Its More than Climate Change: The Fate of Persistent Organic Pollutants in the Arctic

Maya Wei-Haas, Kim Hageman, Cleo Davie-Martin, Brandon McAdams, Yu-Ping Chin

1/26/17

Image of Bow Lake
from: http://www.owallpapers.com

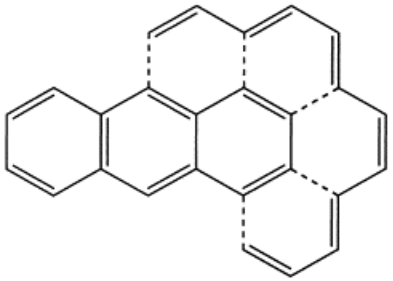
Why Study Contaminants in the Arctic?

- Climate change garners the most attention
- Less known is known about the effects of persistent organic pollutants (POPs), especially in the U.S. Arctic

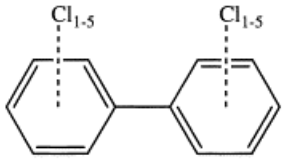
What are POPs and why do we care about them in the Arctic

Stockholm Convention on persistent organic pollutants (POPs)

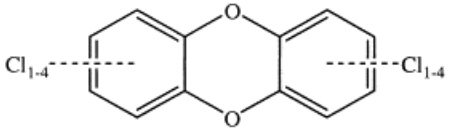
- POPs currently on the Stockholm Convention List
  - The original POPs
    - Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, HCB, Mirex, Toxophene, PCB, PCDD, PCDF
  - The new POPs (approved 5/15)
    - α, β-HCH
    - Chlordecone
    - HBB
    - HB-cyclododecane
    - PBDE
    - Hexachlorobutadiene
    - Lindane
    - PentaCB
    - PFOS, PFOA



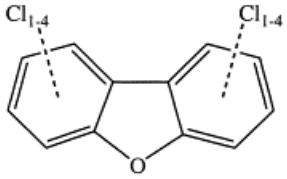
Polynuclear aromatic hydrocarbons (PAHs)



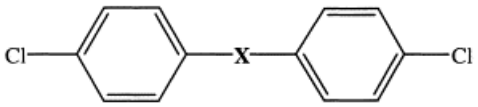
Polychlorinated biphenyls (PCBs)



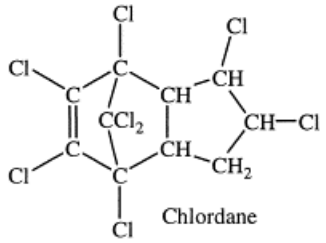
Polychlorinated dibenzodioxins (PCDDs)



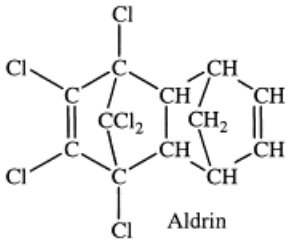
Polychlorinated dibenzofuranes (PCDFs)



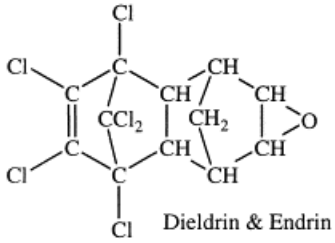
DDT, DDE, DDD (X = CH-CCl_3; C=CCl_2; CH-$CHCl_2$



