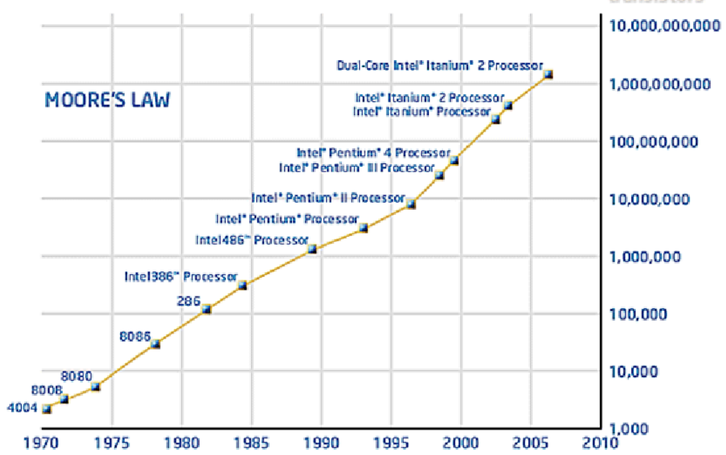
The Information Technology Revolution



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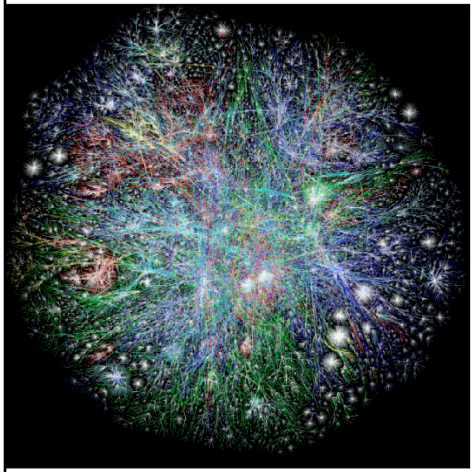
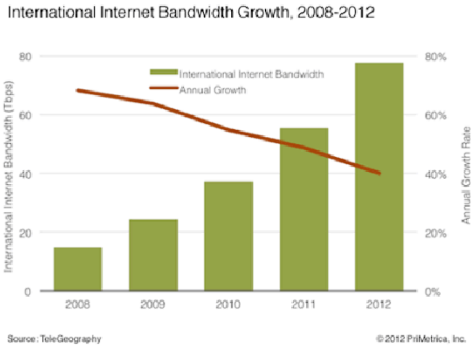
NJTechReviews

The Information Technology Revolution



2010 Map of the Global Internet by Cisco Systems



International Internet Bandwidth Growth, 2008-2012

Source: TeleGeography

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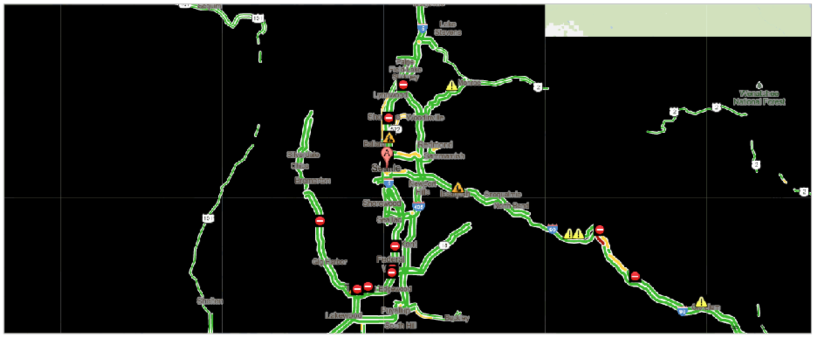
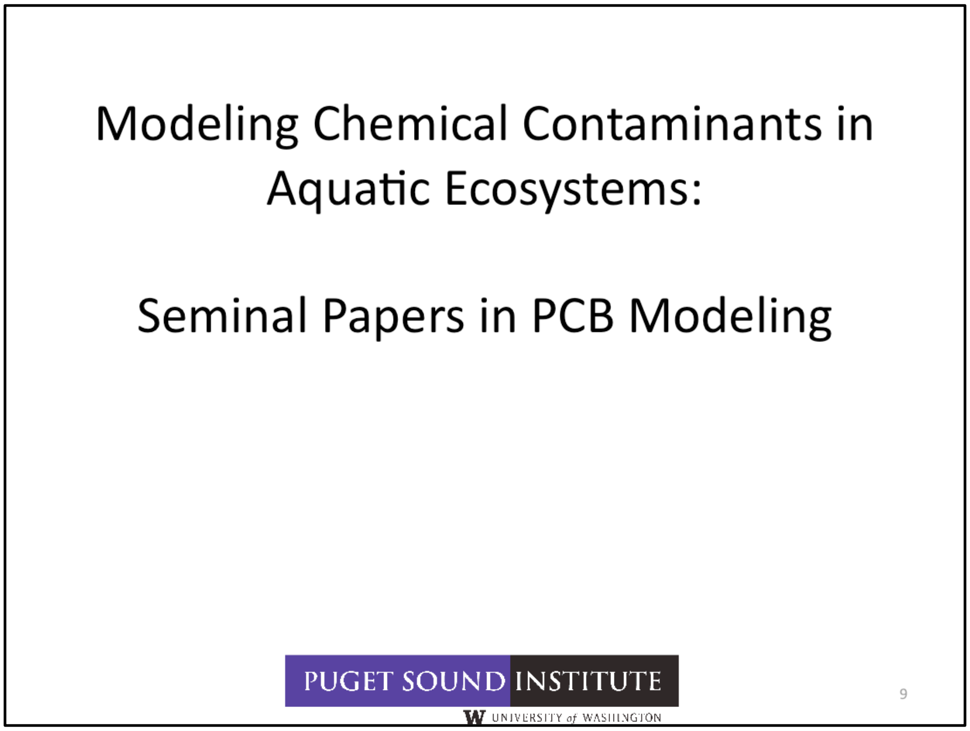
The Information Technology Revolution





Modeling Chemical Contaminants in Aquatic Ecosystems:

Seminal Papers in PCB Modeling

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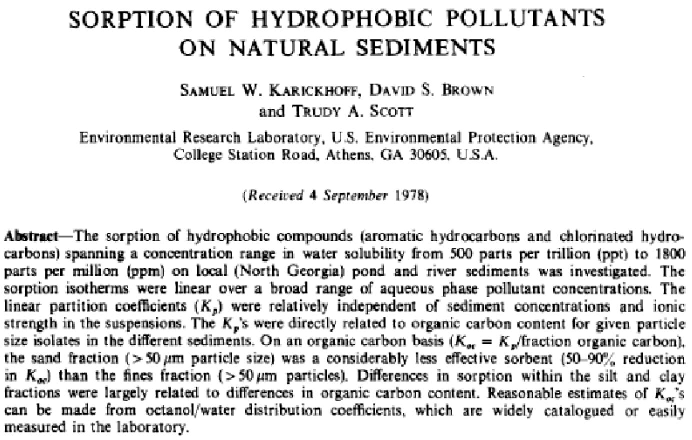
Modeling Chemical Contaminants in Aquatic Ecosystems: Karickhoff *et al.* 1979



SORPTION OF HYDROPHOBIC POLLUTANTS ON NATURAL SEDIMENTS

SAMUEL W. KARICKHOFF, DAVID S. BROWN
and TRUDY A. SCOTT

Environmental Research Laboratory, U.S. Environmental Protection Agency,
College Station Road, Athens, GA 30605, U.S.A.

(*Received 4 September 1978*)

Abstract—The sorption of hydrophobic compounds (aromatic hydrocarbons and chlorinated hydrocarbons) spanning a concentration range in water solubility from 500 parts per trillion (ppt) to 1800 parts per million (ppm) on local (North Georgia) pond and river sediments was investigated. The sorption isotherms were linear over a broad range of aqueous phase pollutant concentrations. The linear partition coefficients (K_p) were relatively independent of sediment concentrations and ionic strength in the suspensions. The K_p's were directly related to organic carbon content for given particle size isolates in the different sediments. On an organic carbon basis ($K_{oc} = K_p$/fraction organic carbon), the sand fraction (> 50 μm particle size) was a considerably less effective sorbent (50–90% reduction in K_{oc}) than the fines fraction (> 50 μm particles). Differences in sorption within the silt and clay fractions were largely related to differences in organic carbon content. Reasonable estimates of K_{oc}'s can be made from octanol/water distribution coefficients, which are widely catalogued or easily measured in the laboratory.

Modeling Chemical Contaminants in Aquatic Ecosystems: Karickhoff *et al.* 1979

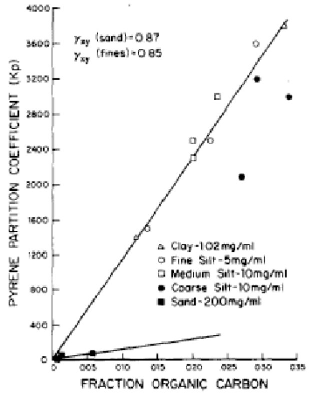


Fig. 3. Pyrene K_p as a function of sediment organic carbon.

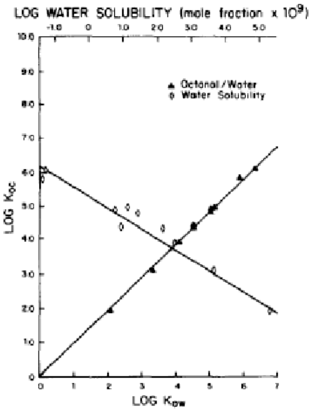


Fig. 5. Sorption K_{oc} as a function of compound water solubility and octanol/water distribution coefficients.

