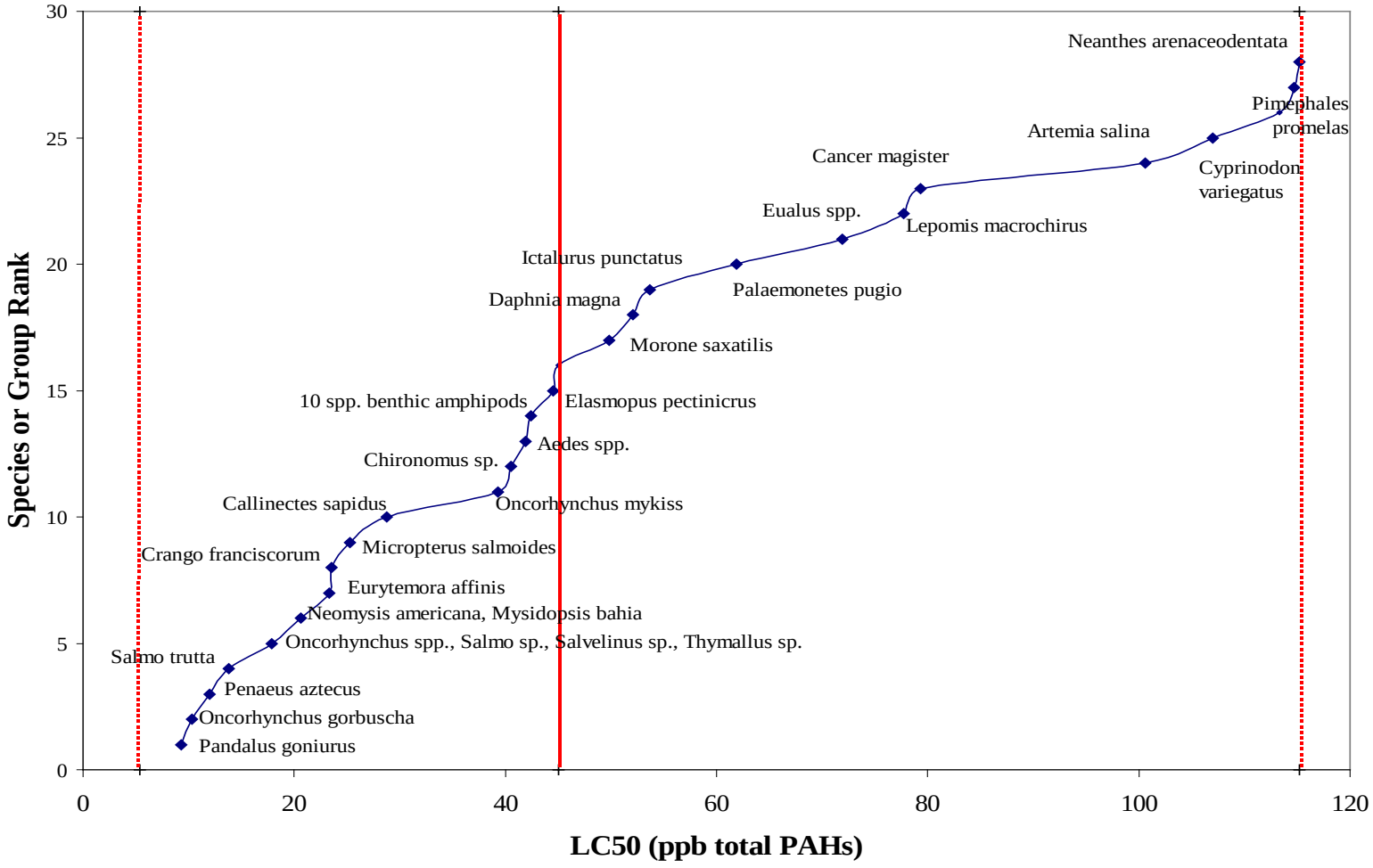
Oil-in-Ice: Transport, Fate and Potential Exposure (JIP P9) Report on October 22, 2008

Nancy Kinner and Whitney Blanchard, University of New Hampshire (UNH), Coastal Response Research Center (CRRC), , Amy A. Merten, NOAA's Office of Response and Restoration, CRRC, Per Johan Brandvik, SINTEF, Liv-Guri Faksness (SINTEF), Odd Gunnar Brakstad (SINTEF), Mark Reed (SINTEF), W. Scott Pegau (OSRI), John Whitney (NOAA ORR), Rainer Lohmann (URI), Chris Petrick (UAF) and Hajo Eiken (UAF)

Overall CRRC Mission

- Joint partnership between NOAA's Office of Response and Restoration (ORR) and the University of New Hampshire
- Develop new approaches to spill response and restoration through research/synthesis of information
- Serve as a hub for spill research, development, and technical transfer
  - Oil spill community (national and international)

Species Sensitivities to Oil



French-McCay 2002.

Measuring Biological Effects

- **Estimating "impacts"?**
- **Basic Risk Equation**

Chemical Exposure → **Toxicological Response**

-Route of Uptake

-Concentration

-Duration

-Bioavailability, absorption, metabolism

-Mode/Mechanism of toxicity →

- Lethality

-Changes in growth and reproduction

-Changes in behavior

-Population level parameters

Measuring Biological Effects

- **Estimating "impacts"?**
- **Basic Risk Equation**

Chemical Exposure	→	Toxicological Response

-Route of Uptake

-Concentration

-Duration

-Bioavailability, absorption, metabolism

Known

-Mode/Mechanism of toxicity →

- Lethality

-Changes in growth and reproduction

-Changes in behavior

-Population level parameters

Measuring Biological Effects

- **Estimating "impacts"?**
- **Basic Risk Equation**

Chemical Exposure		Toxicological Response
-Route of Uptake	Known	-Mode/Mechanism of toxicity →
-Concentration	Unknown	- Lethality
-Duration		-Changes in growth and reproduction
-Bioavailability, absorption, metabolism		-Changes in behavior
		-Population level parameters