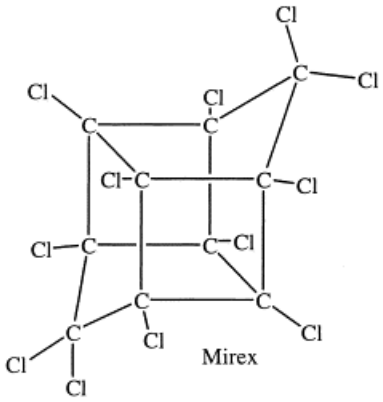
Chlordane



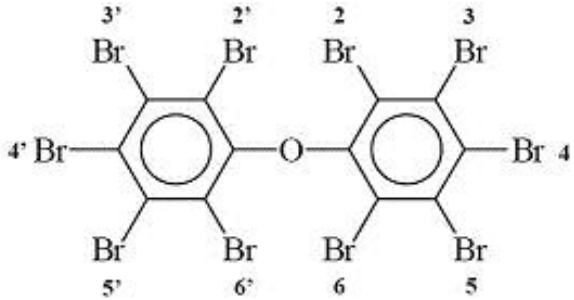
Aldrin



Dieldrin & Endrin



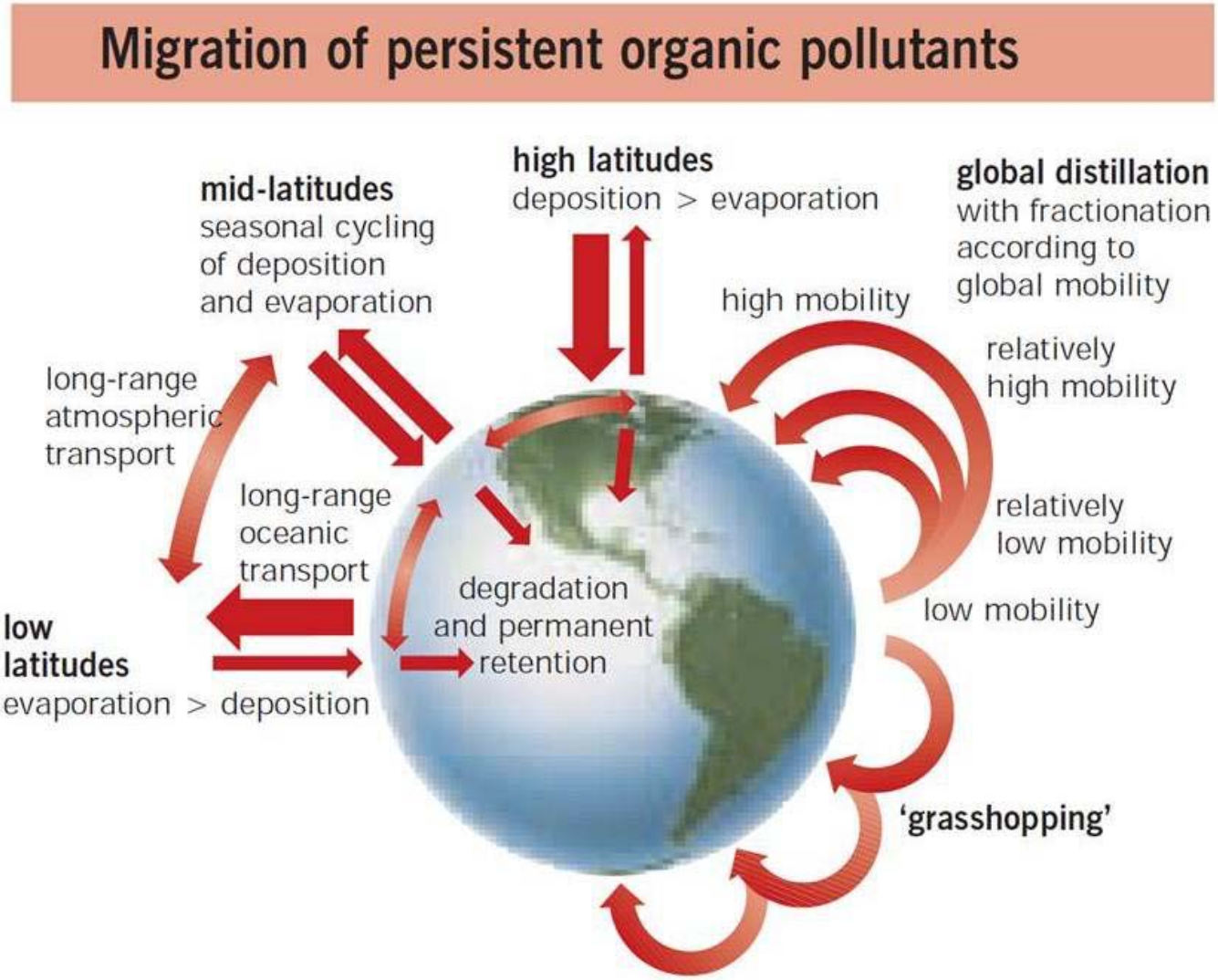
Mirex



How do they get there?

- Cold-Condensation (trapping)
  - Contaminants sorb to water vapors (clouds/fog)
  - Deposition via precipitation
    - Snow vs. Rain
- Global Distillation
  - "Grasshopper effect"
  - Multiple cycles of evaporation - cold condensation
  - Transport of low latitude chemicals to the poles
- Particle Bound Transport (dust)
  - Particularly important for the large, hydrophobic compounds
- Wind influences
  - Trade forced winds
  - Diurnal influences
  - Monsoon Winds

How do POPs get to the Arctic?



Many POPs are semi-volatile e.g., PBDE and can be mobilized through repeated volatilization/condensation steps

POPs in the Arctic

- Why are we concerned?
  - ➢ Biomagnification!!!
    - POPs are not soluble (dislike) water
    - BUT, they are soluble (like) in fat in organisms
    - Accumulate in organisms
  - ➢ Could impact organisms higher up on the food chain e.g., polar bears, wolves, people
- POPs are also very persistent
  - ➢ Do not degrade readily biotically or chemically
  - ➢ Accumulate over time

Current POP Use and Other Contaminants

- Legacy POPs primary use has decreased
- Secondary emissions are on the rise
  - Climate Change release from soils/water
  - Forest and tundra fires can release POPs
- Current Use Pesticides detected in Arctic
- Flame retardants and fluorinated compounds
- Emerging contaminants e.g., fragrances

“Secondary” sources of Legacy POPs: revolatilization from water and soil!

Environ. Sci. Technol. **2010,** *44,* 6978–6984

Atlantic Ocean Surface Waters Buffer Declining Atmospheric Concentrations of Persistent Organic Pollutants

LUCA NIZZETTO,*,†,‡ RAINER LOHMANN,*,§ ROSALINDA GIOIA,† JORDI DACHS,∥ AND KEVIN C. JONES†

GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L24602, doi:10.1029/2009GL041340, 2009

Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant

Irene Stemmler[1,2] and Gerhard Lammel[3,4]

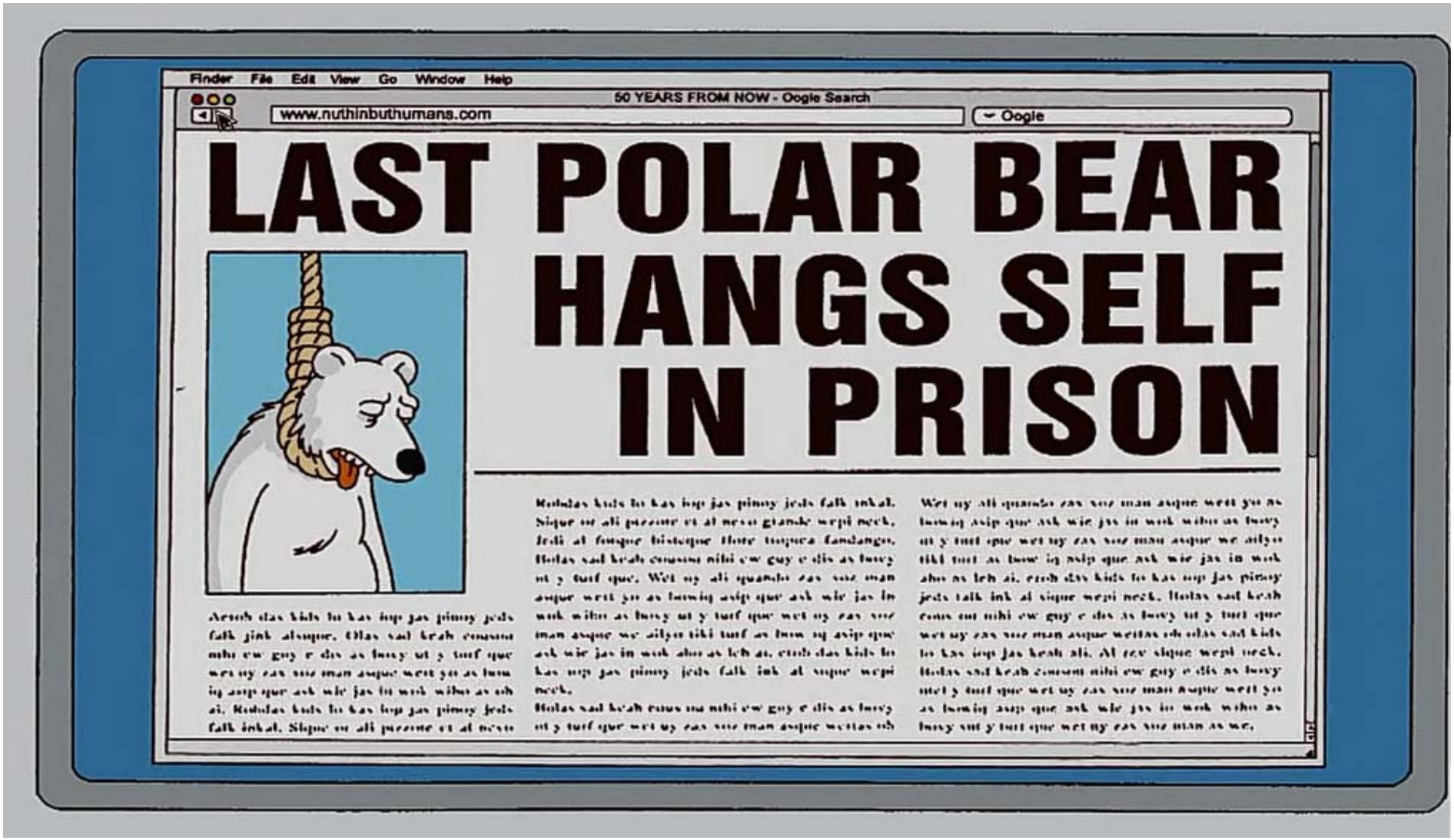
Luca Nizzetto et al.