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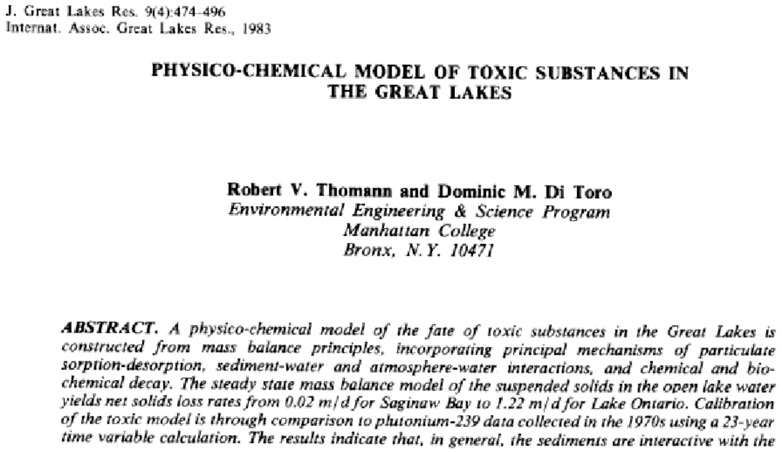
Modeling Chemical Contaminants in Aquatic Ecosystems: Thomann and DiToro, 1983



J. Great Lakes Res. 9(4):474-496
Internat. Assoc. Great Lakes Res., 1983

PHYSICO-CHEMICAL MODEL OF TOXIC SUBSTANCES IN THE GREAT LAKES

Robert V. Thomann and Dominic M. Di Toro
Environmental Engineering & Science Program
Manhattan College
Bronx, N.Y. 10471

ABSTRACT. *A physico-chemical model of the fate of toxic substances in the Great Lakes is constructed from mass balance principles, incorporating principal mechanisms of particulate sorption-desorption, sediment-water and atmosphere-water interactions, and chemical and biochemical decay. The steady state mass balance model of the suspended solids in the open lake water yields net solids loss rates from 0.02 m/d for Saginaw Bay to 1.22 m/d for Lake Ontario. Calibration of the toxic model is through comparison to plutonium-239 data collected in the 1970s using a 23-year time variable calculation. The results indicate that, in general, the sediments are interactive with the*

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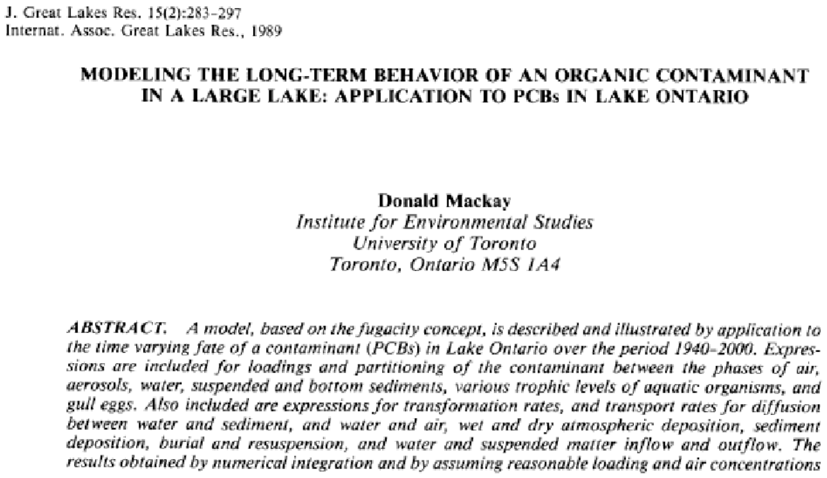
Modeling Chemical Contaminants in Aquatic Ecosystems: Mackay, 1989



J. Great Lakes Res. 15(2):283–297
Internat. Assoc. Great Lakes Res., 1989

MODELING THE LONG-TERM BEHAVIOR OF AN ORGANIC CONTAMINANT IN A LARGE LAKE: APPLICATION TO PCBs IN LAKE ONTARIO

Donald Mackay
Institute for Environmental Studies
University of Toronto
Toronto, Ontario M5S 1A4

ABSTRACT. A model, based on the fugacity concept, is described and illustrated by application to the time varying fate of a contaminant (PCBs) in Lake Ontario over the period 1940–2000. Expressions are included for loadings and partitioning of the contaminant between the phases of air, aerosols, water, suspended and bottom sediments, various trophic levels of aquatic organisms, and gull eggs. Also included are expressions for transformation rates, and transport rates for diffusion between water and sediment, and water and air, wet and dry atmospheric deposition, sediment deposition, burial and resuspension, and water and suspended matter inflow and outflow. The results obtained by numerical integration and by assuming reasonable loading and air concentrations

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Modeling Chemical Contaminants in Aquatic Ecosystems: Mackay, 1989

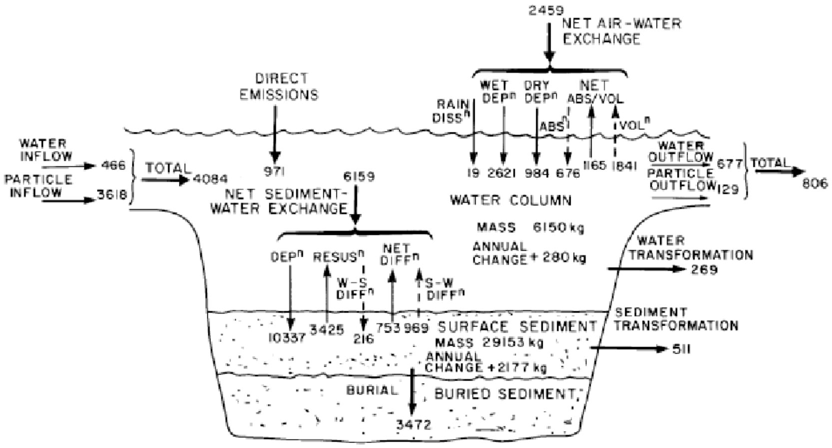

FIG. 5. Estimated PCB flows in 1965 (kg/year).

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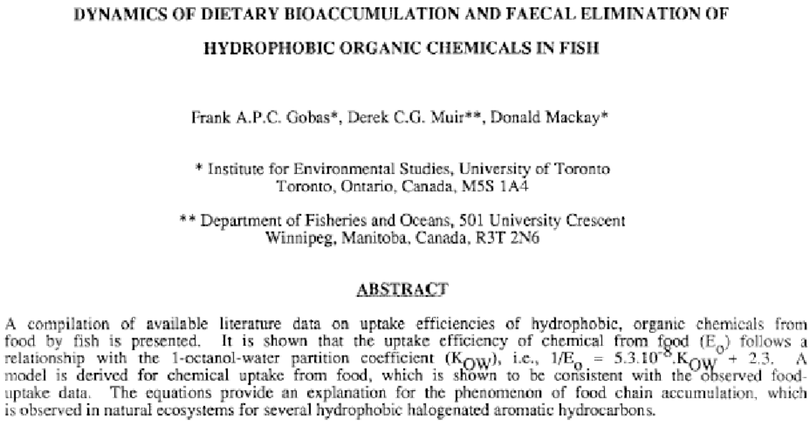
Modeling Chemical Contaminants in Aquatic Ecosystems: Gobas and Mackay, 1988



DYNAMICS OF DIETARY BIOACCUMULATION AND FAECAL ELIMINATION OF HYDROPHOBIC ORGANIC CHEMICALS IN FISH

Frank A.P.C. Gobas*, Derek C.G. Muir**, Donald Mackay*

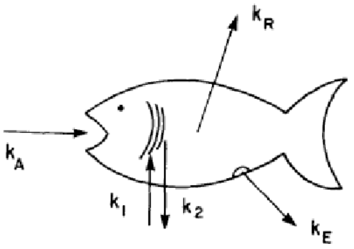
* Institute for Environmental Studies, University of Toronto
Toronto, Ontario, Canada, M5S 1A4

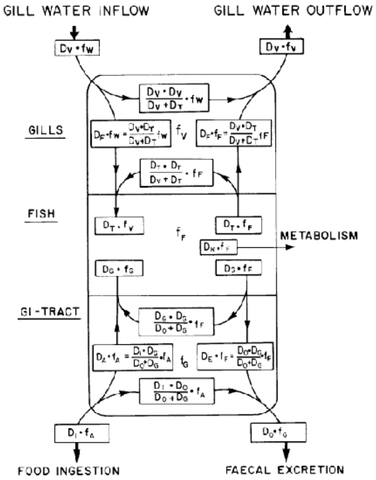
** Department of Fisheries and Oceans, 501 University Crescent
Winnipeg, Manitoba, Canada, R3T 2N6

ABSTRACT

A compilation of available literature data on uptake efficiencies of hydrophobic, organic chemicals from food by fish is presented. It is shown that the uptake efficiency of chemical from food (E_o) follows a relationship with the 1-octanol-water partition coefficient (K_{OW}), i.e., $1/E_o = 5.3.10^{-8}.K_{OW} + 2.3$. A model is derived for chemical uptake from food, which is shown to be consistent with the observed food-uptake data. The equations provide an explanation for the phenomenon of food chain accumulation, which is observed in natural ecosystems for several hydrophobic halogenated aromatic hydrocarbons.