Measuring Biological Effects

- **Estimating "impacts"?**
- **Basic Risk Equation**

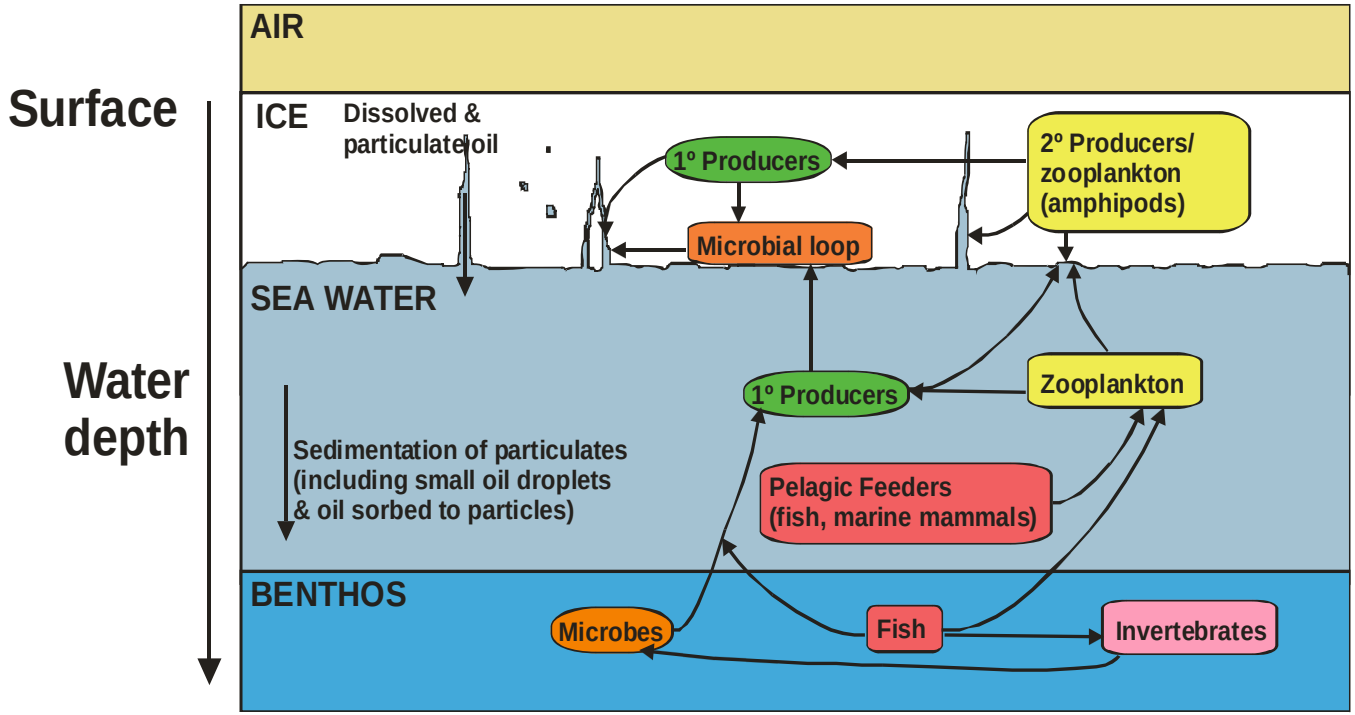
Chemical Exposure		Toxicological Response
-Route of Uptake	Known	-Mode/Mechanism of toxicity →
-Concentration	Unknown	- Lethality
-Duration	Unknown	-Changes in growth and reproduction
-Bioavailability, absorption, metabolism		-Changes in behavior
		-Population level parameters

Measuring Biological Effects

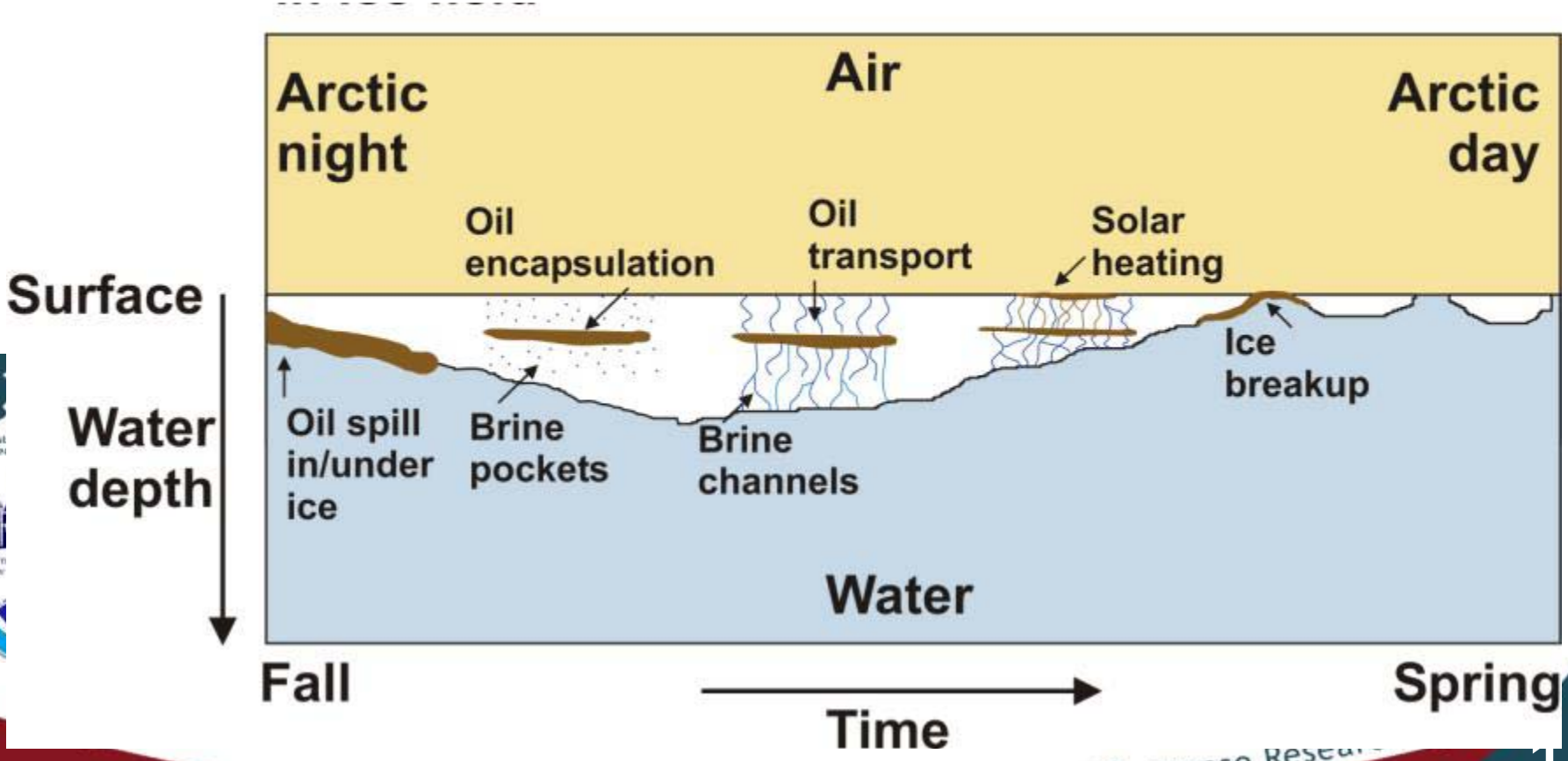
- **Estimating "impacts"?**
- **Basic Risk Equation**

Chemical Exposure		Toxicological Response
-Route of Uptake	Known	-Mode/Mechanism of toxicity →
-Concentration	Unknown	- Lethality
-Duration	Unknown	-Changes in growth and reproduction
-Bioavailability, absorption, metabolism	Unknown	-Changes in behavior
		-Population level parameters

Idealized Arctic First Year Ice Food Web



Seasonal Progression of Oil Frozen into Ice Field in Winter, and Released During Melting and Breakup in Spring



Primary components of study are:

1. Transport of dissolved crude oil hydrocarbons in ice
2. Biodegradation of crude oil hydrocarbons in ice
3. Modeling of the transport and biodegradation of crude oil hydrocarbons in ice

Questions study addresses are:

What are transport and degradation processes (partitioning, advection, diffusion, and biodegradation) and rates that govern fate of oil components frozen in ice?