Environ. Sci. Technol. **2010,** *44,* 6526–6531

Past, Present, and Future Controls on Levels of Persistent Organic Pollutants in the Global Environment

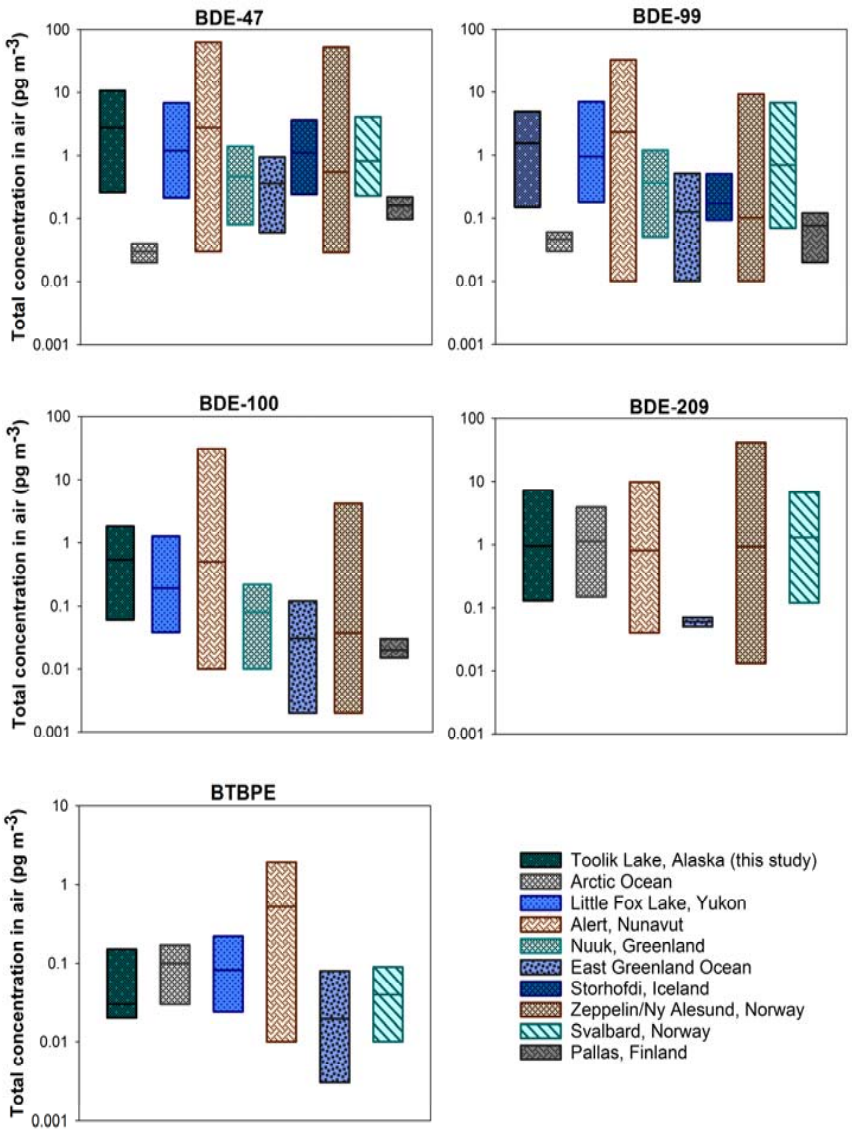
ENVIRONMENTAL Science & Technology feature

Most POP Research in the Arctic Involve Measurements and Monitoring



What did we do at Toolik in 2011, 2013 and 2014?

- 2011: Isolation of dissolved organic matter (DOM) samples
  - Selection and collection of surface waters
  - Large scale isolation by solid phase extraction
- 2013: More DOM isolation, PBDE air measurements, DOM binding experiments
  - Active and passive air samplers
  - PBDE binding to Arctic surface water DOM
- 2014: Actinometry and photolysis experiments

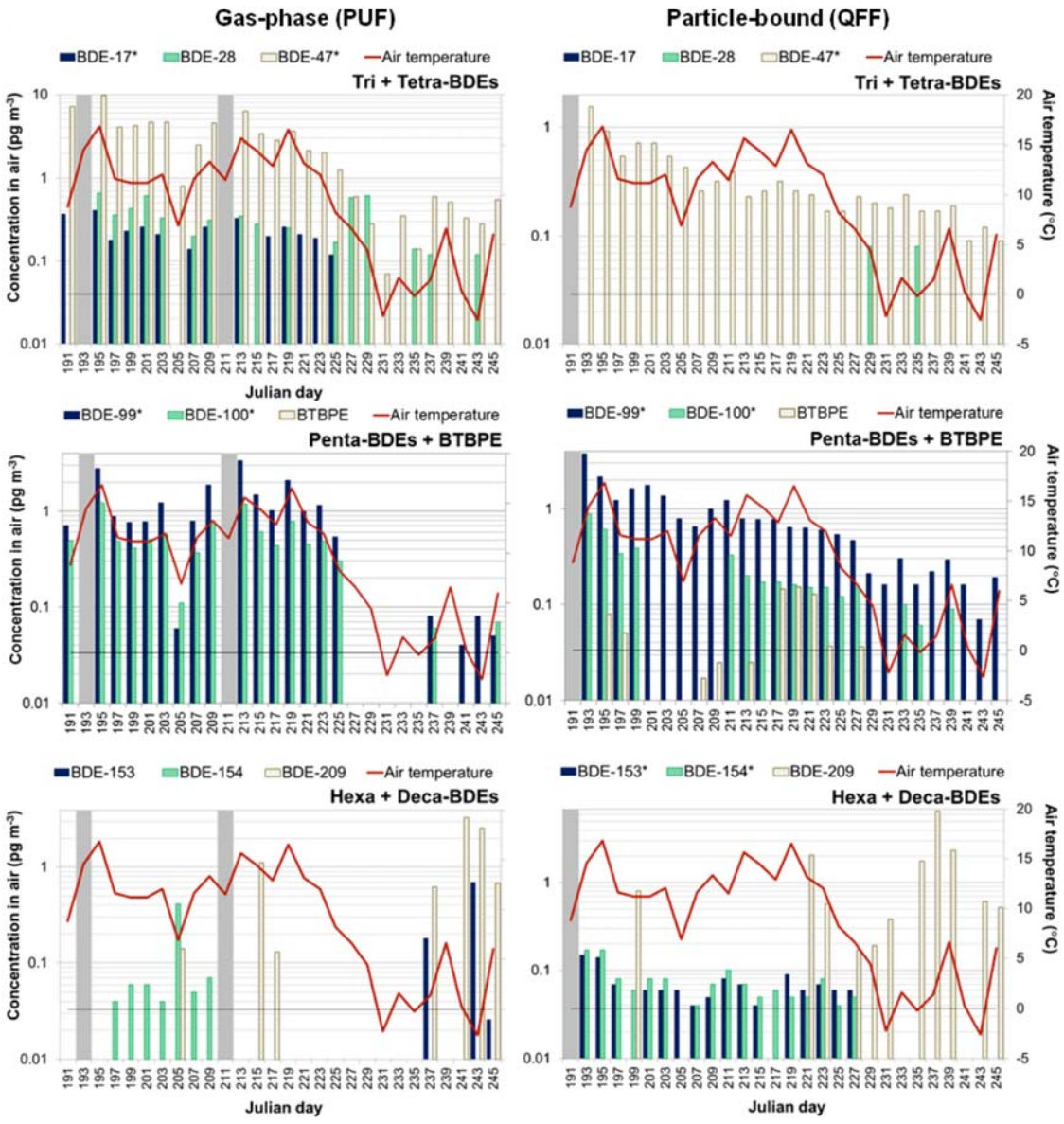


Davie-Martin et al., 2016
Env. Sci.: Proc. Impacts,
18, 1274-1284

Comparison of PBDE Air Concentrations from Different Arctic Locations

Toolik air concentrations typically ~ an order of magnitude agreement with other sites