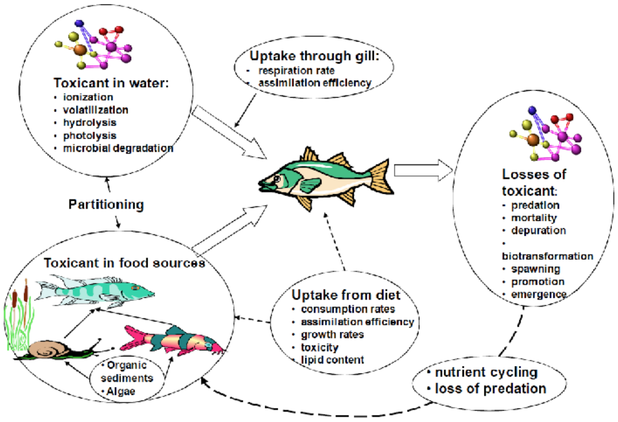
Modeling Chemical Contaminants in Aquatic Ecosystems: Gobas and Mackay, 1988





Modeling Chemical Contaminants in Aquatic Ecosystems: Current Models

Bioaccumulation in AQUATOX



Toxicant in water:
- ionization
- volatilization
- hydrolysis
- photolysis
- microbial degradation

Uptake through gill:
- respiration rate
- assimilation efficiency

Partitioning

Toxicant in food sources

- Organic sediments
- Algae

Uptake from diet
- consumption rates
- assimilation efficiency
- growth rates
- toxicity
- lipid content

Losses of toxicant:
- predation
- mortality
- depuration
- biotransformation
- spawning
- promotion
- emergence

- nutrient cycling
- loss of predation

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R.A. Park et al., 2010

Modeling Chemical Contaminants in Aquatic Ecosystems: NY/NJ Harbor CARP Model

Management Question

- Which **sources of contaminants** need to be reduced or eliminated to render future dredged material clean?

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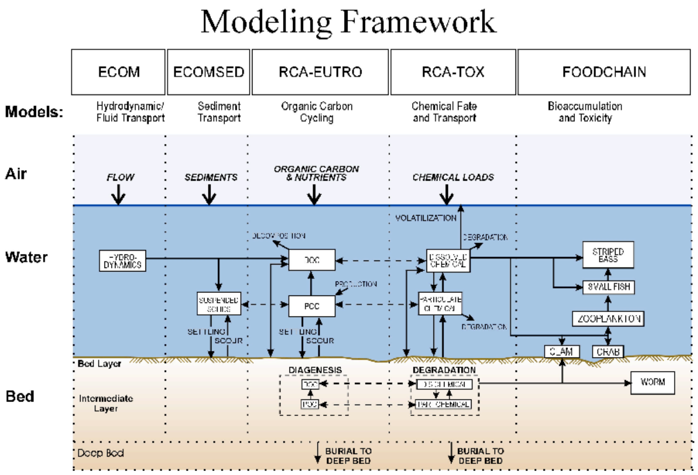
Modeling Chemical Contaminants in Aquatic Ecosystems: NY/NJ Harbor CARP Model



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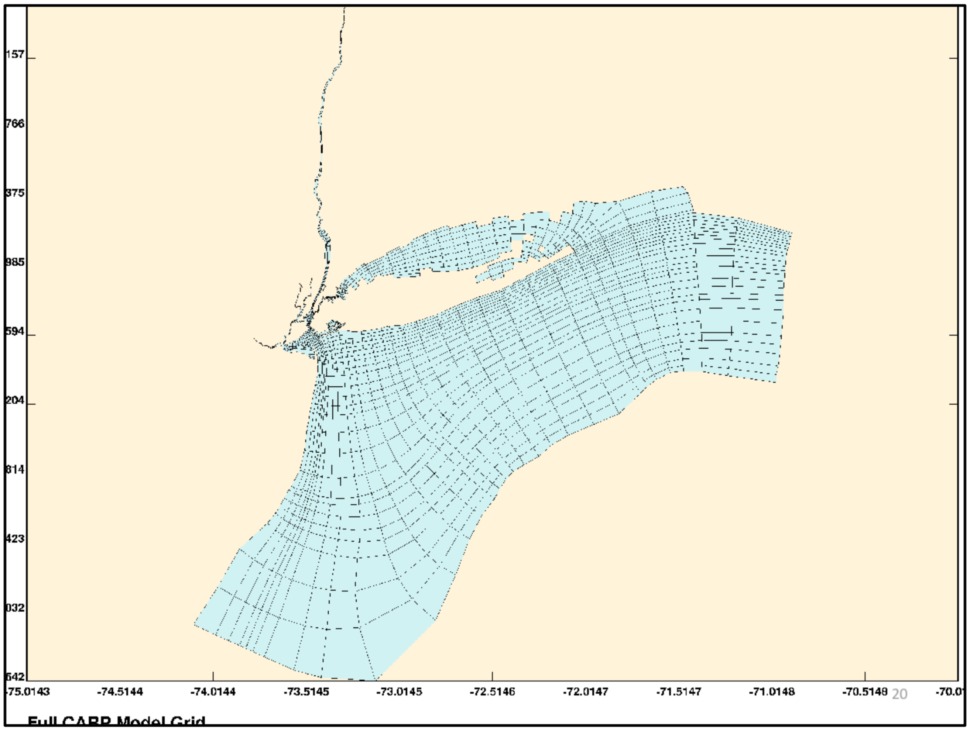
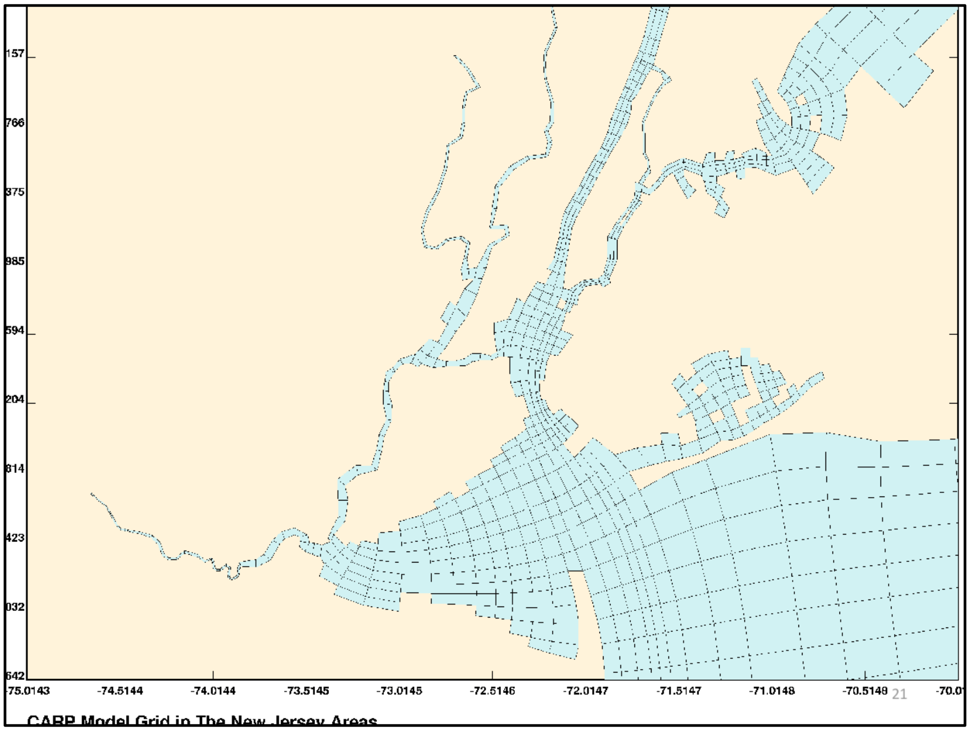
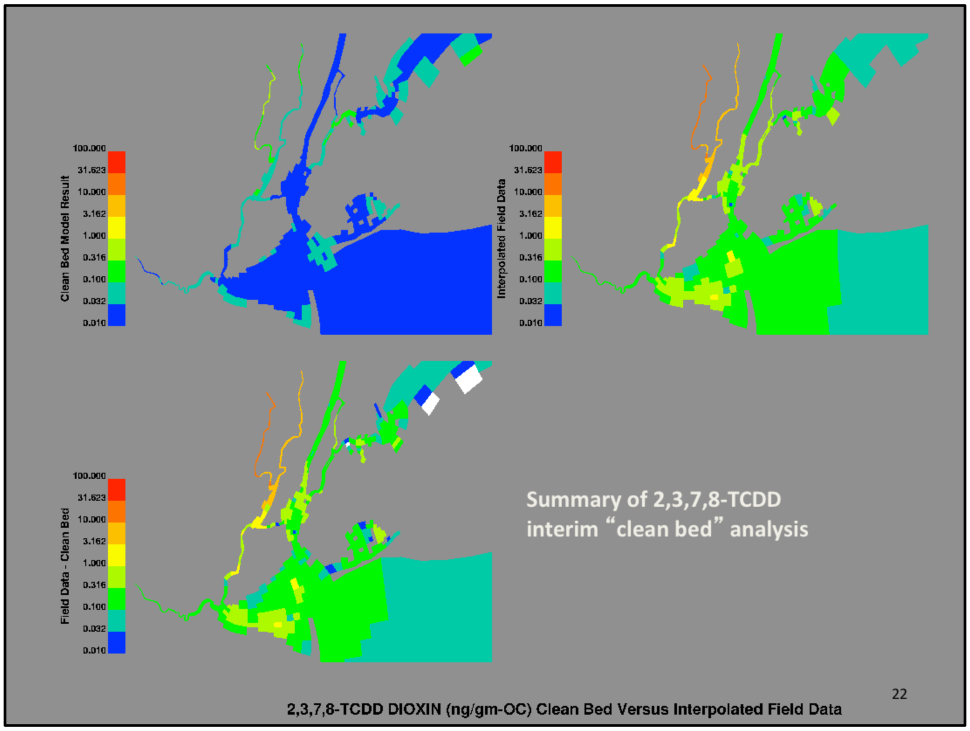