How does change of ice microstructure dynamics affect transport?

What are exposures (e.g., composition, concentrations and durations) to which ice-associated organisms (e.g., microbes and protists) may be exposed?

How will response options affect transport and biodegradation processes?

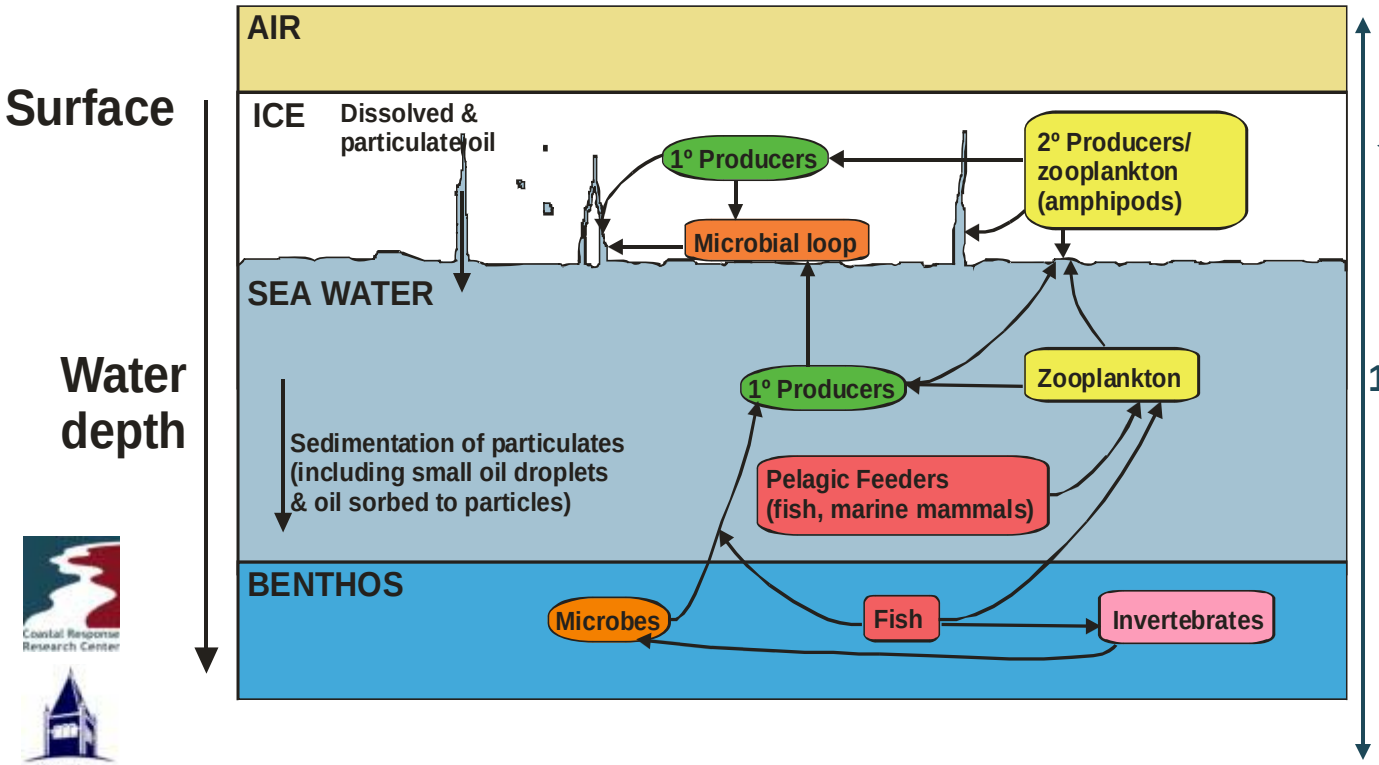
Peer Review Process for Proposal

- Team meeting at SINTEF in January 2008
- Proposal peer reviewed by 5 external reviewers
  - Confidentiality
- Team response to reviewers comments
- Resubmittal to peer reviewers for approval
- Proposal approved
- QA plans submitted and approved
- UAF and URI contracts signed
- SINTEF contract being signed
- $ 548,000 (CRRC + OSRI)

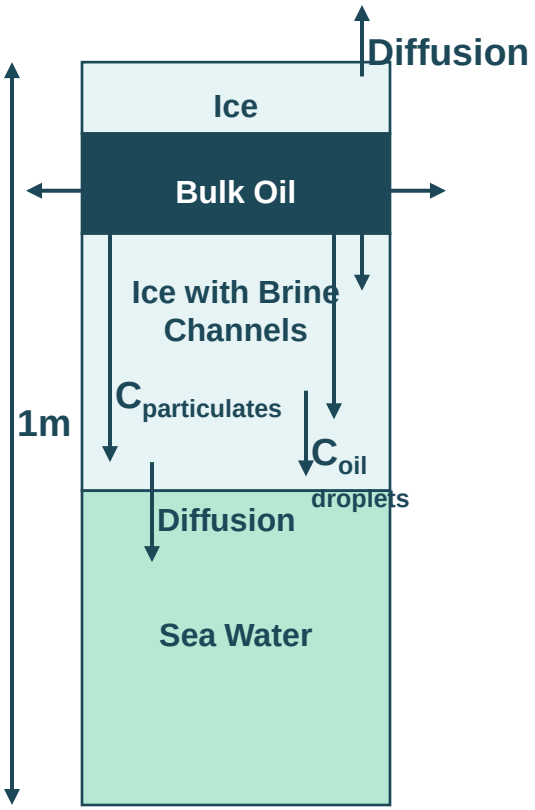
Step-wise Approach

- **Transport/exposure laboratory studies:**
  - **Determine how ice growth conditions affect transport and fate of entrapped oil in ice**
  - **Collect quantitative data on partitioning of oil components (bioavailable fractions) into brine inclusions and channels**
  - **Determine rates of vertical transport;**
- **Biodegradation laboratory studies:**
  - **Determine extent of crude oil biodegradation in marine sea ice;**
  - **Quantify contribution of biodegradation to depletion of hydrocarbons compared to other depletion processes;**
- **Develop oil-in-ice sub-model**

Idealized Arctic Food Web

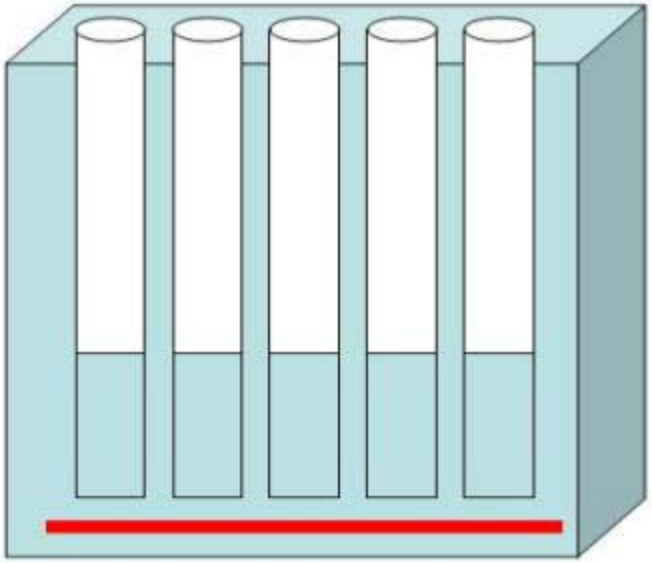


Bulk oil in ice



Behavior Experiments – SINTEF
Liv-Guri Faksness (PI)