PBDE Concentrations in Toolik Air



Davie-Martin et al., 2016
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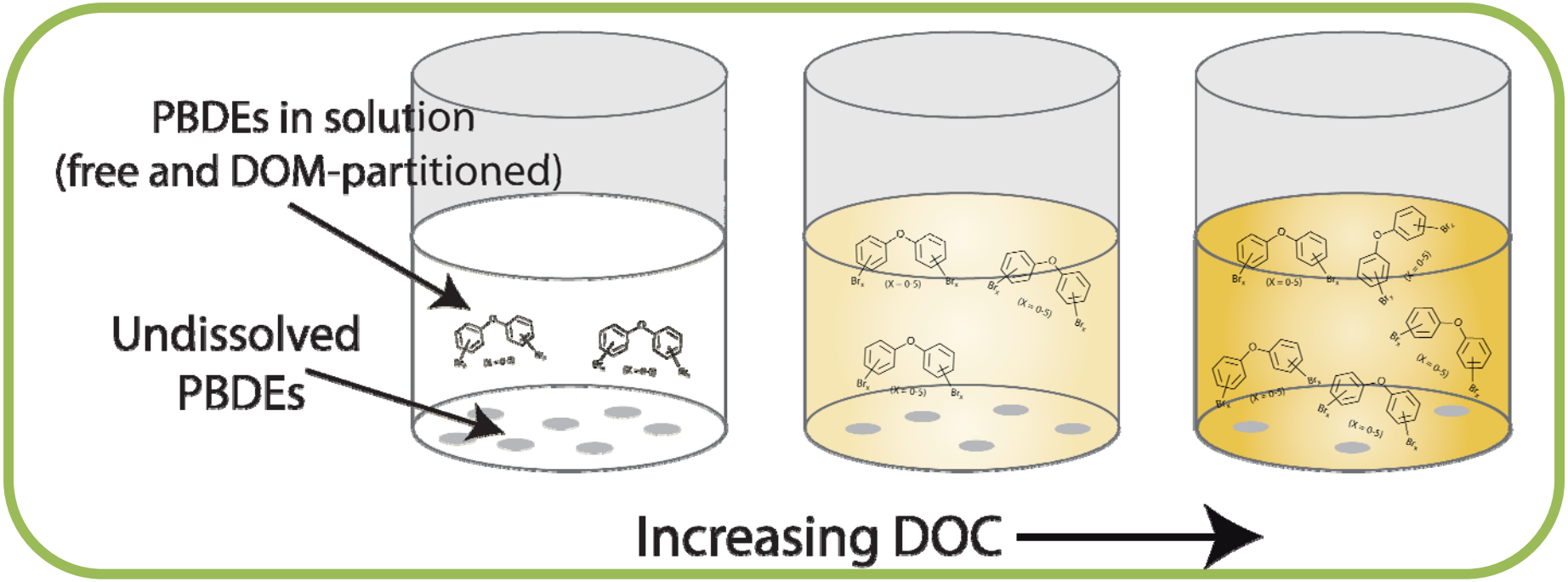
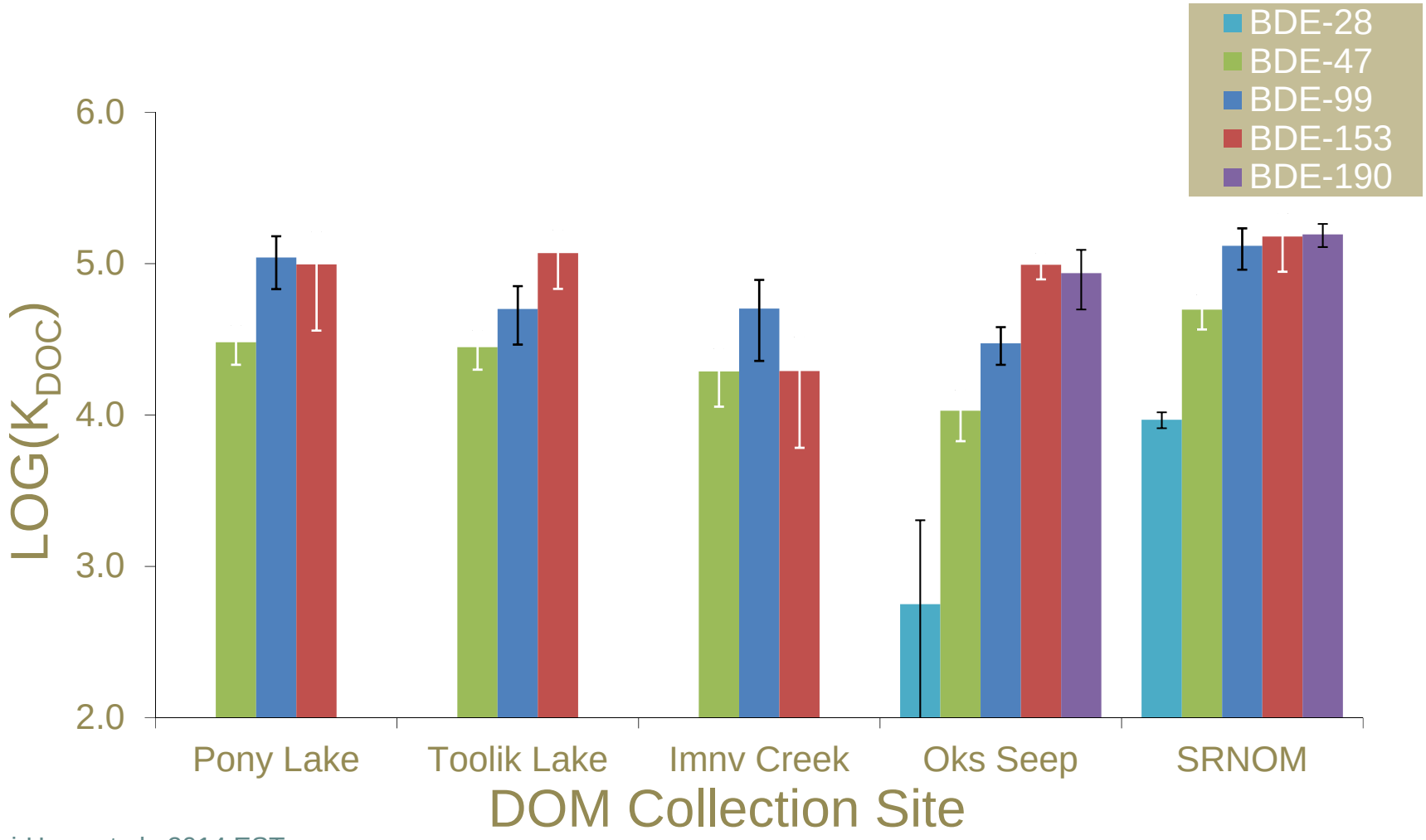
Solubility Enhancement