Full CARP Model Grid



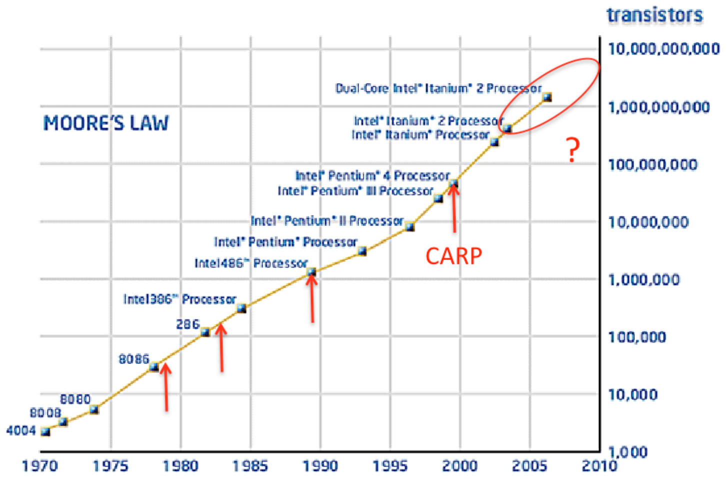
CARP Model Grid in The New Jersey Areas



Summary of 2,3,7,8-TCDD interim “clean bed” analysis

2,3,7,8-TCDD DIOXIN (ng/gm-OC) Clean Bed Versus Interpolated Field Data

The Information Technology Revolution



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NJTechReviews

Premise of Today's Talk

Tools to model contaminant behavior and effects in aquatic ecosystems have not kept up with the information technology revolution

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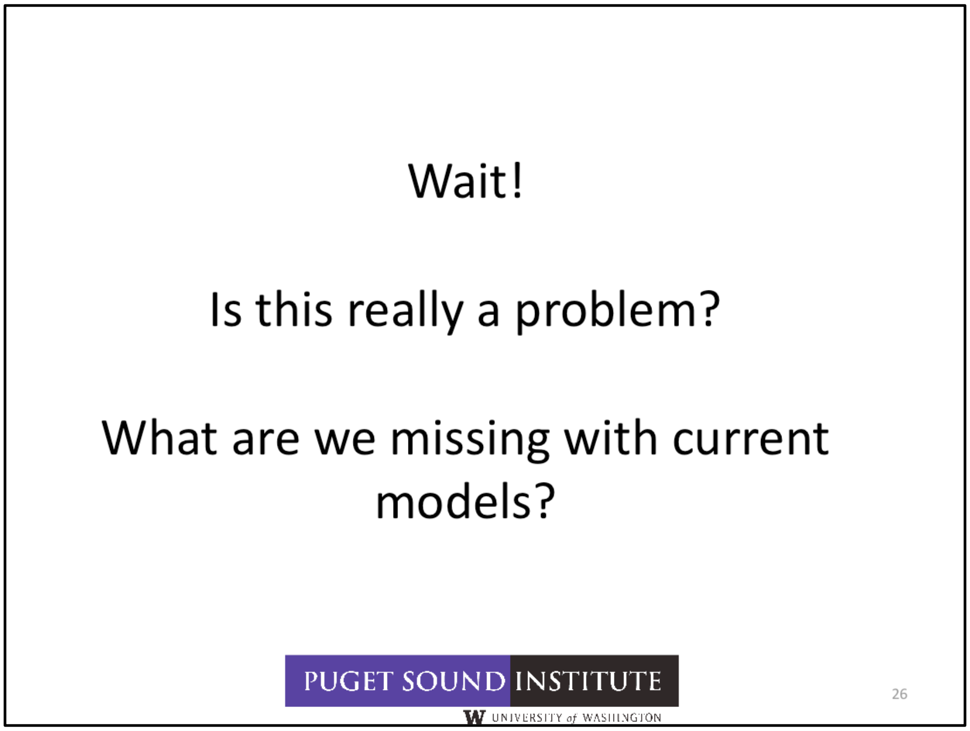
Corollaries

1. We assume that technology is frozen in time to what tools we had available in grad school (computers, IT, and analytical chemistry)

2. Innovation and experimentation may be seen at odds with stability and confidence



Wait!

Is this really a problem?

What are we missing with current models?

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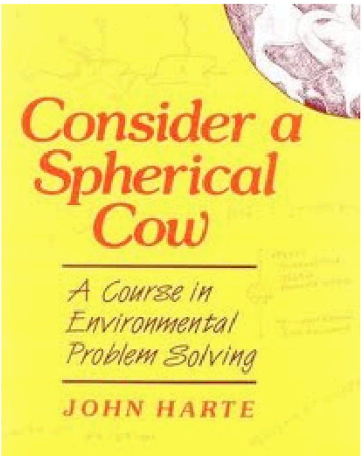

Consider a Spherical Cow

A Course in Environmental Problem Solving

JOHN HARTE

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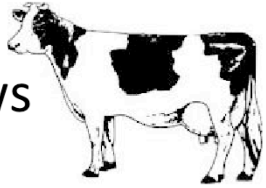
Non-Spherical Cows



1. Phase partitioning in the water column

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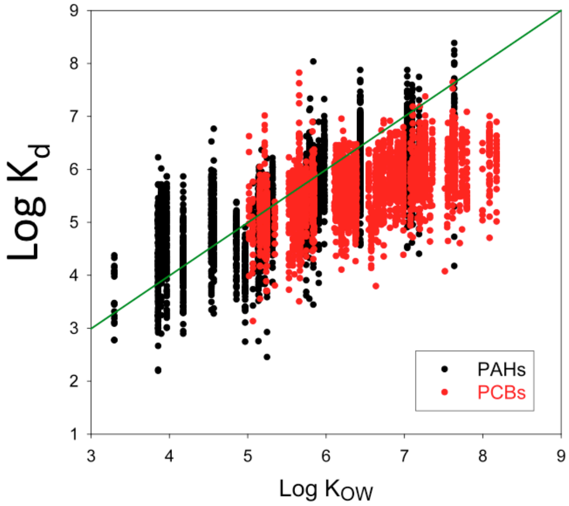
- Use PCB and PAH distribution coefficients measured in the Chesapeake Bay to explore the mechanism driving observed variability
  - three-phase partitioning?
  - slow sorption kinetics?
  - highly sorbent particles?

[Mass on Filter/Volume Filtered]
Kd= ---
[Mass on XAD/Volume Processed][TSS]



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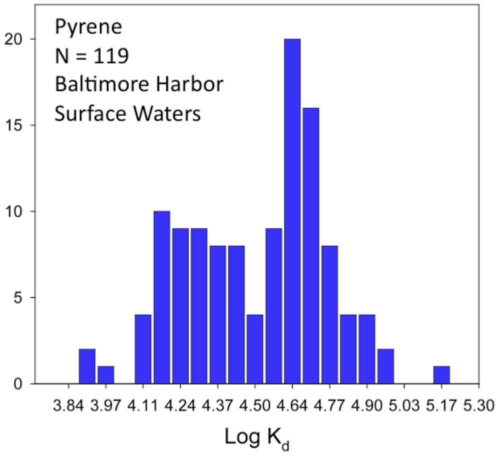

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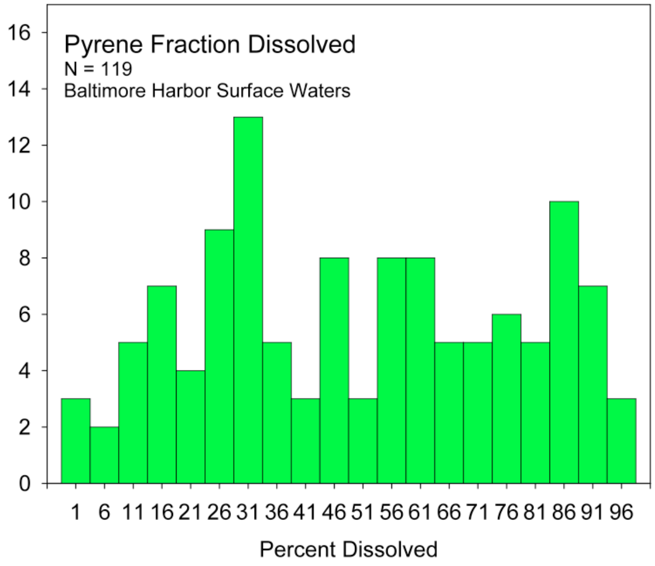

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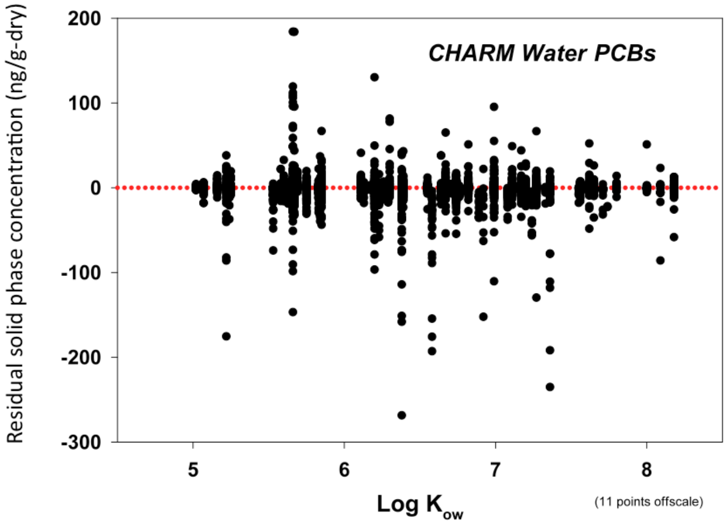
Investigating the sources of variability in partitioning