- Objective: investigate how temperature influences oil behavior during thawing
- Freezing ice cores
  - 8 Transparent poly carbonate cylinders
    - inner dia. 144 mm
    - height < 80 cm
  - Temperature controlled, -20 °C
  - Insulated, heating panels placed at bottom
  - 3 mm oil (Statfjord) film in ice



Schematic of equipment for freezing ice cores in the laboratory

Experimental Design

Phase I: (no oil)

- Freeze-thaw cycles times
- Sampling techniques
  - Initial SPME testing

Phase II:

- Sampling techniques

Phase III:

- Replicate

Chemical Analysis

- SVOC (PAHs and phenols): GC/MS
- TPH: GC/FID
- Volatile organic compounds (C5-C9), BTEX: P&T GC/MS

Ice Characterization (UAF)

- X-ray computed tomography (CT)

Phases 1, 2 and 3

Table 2. *Suggested experimental design for oil behavior experiments. The results from one phase will be evaluated before a detailed plan for next phase is made.*

	freezing temp °C	time (to generate ice) days	expected ice thickness cm	oil film thickness mm	Description
Phase I	-20				
Phase II	-20				
Phase III	-20				

Table 3. *Suggested sampling intervals methods for phase II: Comparison of different sampling techniques. The freezing/thawing cycles are based on the finding from phase 1.*

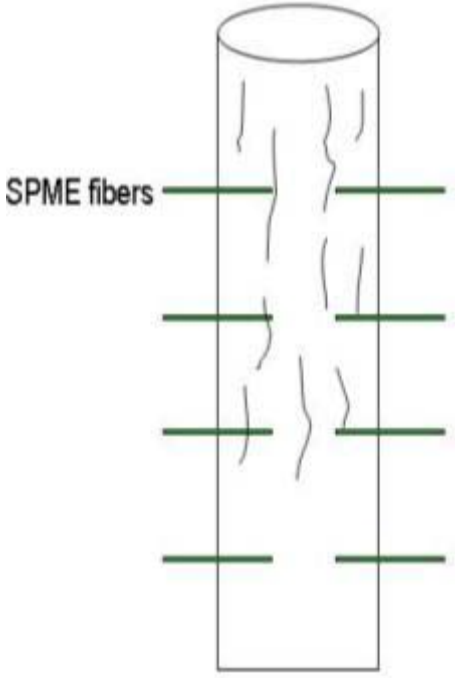
	Oil application	sampling intervals (after oil application)				
		1	2	3	4	
Col 1	no oil					
Col 2	oil					
Col 3	oil					
Col 4	oil					
Col 5	oil					
Col 6	oil					
Col 7	oil					
Col 8	oil					

Table 4. *Suggested sampling intervals and sampling methods for phase III: Replicate experiments.*

	Oil application	sampling intervals (after oil application)				
		1	2	3	4	
Col 1	no oil				x	Reference and temperature logging (characterize ice properties)
Col 2	oil				x	The whole column, cut in sections and melted
Col 3	oil				x	The whole column, cut in sections and melted
Col 4	oil				x	The whole column, cut in sections and melted
Col 5	no oil	x	x	x	x	Reference ice core (blank), passive samplers
Col 6	oil	x	x	x	x	Column with passive samplers
Col 7	oil	x	x	x	x	Column with passive samplers
Col 8	oil	x	x	x	x	Column with passive samplers

Passive Samplers

- 2 Sampling techniques
  - Polyethylene (PE) sheets
  - Solid-phase microextraction (SPME)
- Not validated for oil spills in cold climates
- Objective:
  - Verify equilibrium partitioning constants
  - Include performance reference compounds (PRCs) in PE matrix (for kinetic uptake)