- 7 concentrations of DOM (+1 experiment with Milli-Q only)
- 4 replicates of each DOM concentration (+1 control w/o PBDE)
- 6 day minimum equilibration (kinetics study verification)
- 2:1 Liquid-liquid extraction with hexane
- GC – ECD analysis, S/SL injector, 15m RTX-1614 column

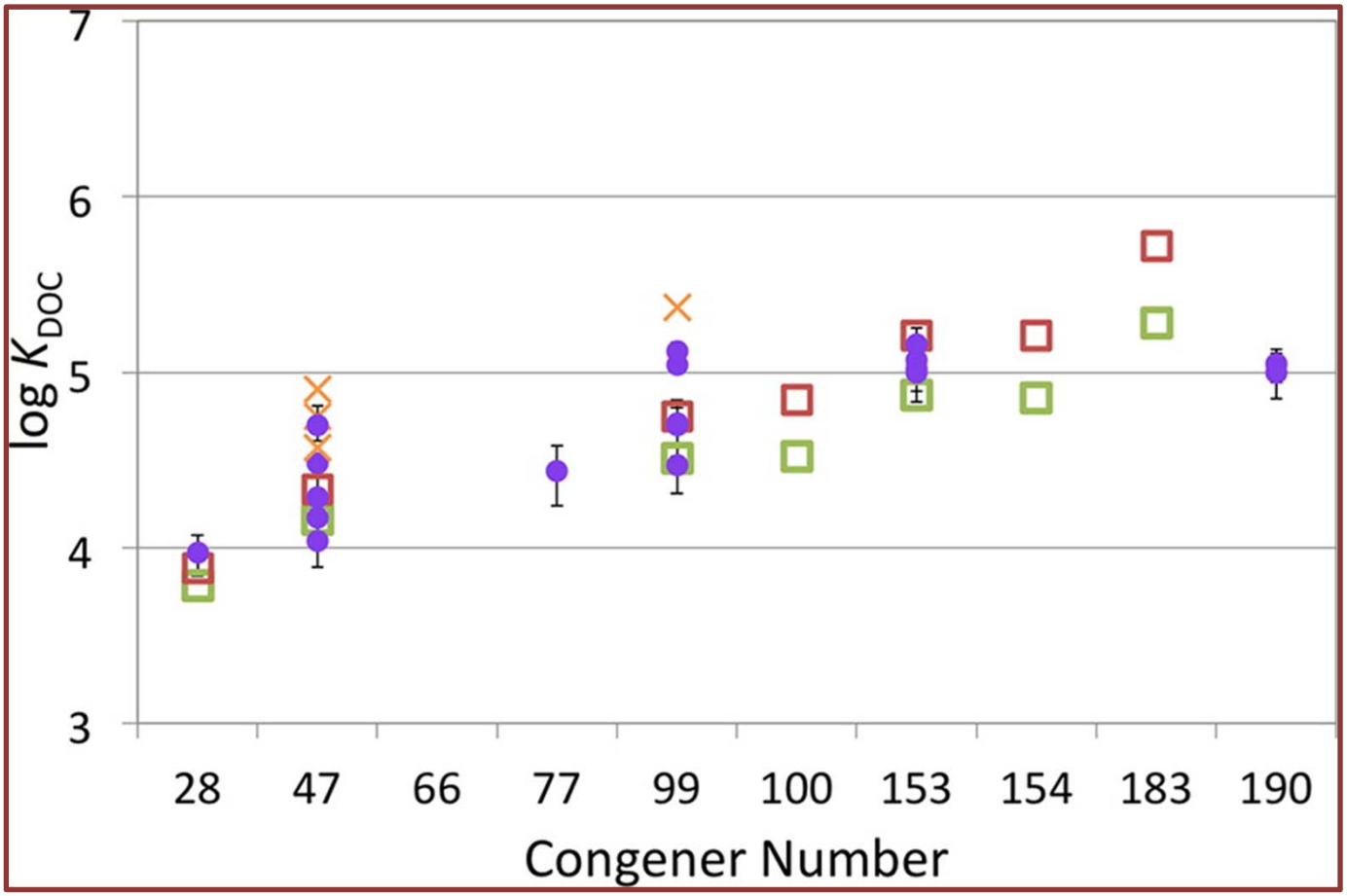
Partition Coefficient Summary



Wei-Haas et al., 2014 EST

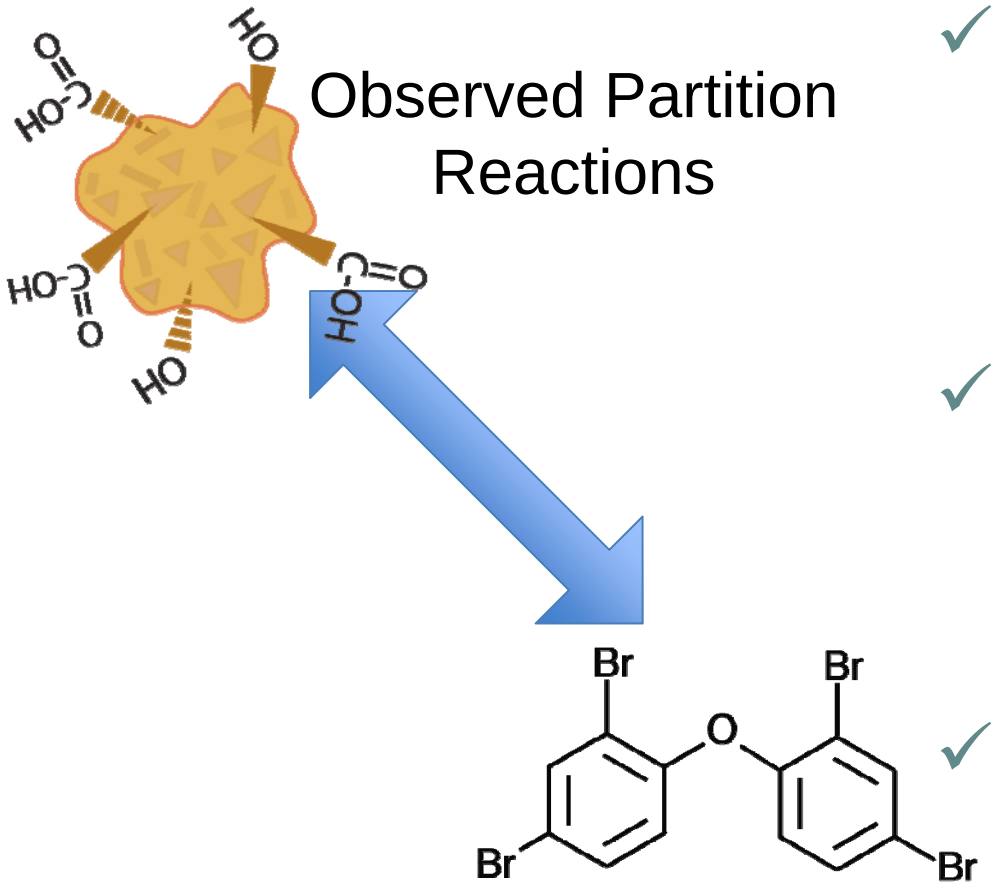
Molecular Modeling Results

ESABV = red squares
LSABV = green squares
Our data = filled purple circles
Lit. Data = orange X