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Investigating the sources of variability in partitioning

1. The presence of colloids

Critical Review

Estimating Dissolved Organic Carbon Partition Coefficients for Nonionic Organic Chemicals

LAWRENCE P. BURKHARD*
U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division, 6201 Congdon Boulevard, Duluth, Minnesota 55804

$$K_{DOC} = 0.08K_{ow}$$

High variation due to:
- the nature of DOC
- the methods used

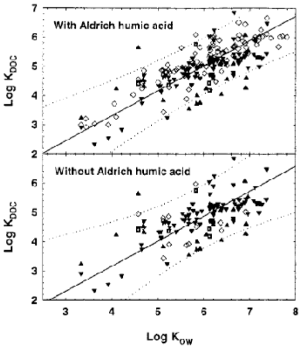

FIGURE 2. Average K_{DOC} values for individual chemicals for different DOC sources: humic and fulvic acids (open diamond), sediment porewaters (downward triangle), soil porewaters and groundwaters (plus square), and surface waters (upward triangle). The geometric mean regression and their 95% prediction confidence limits are plotted.

Environmental Science and Technology, 2000, 34, 4663-4668

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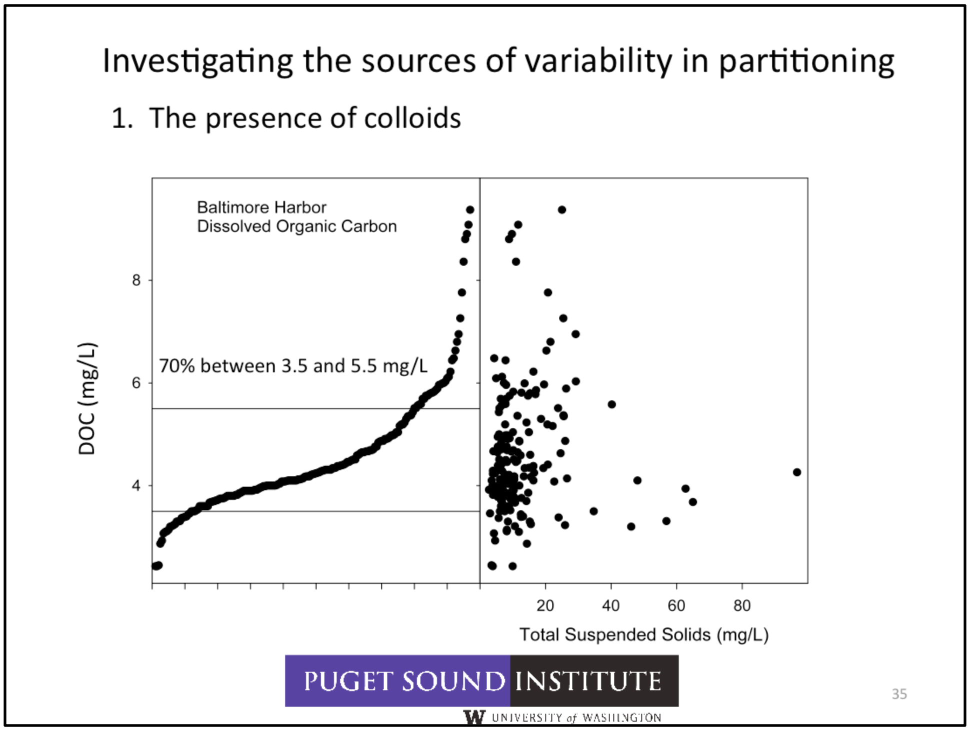

Investigating the sources of variability in partitioning

1. The presence of colloids

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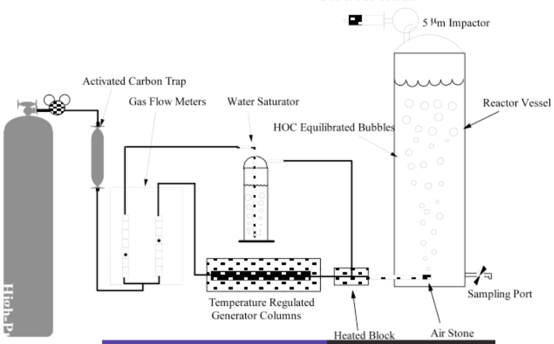
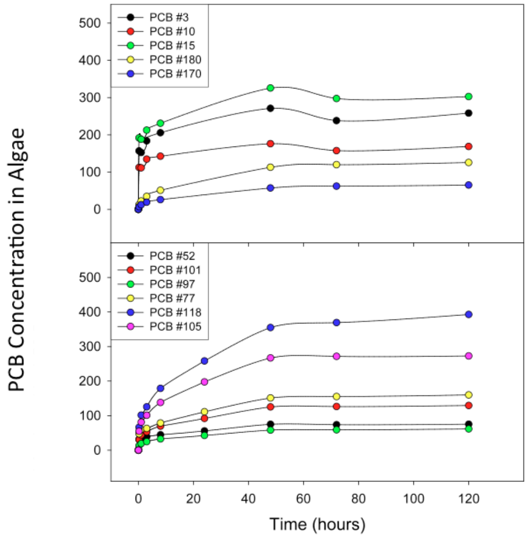
Investigating the sources of variability in partitioning

2. Kinetics of Partitioning

Laboratory PCB congener sorption experiments

- Gas-phase equilibration maintains constant <u>dissolved</u> PCB congener concentrations.
- Stationary-phase chrysophyte *Isochrysis galbana*
- 18 congeners studied over 120 hours





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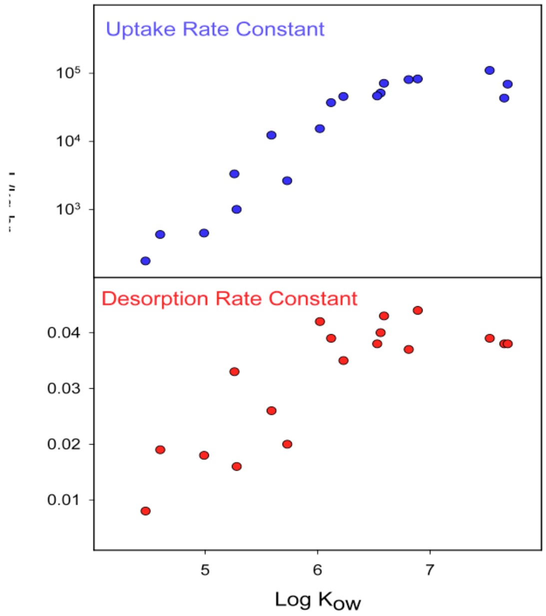
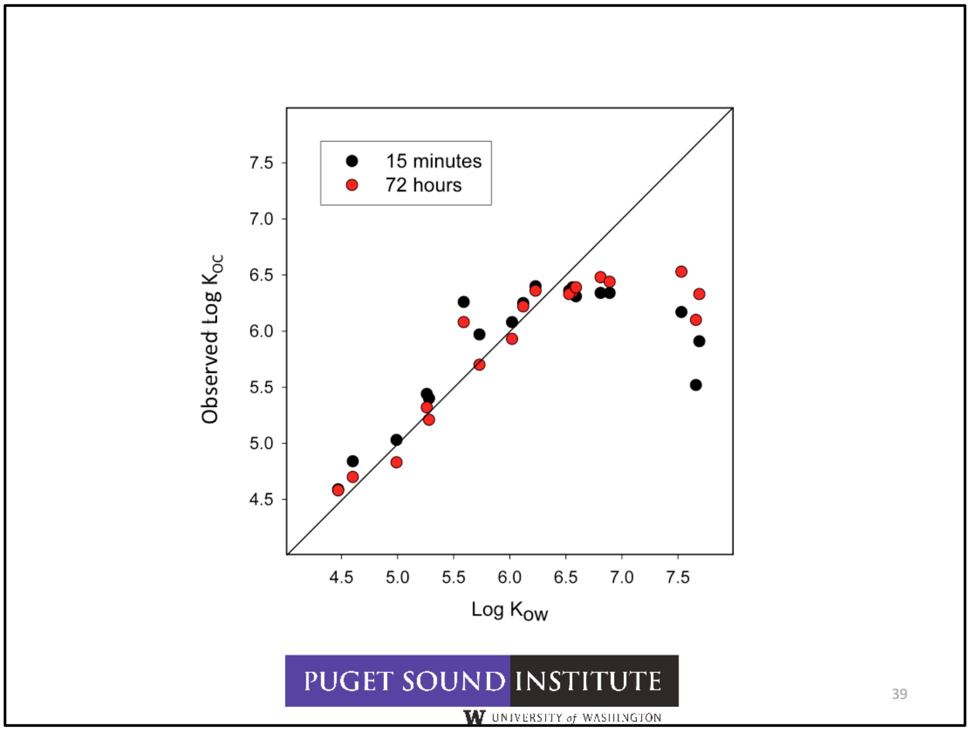