Possible experimental approach for SPMEs in ice core columns

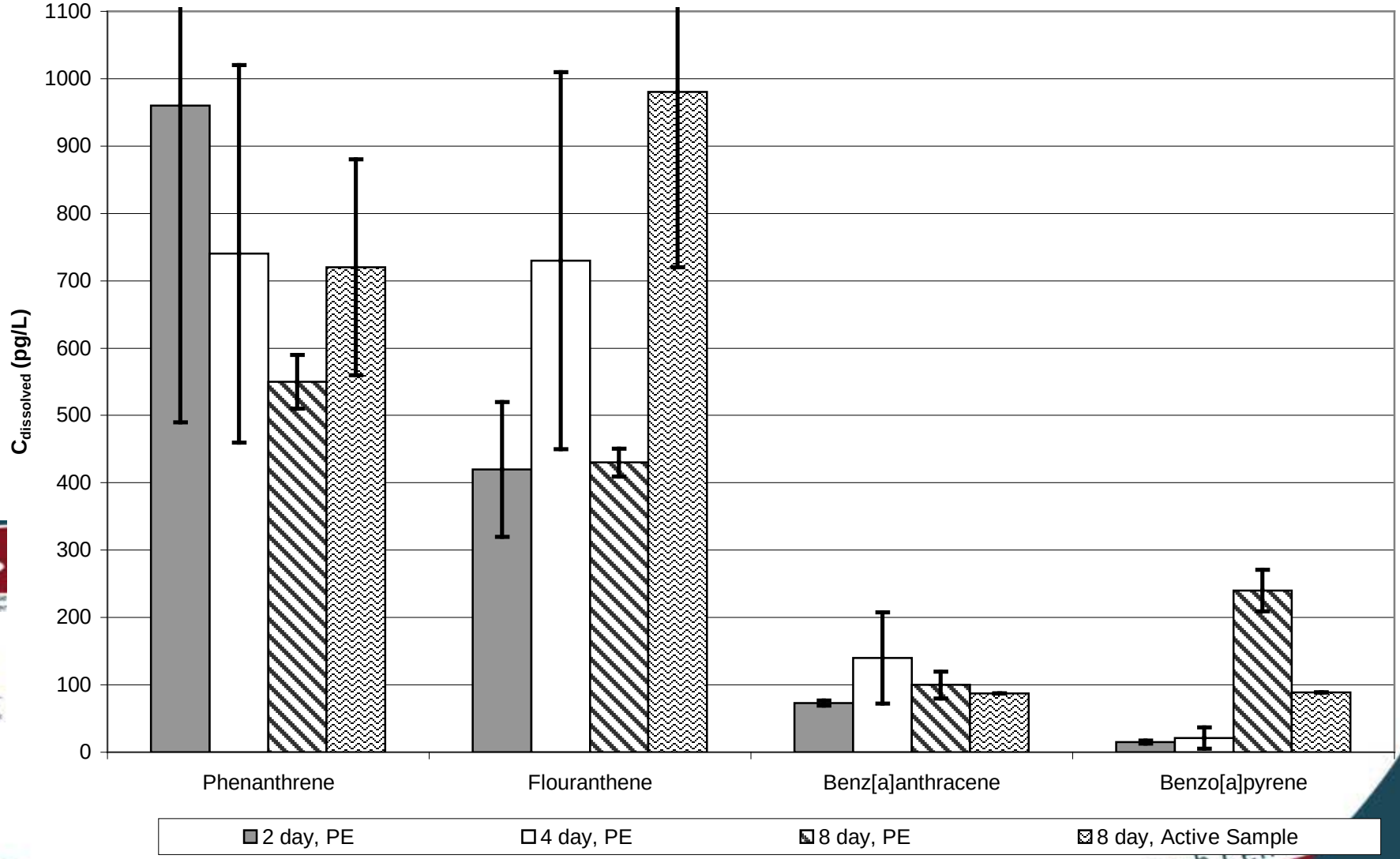
Update: Use of passive samplers

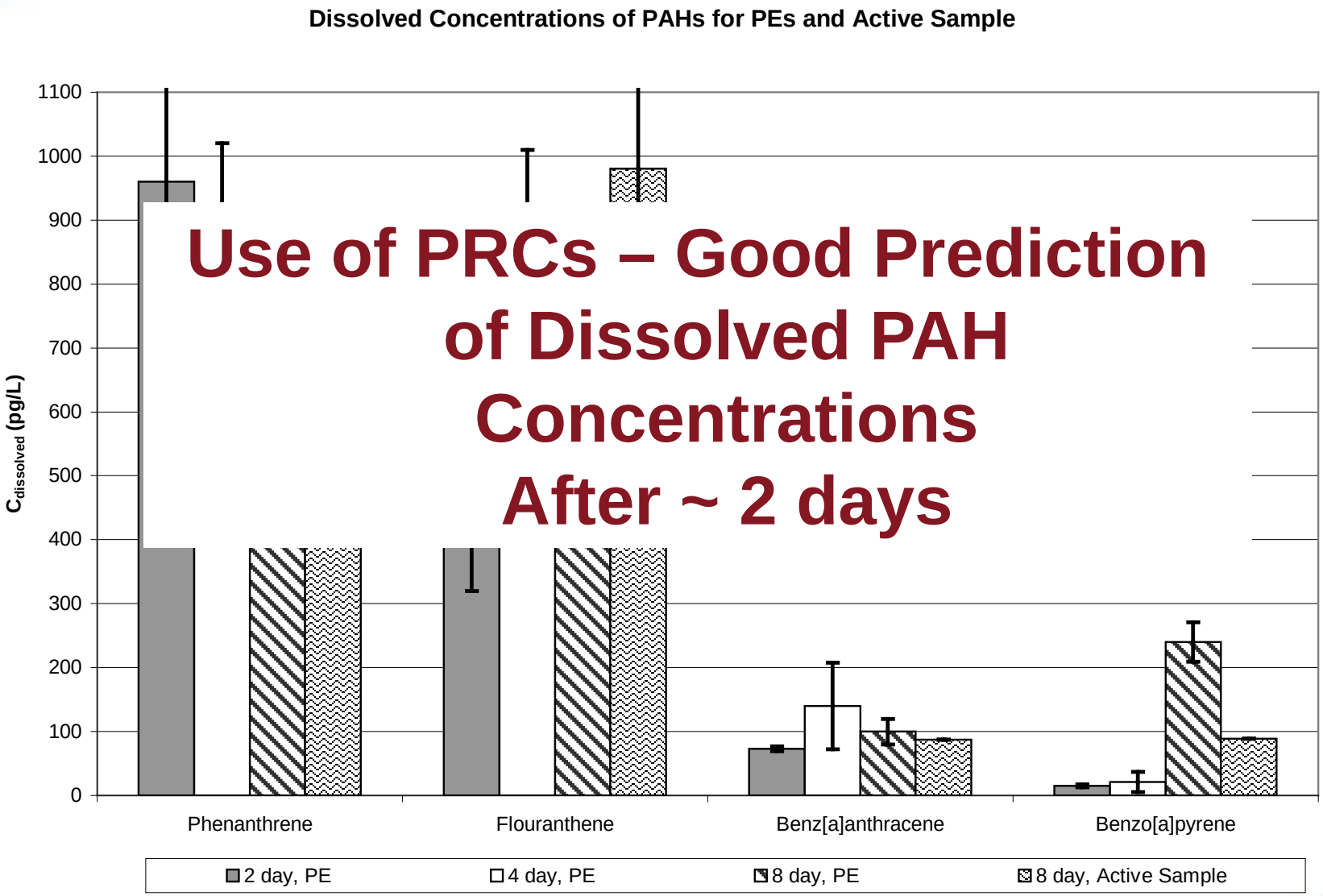
Rainer Lohmann (Univ. of Rhode Island)

- PE deployments, Summer 2008, Loss of PRCs in Narragansett Bay
- Small PAHs need <10 days to reach equilibrium

Compound	Log K_{PE-w}	% left after 8 days	t_{95}
d10-anthracene	4.3	1%	5
d12-benz(a)anthracene	5.7	32%	17
d12-benzo(a)pyrene	6.2	79%	124

Dissolved Concentrations of PAHs for PEs and Active Sample





Use of PRCs – Good Prediction of Dissolved PAH Concentrations After ~ 2 days

Update: Oil/WSF Entrainment and Movement in Ice

Hajo Eicken, Jonas Karlsson, Mette Kaufman (UAF)

Cold-lab experiments:

- Synthetic oil & North Slope sweet crude
- Oil entrainment and migration experiments:
  - Temperature
  - Salinity
  - Oil flow rate after onset of migration
  - Oil content and micro-distribution

Update: Oil/WSF Entrainment and Movement in Ice

- Progress on experiments/ data analysis
  - Oil properties
  - Small-scale experiment
- Meeting with Liv-Guri Faksness (SINTEF) in Nov 08 to discuss experiment progress
- Financial support of this component of JIP through Oil Spill Recovery Institute (OSRI), Cordova, AK (Contract 10-13-08)

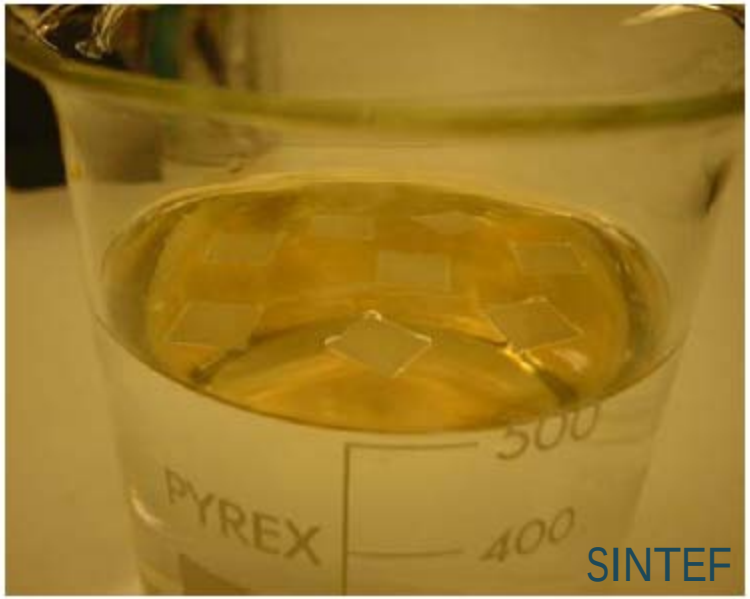
Biodegradation - SINTEF

Will biodegradation contribute to the HC depletion in ice (WSF and oil droplets)?