Wei-Haas et al., 2014 EST

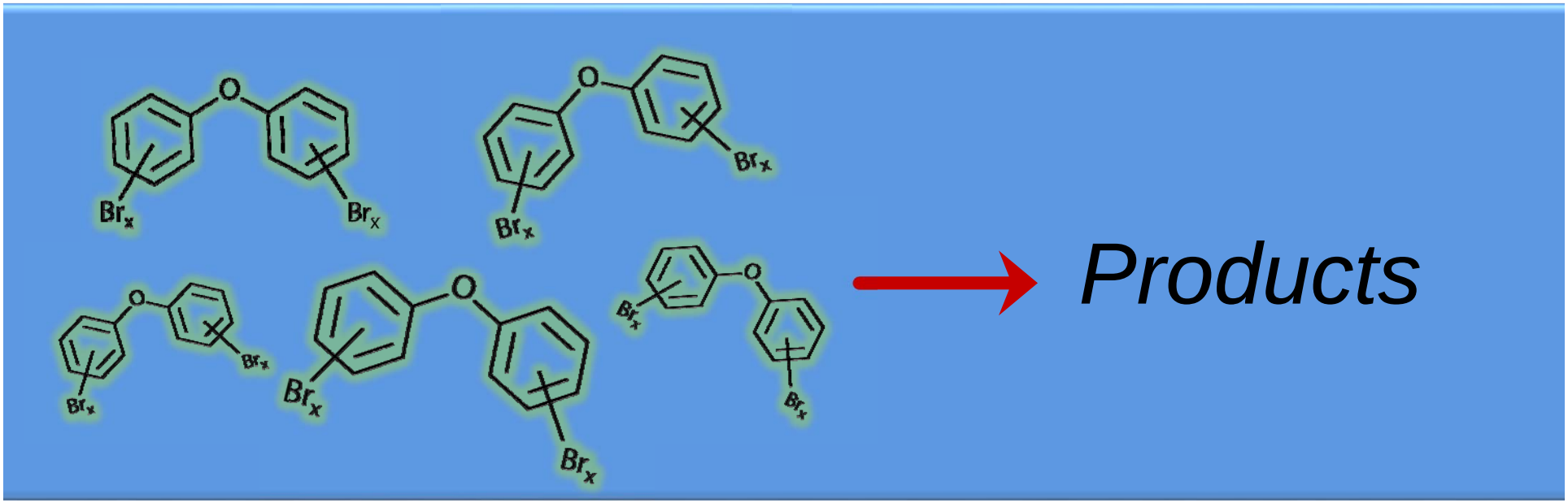
Conclusions 1:



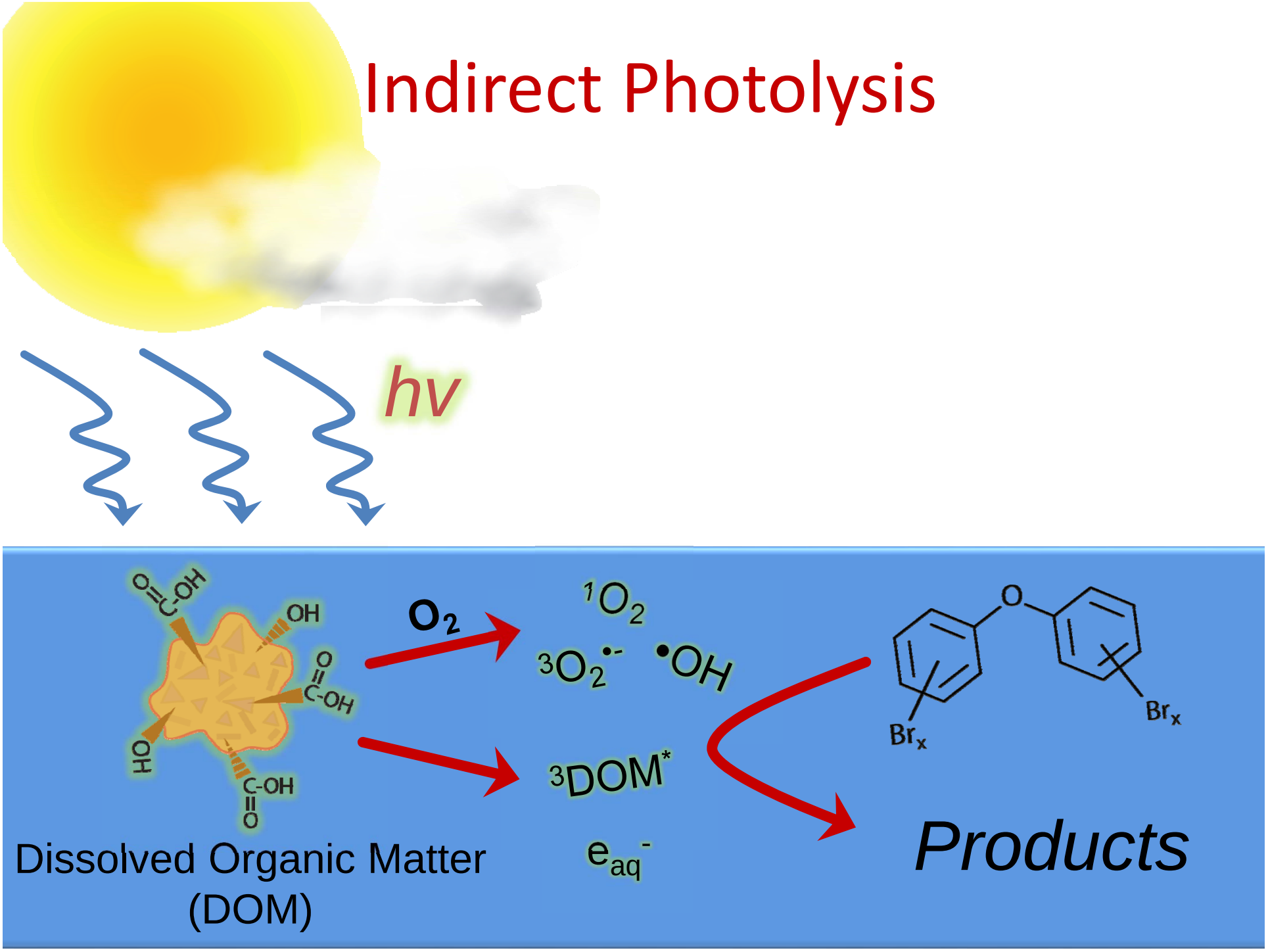
- ✓ K_{DOC} is a function of bromination and DOC properties
- ✓ pp-LFER accurately estimates this reaction
- ✓ Both ESABV and LSABV robust