Uptake Rate Constant
10^5
10^4
10^3
Desorption Rate Constant
0.04
0.03
0.02
0.01
5
6
7
Log Kow



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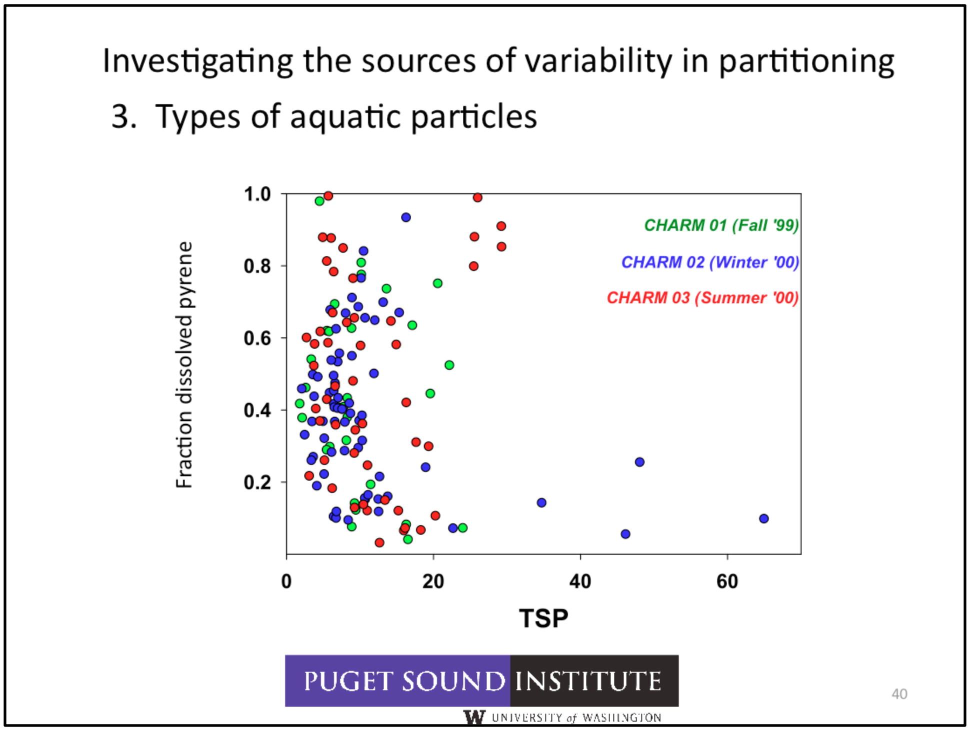

Investigating the sources of variability in partitioning

3. Types of aquatic particles

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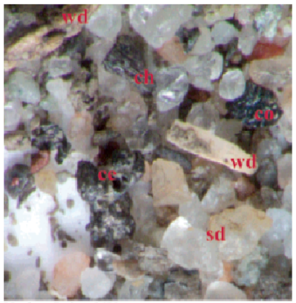
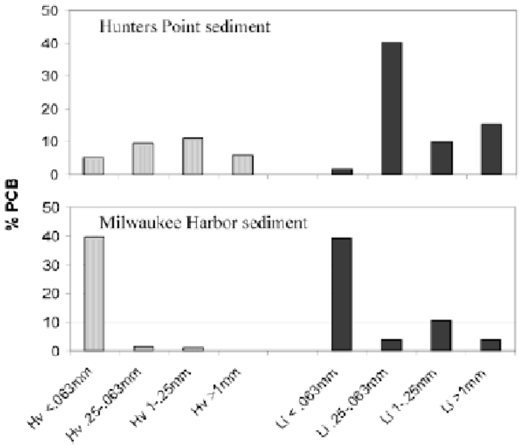
PCB and PAH Speciation among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

UPAL GHOSH,*
JOHN R. ZIMMERMAN, AND
RICHARD G. LUTHY
Department of Civil and Environmental Engineering, Stanford University, Stanford, California 94305-4020



Harbor Point, NY



Environ. Sci. Technol. **2003**, *37*, 2209−2217

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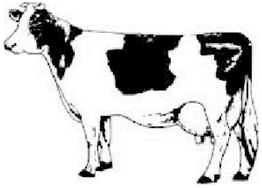
1. Phase partitioning in the Water Column



The observed variations in dissolved-particulate distributions of PCBs, PAHs, *etc.* are large and real.

Although organic colloids likely moderate dissolved HOC concentrations, DOC does not vary enough to explain the observed partitioning.

In studies with well-characterized solids, sorption kinetics are sufficiently fast (at least on a log-log plot).

Remarkably large (*i.e.,* order of magnitude) variations in HOC-solid interactions among particle types.

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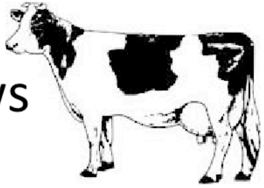
Non-Spherical Cows



2. Interactions among particles

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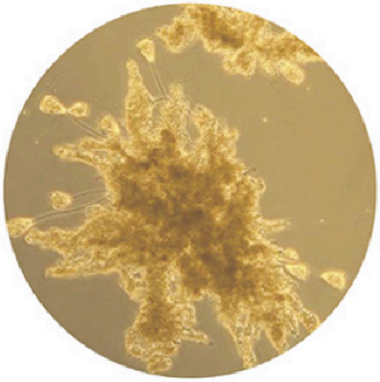
Physical characteristics of flocs

- Lower settling velocity
- Lower bulk density
- Higher contact area (porosity)



http://www.water-technology.net/contractor_images/cu_water/flocke.jpg

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How are flocs formed?

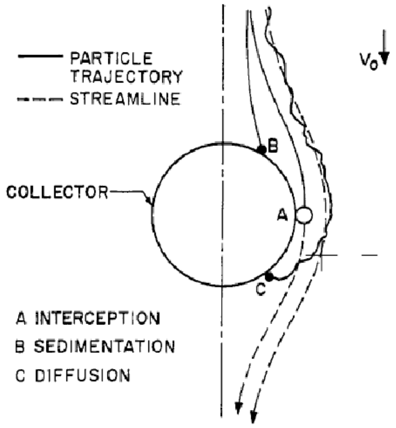

Figure 1. Basic transport mechanisms in water filtration

Yao and O'Melia (1971)

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Flocculation and PCB Models

- The model simulated the floc size among 2 to 1000 µm
- The multi-class flocculation model equations are based on the concept of O'Melia (1982)
- The floc porosity and settling velocity are based on the concept of Winterwerp (1998)
- The floc settling velocity, floc density, stickiness coefficient, and fraction of organic carbon (f_{OC}) are calculated simultaneously and temporally at each class of flocculation particle
- The PCB mass transfer coefficient is varied with floc properties

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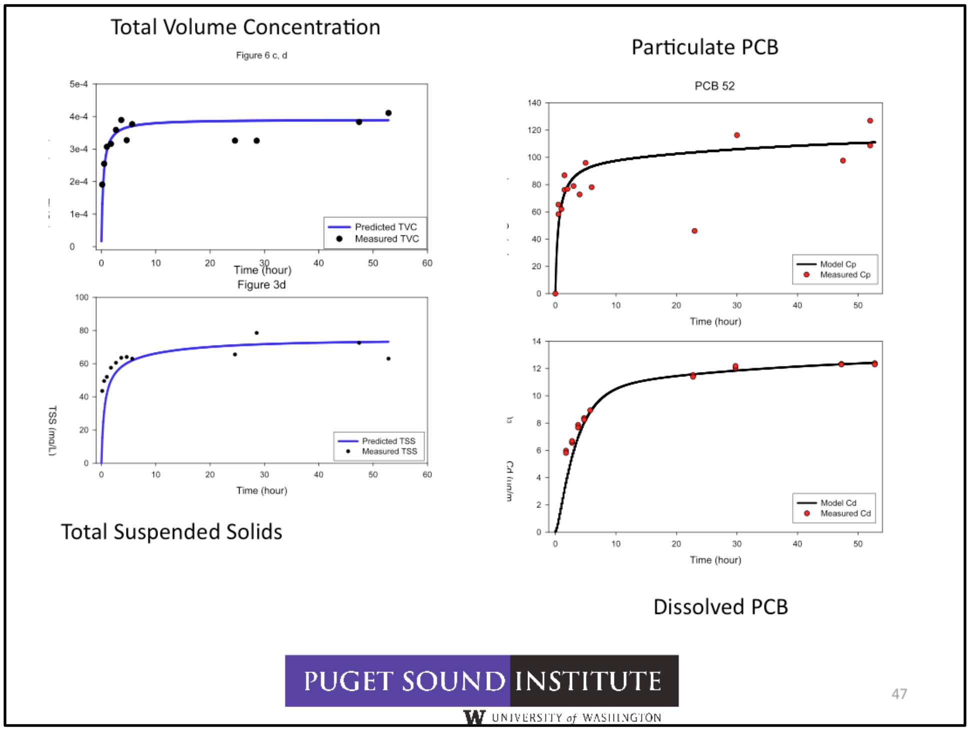