- Artificial brine
  - -5°C, 100 psu
  - -10°C,145 psu
- Bacterial inocula
  - 90 m depth, SINTEF lab
- Water-soluble fractions (WSFs), CROSERF method
  - 1: 1000, oil: water
  - 1: 10000, oil: water
- Nutrients

  (100: 5: 0.1, C: N: P)

- Simulated oil Droplet/adsorbed oil
  - Oil films (10-20 µm thick)
  - Fluortex fabric adsorbents (1 cm^2)



Experiment 1 and 2

Table 5. Suggested experimental setup for biodegradation experiments BE1, with oil/water (O/W) ratios of 1/1000 and 1/10000.

Temp. (°C)	O/W (ratio)	Sampling (weeks)								
		0	1	2	4	8	12	16	20	24
+5	1/10000	X			X	X				
0	1/10000	X			X	X		(X)		(X)
-5	1/1000	X		X	X	X	X	X	X	X
	1/10000	X	X	X	X	X	X	X	X	X
	Adsorbents	X	X	X	X	X	X	X	X	X
-10	1/1000	X					X			X
	1/10000	X					X			X
	Adsorbents	X					X			X

Table 6. Suggested experimental setup for biodegradation experiments BE2.

Temperature (°C)	Nutrients	Sampling time						
		0	1	2	3	4	5	6
-5 (static)	+	X	X	X	X	X	X	X
	-			X		X		X
-5 (agitation)	+	X	X	X	X	X	X	X
	-			X		X		X
-10 (static)	+	X	X	X	X	X	X	X
	-			X		X		X
-20 (optional)	+	X		X		X		X
	-					X		X

Coastal Response Research Center

University of New Hampshire

Experiment 3

Effect of Protist Predation on Biodegradation

Temp. (C)	Protists	Sampling time (days)						
		0	3	6	9	12	15	15 – 84 (every 3rd day)
+5	+	X	X	X	X	X	X	X
	-	X	X	X	X	X	X	X
0	+	X	X	X	X	X	X	X
	-	X	X	X	X	X	X	X
-5	+	X	X	X	X	X	X	X
	-	X	X	X	X	X	X	X
-10	+	X	X	X	X	X	X	X
	-	X	X	X	X	X	X	X

Analytical Methods

- Decalines, phenols, napthalenes, PAHs: GC-MS
- BTEX: P&T GC-MS
- Microbiological: epifluorescence (DAPI)
- Heterotrophic microbes and oil-degrading prokaryotes: viable counts
- Eukaryotic protists: most probable number
- Chlorophyll: fluorometric analysis
- Change in microbial communities: DGGE

Modeling SINTEF

Objective: to develop and test module that can eventually link oil spill models to large-scale coupled sea ice-hydrodynamic models

- **Model development**
  - **2D single-phase flow (Petrich et al. 2006)**
- **Modified**
  - **Include bulk oil as a source for dissolved**
  - **Diffusion-advection of dissolved HCs**
  - **Solar insulation**
  - **Physical-chemical processes governing oil behaviour**
- **Multi-phase version**

- **Anticipated variables:**
  - **Porosity (total)**
  - **Permeability (or effective porosity)**
  - **Thickness**
  - **Temperature gradient (vertical)**
  - **Salinity (brine concentration)**
  - **Oil concentration (by component)**

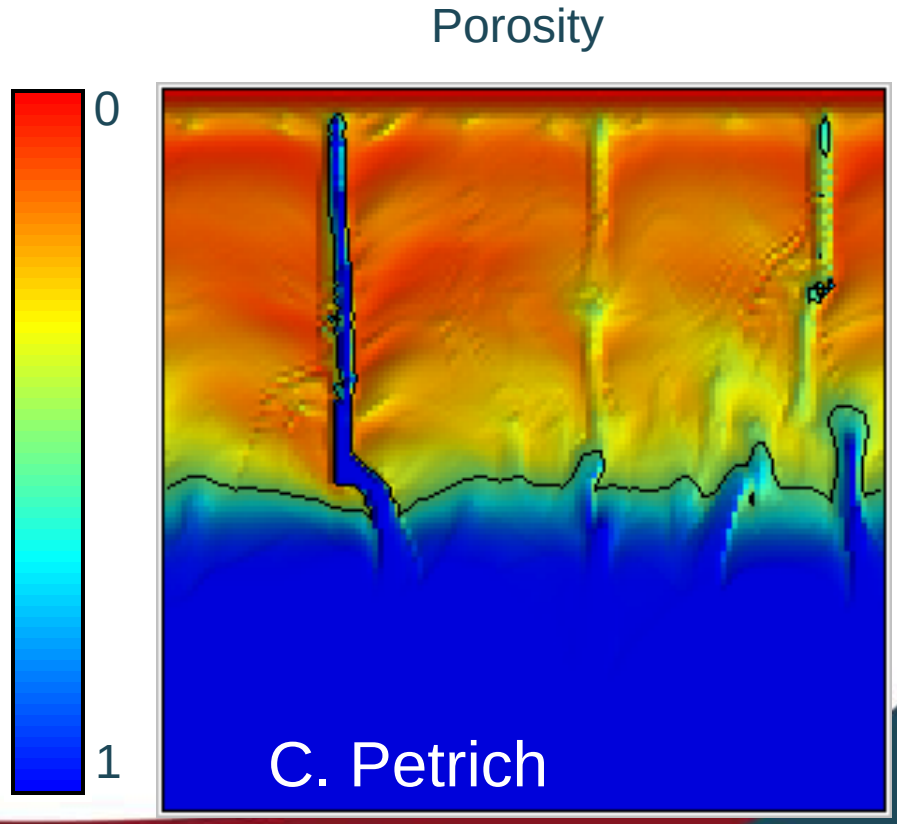
Update: Fluid Dynamics Model

Progress

- Application design developed (open source C code, Linux)
- Entered code at implementation stage
  - Skeleton code w/ primitive boundaries
  - Preliminary matrix solver
  - Not all differential equations solved