Direct Photolysis

hv

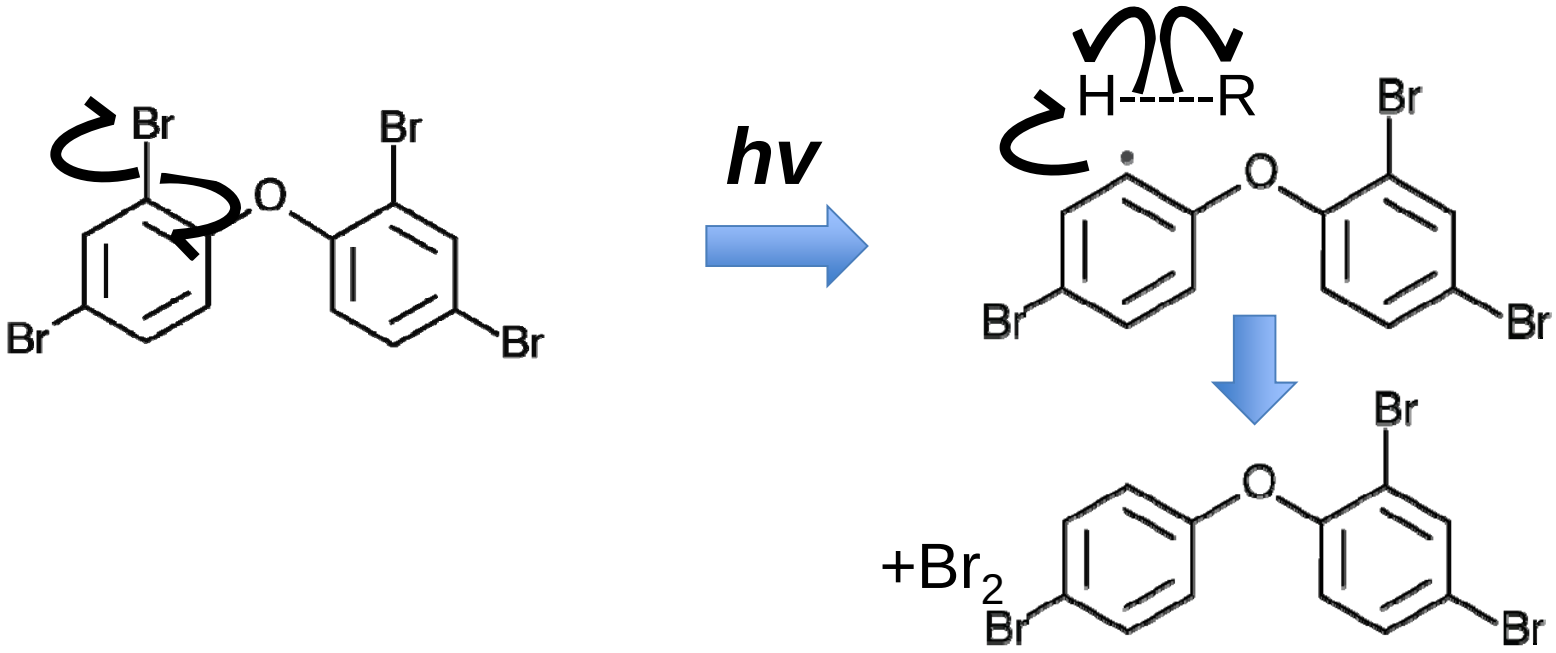


Indirect Photolysis

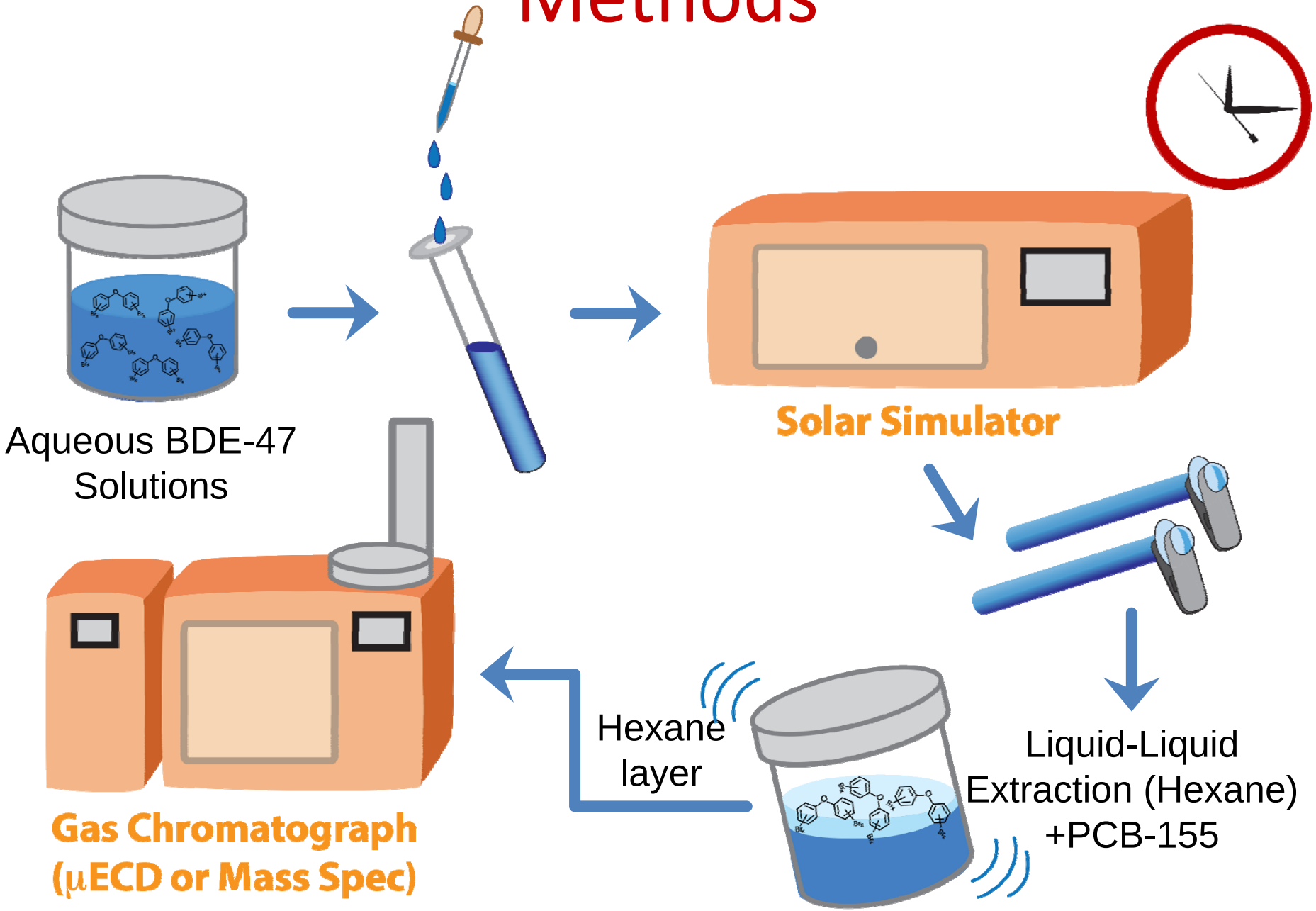


Previous Research

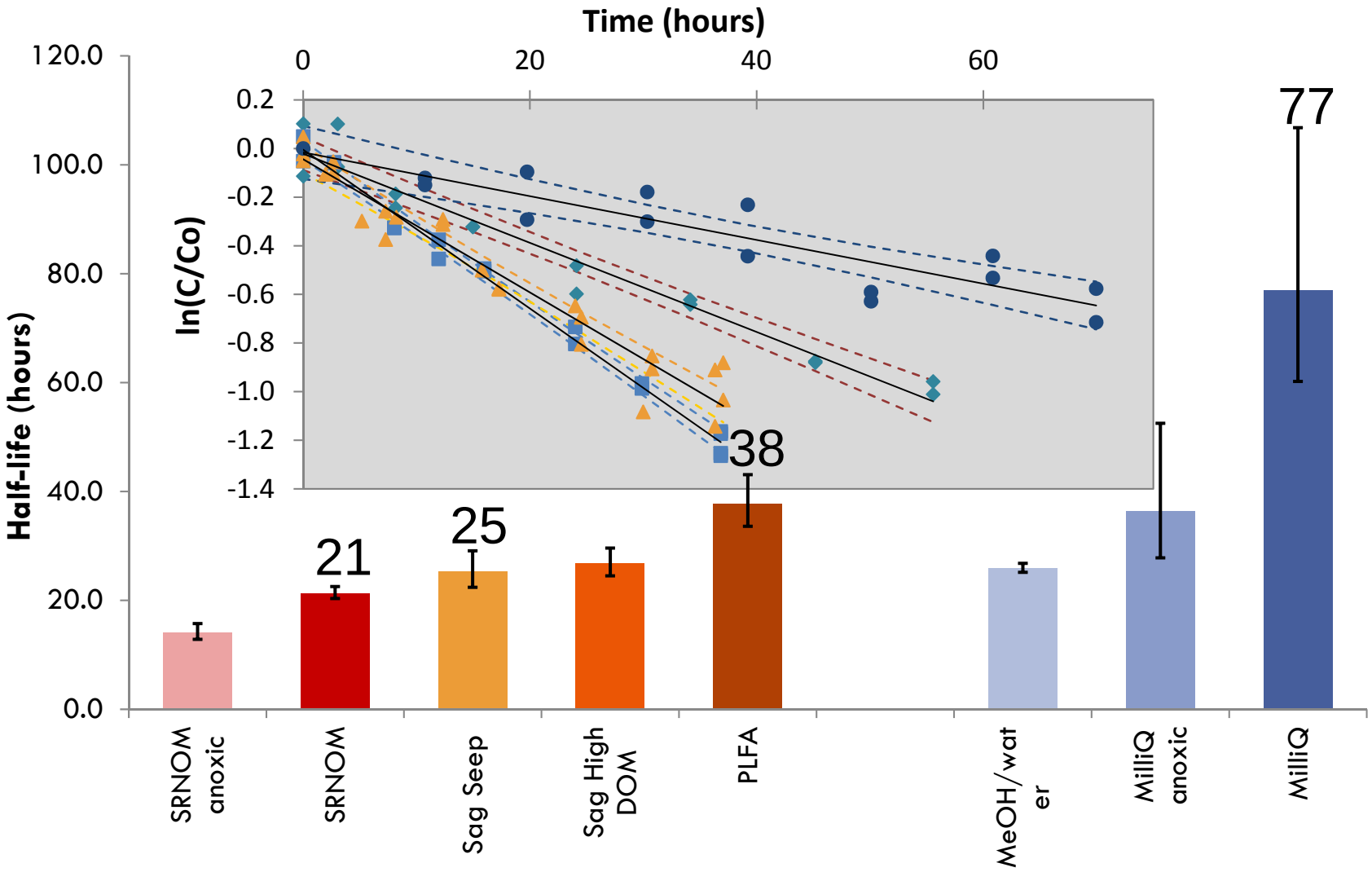
* Direct photolysis in organic solvents
  * $t_{1/2}$ = minutes to hours
* Indirect photolysis and the influence of DOM
  * Conflicting Results (Eriksson et al., 2004 vs. Leal et al., 2013)



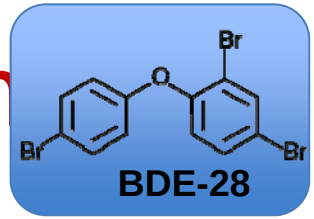