Total Volume Concentration

Total Suspended Solids

Particulate PCB

Dissolved PCB

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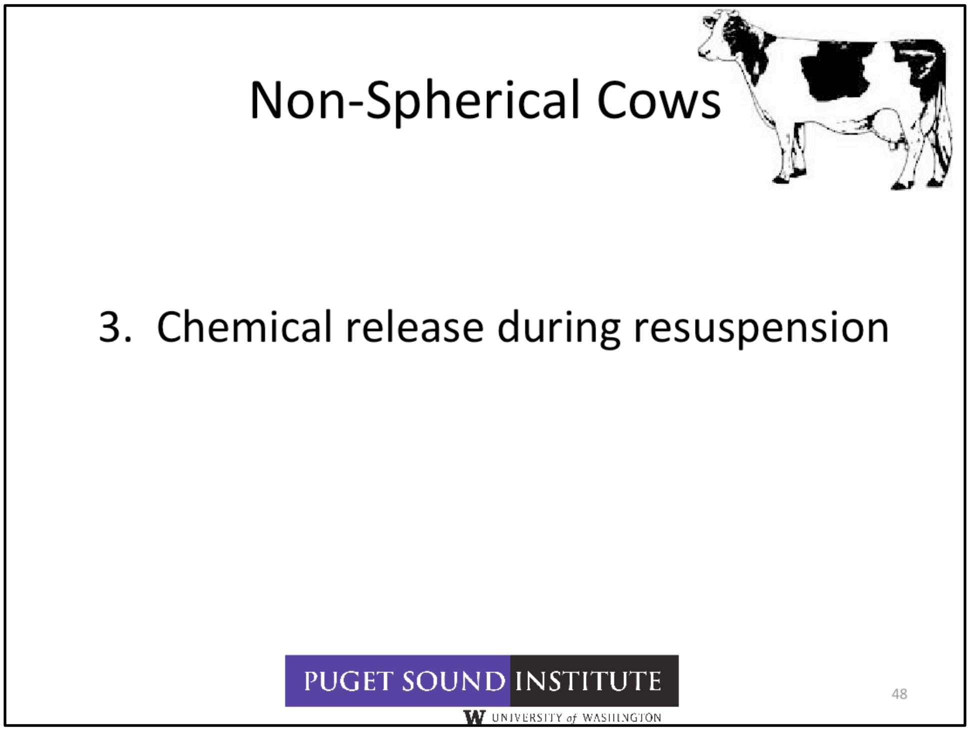
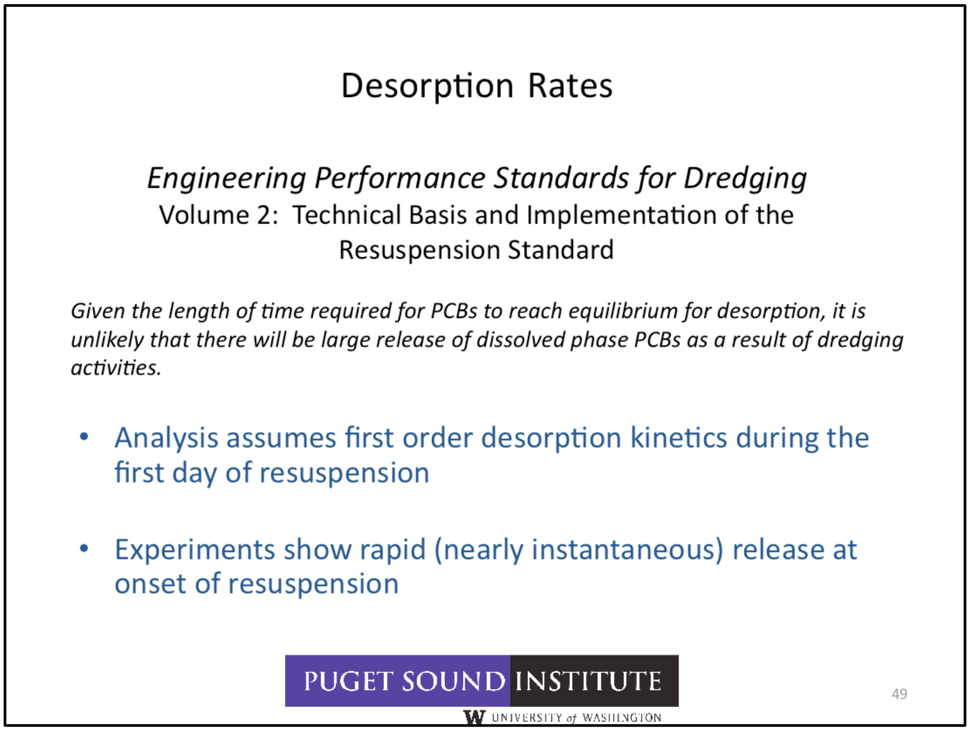


Non-Spherical Cows

3. Chemical release during resuspension



Desorption Rates

Engineering Performance Standards for Dredging
Volume 2: Technical Basis and Implementation of the Resuspension Standard

Given the length of time required for PCBs to reach equilibrium for desorption, it is unlikely that there will be large release of dissolved phase PCBs as a result of dredging activities.

- Analysis assumes first order desorption kinetics during the first day of resuspension
- Experiments show rapid (nearly instantaneous) release at onset of resuspension

Objectives

- What is the initial release of PCBs from quiescent river sediment when it is resuspended (*i.e.* during high flow or dredging)?
- How does the frequency and duration of resuspension events affect PCB desorption?

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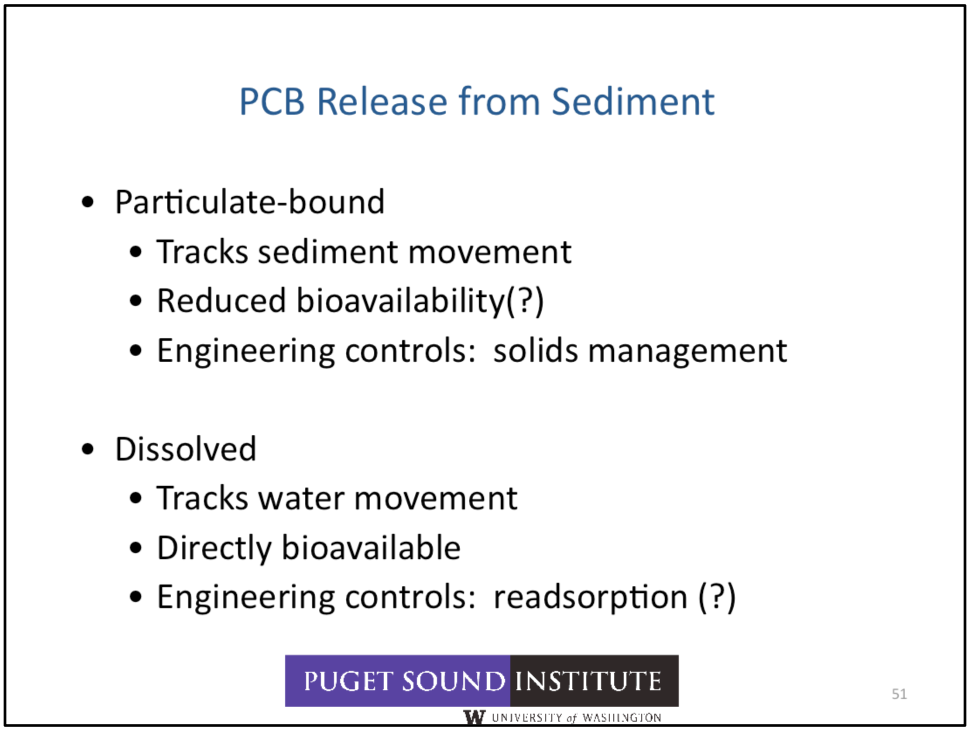

PCB Release from Sediment

- Particulate-bound
  - Tracks sediment movement
  - Reduced bioavailability(?)
  - Engineering controls: solids management

- Dissolved
  - Tracks water movement
  - Directly bioavailable
  - Engineering controls: readsorption (?)

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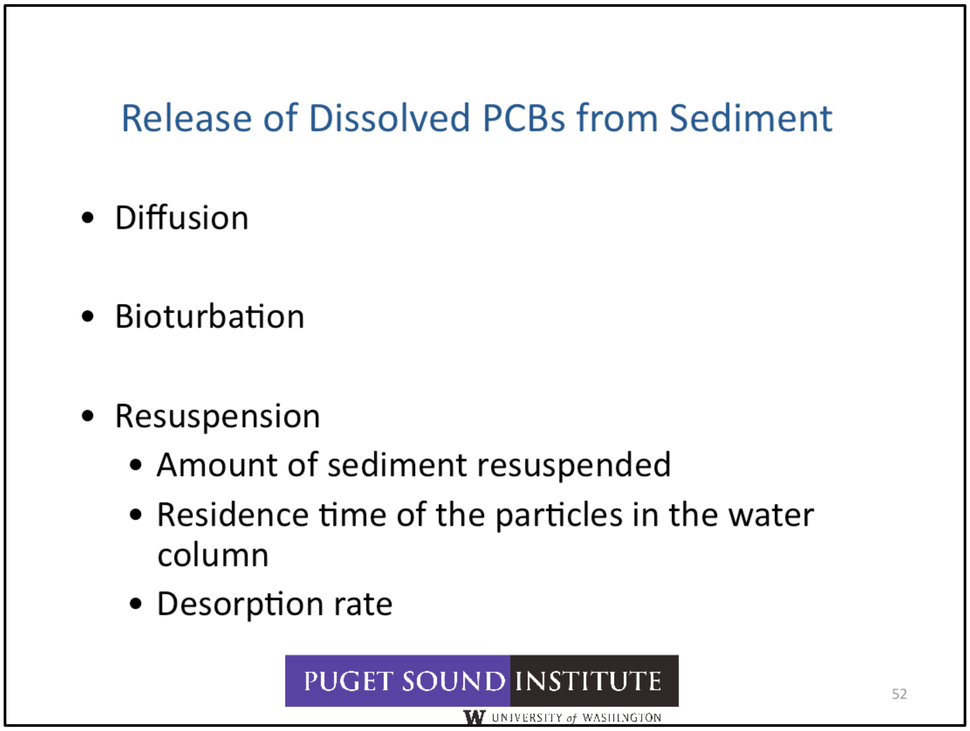