Plans

- Meeting w/ Whitney Blanchard (UNH) in Nov 08 to discuss implementation



Next Steps/Timeline

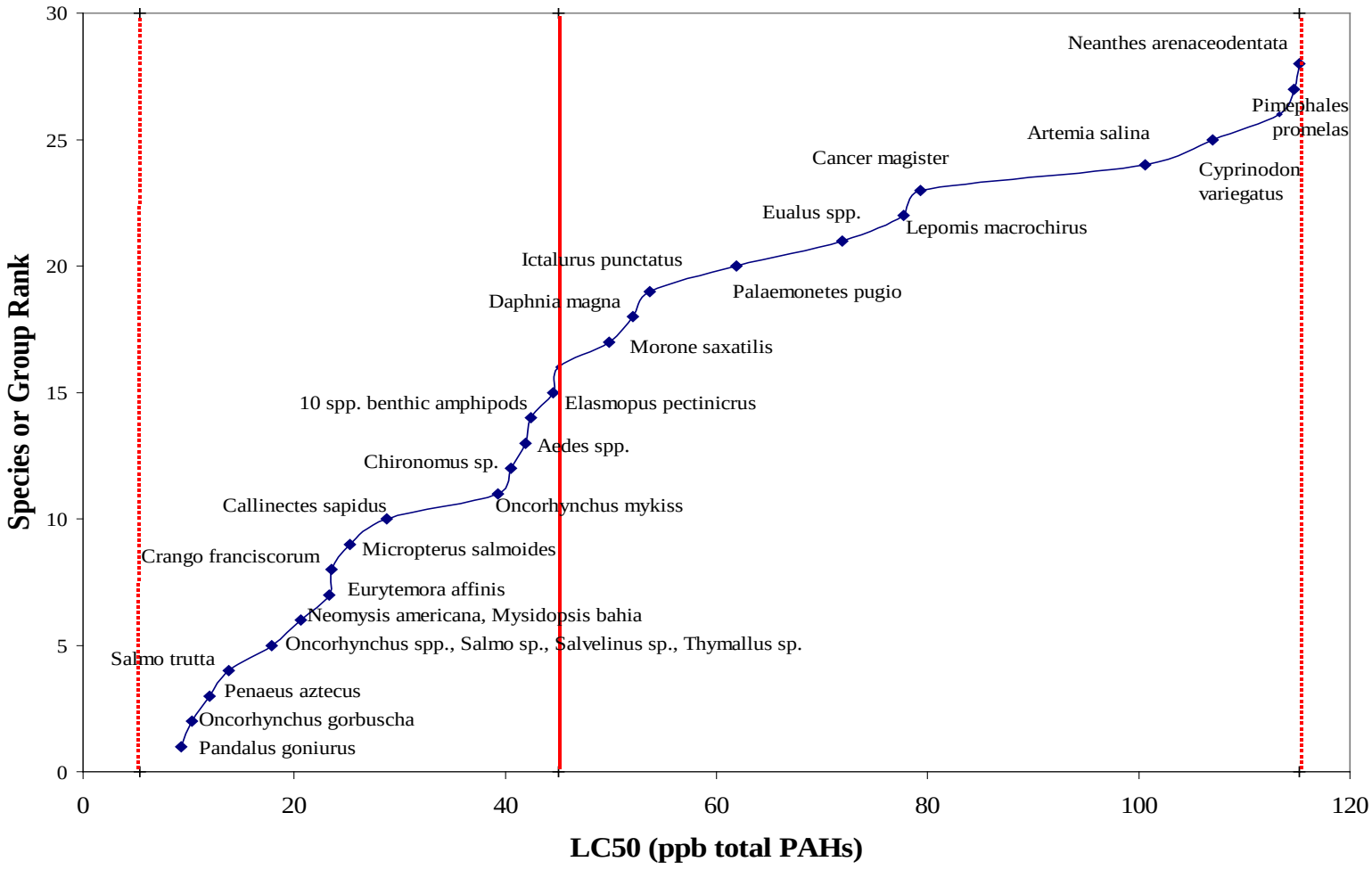
	Proposed SINTEF/UNH Timeline																							
	2008						2009												2010					
Overall Project Activity	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
Behavior																								
Biodegradation																								
Modeling																								
Administration/reporting																								

	Proposed URI Timeline																							
	2008						2009												2010					
Activity	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J
MS method for WSCs																								
Equilibrium and kinetic validation																								
Cold water and salinity experiments																								
Ice-column spill analysis																								
Manuscript, final																								

Discussion and Questions

Extra Slides

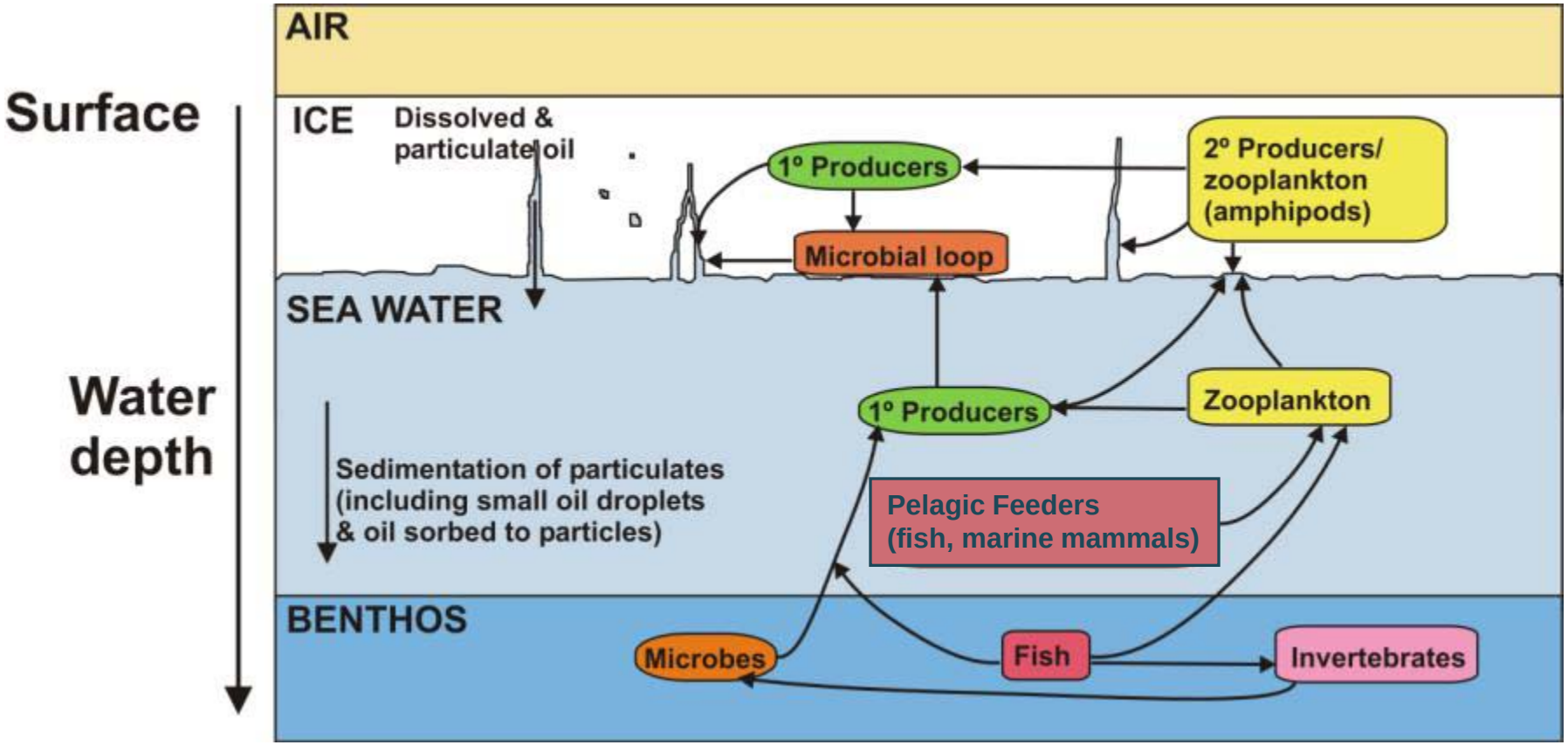
Species sensitivities to Oil



French-McCay 2002.