Release of Dissolved PCBs from Sediment

- Diffusion
- Bioturbation
- Resuspension
  - Amount of sediment resuspended
  - Residence time of the particles in the water column
  - Desorption rate

Methods: STORM Tanks

- The 1000L tanks produce high levels of bottom shear stress without generating excessive water column turbulence

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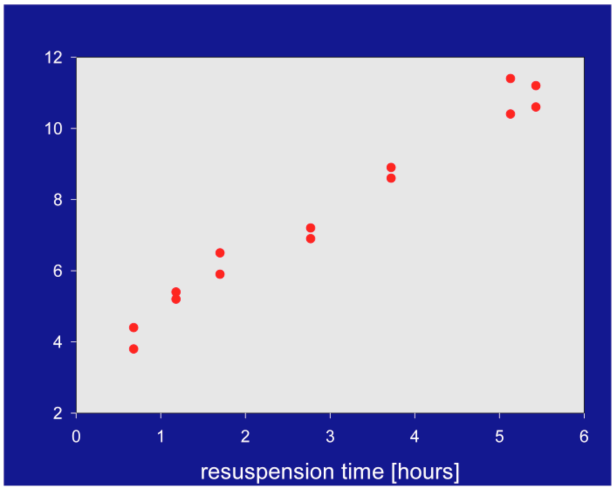
Dissolved PCB 49



Release of Resuspended PCBs into the Dissolved Phase

- After 1 hour of resuspension
  - First Resuspension: 20%
  - Second and Third Resuspensions: 15%
- After 6 hours of resuspension
  - First Resuspension: 40%
  - Second and Third Resuspensions: 25%

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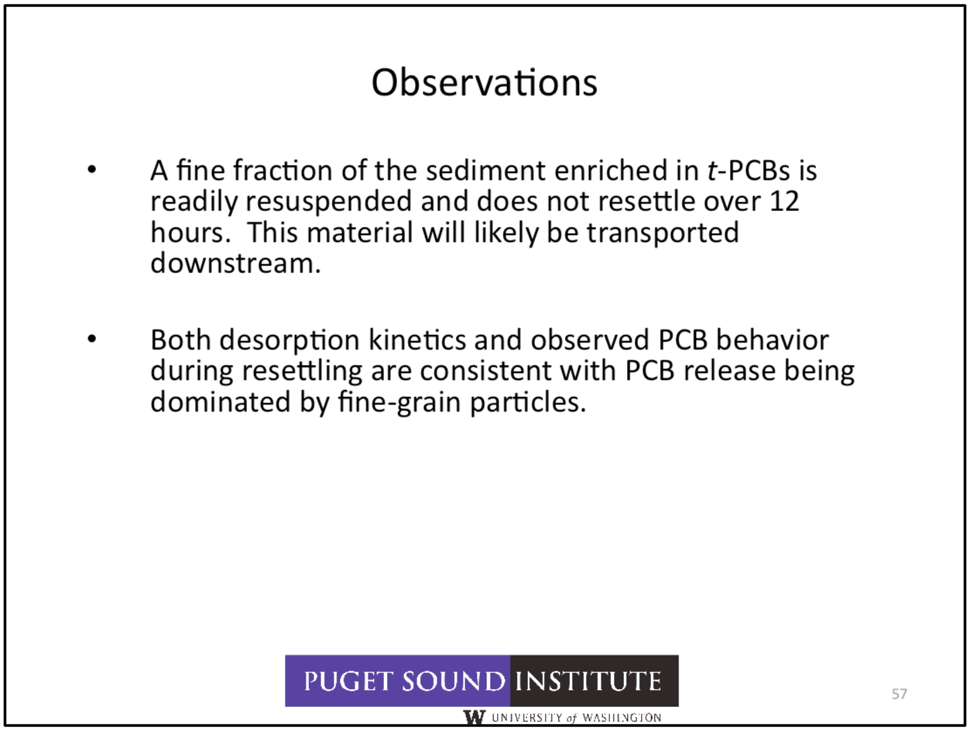
Observations

- After only one hour, resuspension of 7.4 mg/kg *t*-PCB Hudson River sediment under gentle conditions yields:
    - 34 mg/L suspended solids
    - 75 ng/L dissolved *t*-PCB
    - 300 ng/L particulate *t*-PCB
- 20% of the PCB mass resuspended is desorbed into the truly dissolved phase in one hour
- Higher levels of suspended solids and higher *t*-PCB levels in sediments will result in larger dissolved concentrations



Observations

- A fine fraction of the sediment enriched in *t*-PCBs is readily resuspended and does not resettle over 12 hours. This material will likely be transported downstream.
- Both desorption kinetics and observed PCB behavior during resettling are consistent with PCB release being dominated by fine-grain particles.

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Lessons Learned (so far…)

1. “Don’t make me come out of retirement to come back here to fix the loadings estimates” – R. Thomann

2. “Sediment transport is a side show” – D. DiToro
   Keep your eye on the ball

3. “If a simulation won’t finish overnight the model is too complex”
   The modeling effort must generate something that fits on a manager’s laptop

4. Complex systems require continual review during development
   Building inspectors

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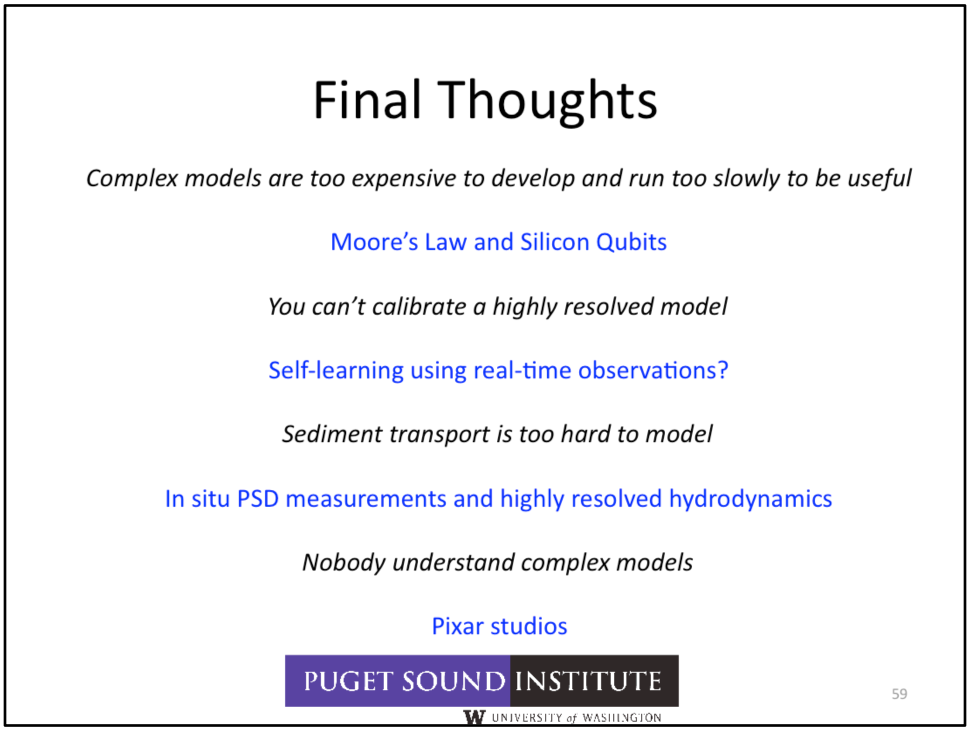

Final Thoughts

Complex models are too expensive to develop and run too slowly to be useful

Moore’s Law and Silicon Qubits

You can’t calibrate a highly resolved model

Self-learning using real-time observations?

Sediment transport is too hard to model

In situ PSD measurements and highly resolved hydrodynamics

Nobody understand complex models

Pixar studios

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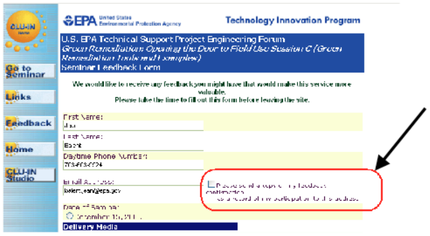
Links page

- Dr. Joel Baker (jebaker@uw.edu)
- Center for Urban Water at University of Washington Tacoma: http://www.tacoma.uw.edu/center-urban-waters
- University of Washington Superfund Research Program: http://depts.washington.edu/sfund/
- US EPA Region 10: http://www.epa.gov/aboutepa/region10.html
- National Institute of Environmental Health Institute (NIEHS)-Superfund Research Program http://www.niehs.nih.gov/research/supported/srp/

Thank you for your time!

Please click here to give the UW-SRP your feedback!



U.S. EPA Technical Support Project Engineering Forum
Green Remediation: Opening the Door to Field Use Session C (Green Remediation Tools and Examples)
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Katie Frevert, *University of Washington Superfund Research Program (UW-SRP)*
kfrevert@u.washington.edu
Tel (206)685-5379

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Thank you again for your attention and comments. I want to remind each of you that we are looking for your specific responses to many of the issues discussed today in our feedback form following this session.
Also, there are several resources and related documents included in the links to more resources on this page.

If you have any additional questions or comments, please feel free to contact myself or fill out a comment form on CLUIN.

Thank you and have a great afternoon.

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