Conceptual Model

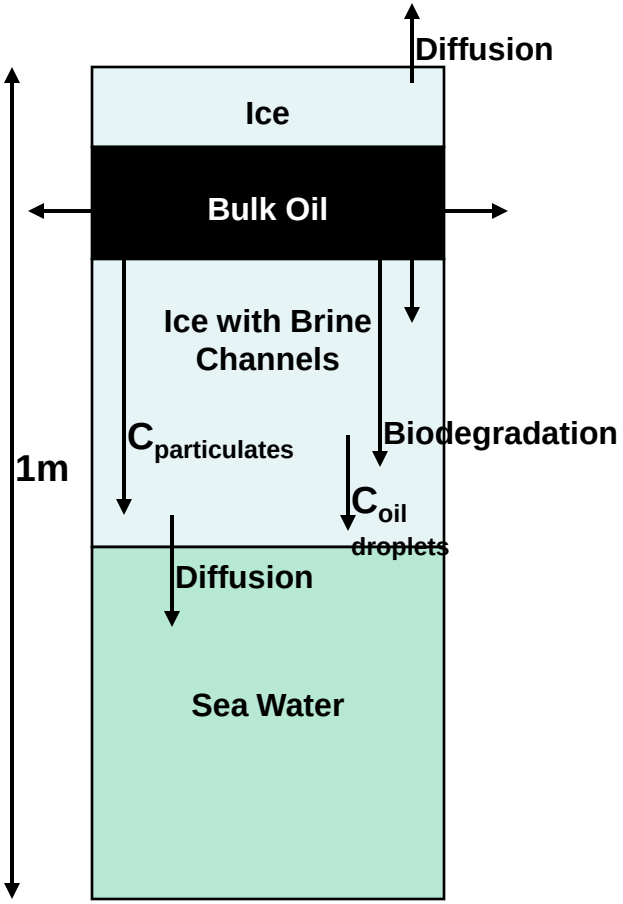
Food Web Cycle



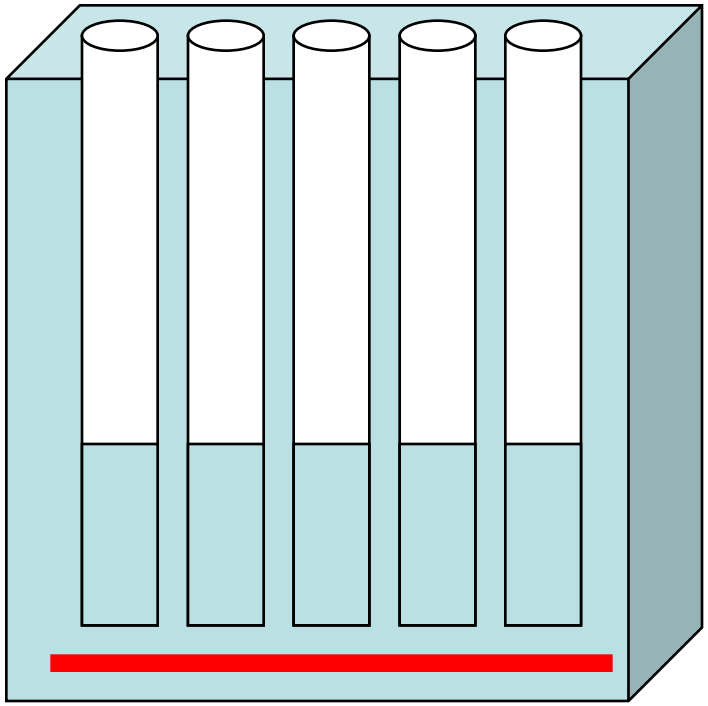
Transport/Exposure Mechanisms

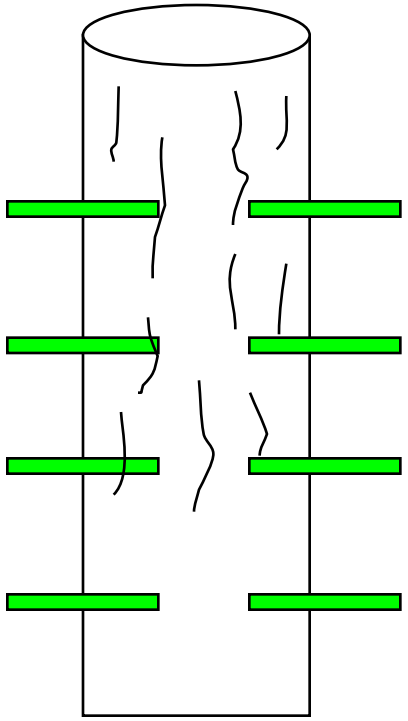
Bulk oil encapsulated in ice from below
→measure dissolved constituents
(WAF - e.g., PAHs)

Density of brine transport downward
→will transport dissolved (bioavailable)
components of oil downward



POSSIBLE EXPERIMENTAL APPROACH FREEZING ICE CORES





SPME fibers

Insulated box in freezer

Heating element

Transport, Fate and Potential Exposure of Oil-in-Ice: Objective(P9)

- Estimate routes and magnitudes of:
  - Potential environmental exposures
  - Concentrations of oil components
- During migration through the ice regime during a freeze-thaw cycle

Transport, Fate and Potential Exposure of Oil-in-Ice: Goals (P9)

- **Transport (Behavior) of water soluble fraction (WSF) from crude oil in ice**
  - **Investigate how ice conditions affect fate and transport of encapsulated oil in ice**
  - **Collect data on the partitioning of oil components (bioavailable fractions) into brine inclusions and channels**
  - **Determine rates of vertical transport**

Transport, Fate and Potential Exposure of Oil-in-Ice: Goals (P9)

- **Biodegradation of WSF from crude oil in ice**
  - **Determine extent and time span crude oil biodegradation takes occurs in ice**
  - **Compare biodegradation rates to other depletion processes**
  - **Determine whether naturally-occurring predation can hinder biodegradation**

Transport, Fate and Potential Exposure of Oil-in-Ice: Goals (P9)

- **Modeling the fate and transport of WSF in ice**
  - **Develop an oil-in-ice transport model**