Methods

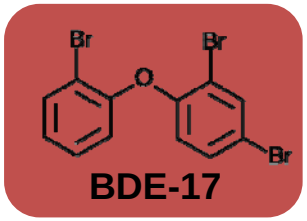

Aqueous BDE-47 Solutions
Solar Simulator
Liquid-Liquid Extraction (Hexane) +PCB-155
Hexane layer
Gas Chromatograph (μECD or Mass Spec)

Results – MQ vs. DOM



Product Form

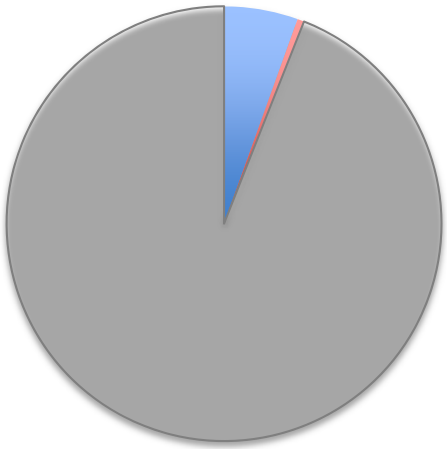




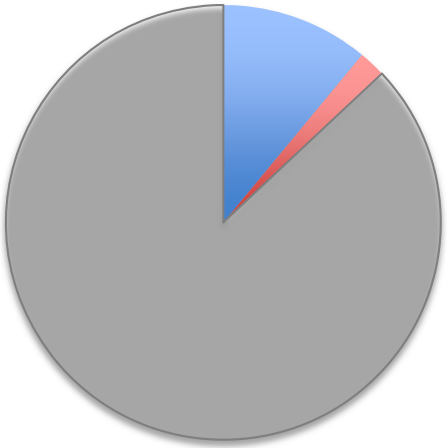
BDE-28
BDE-17
Product
Remainder

SRNOM

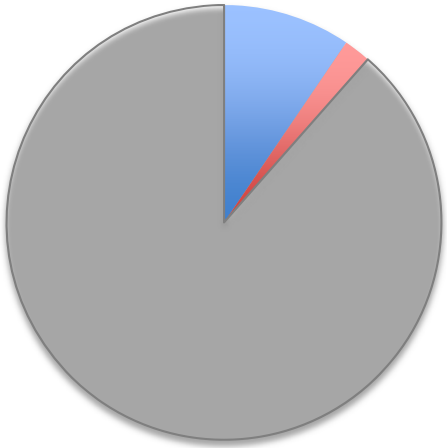
Sag Seep



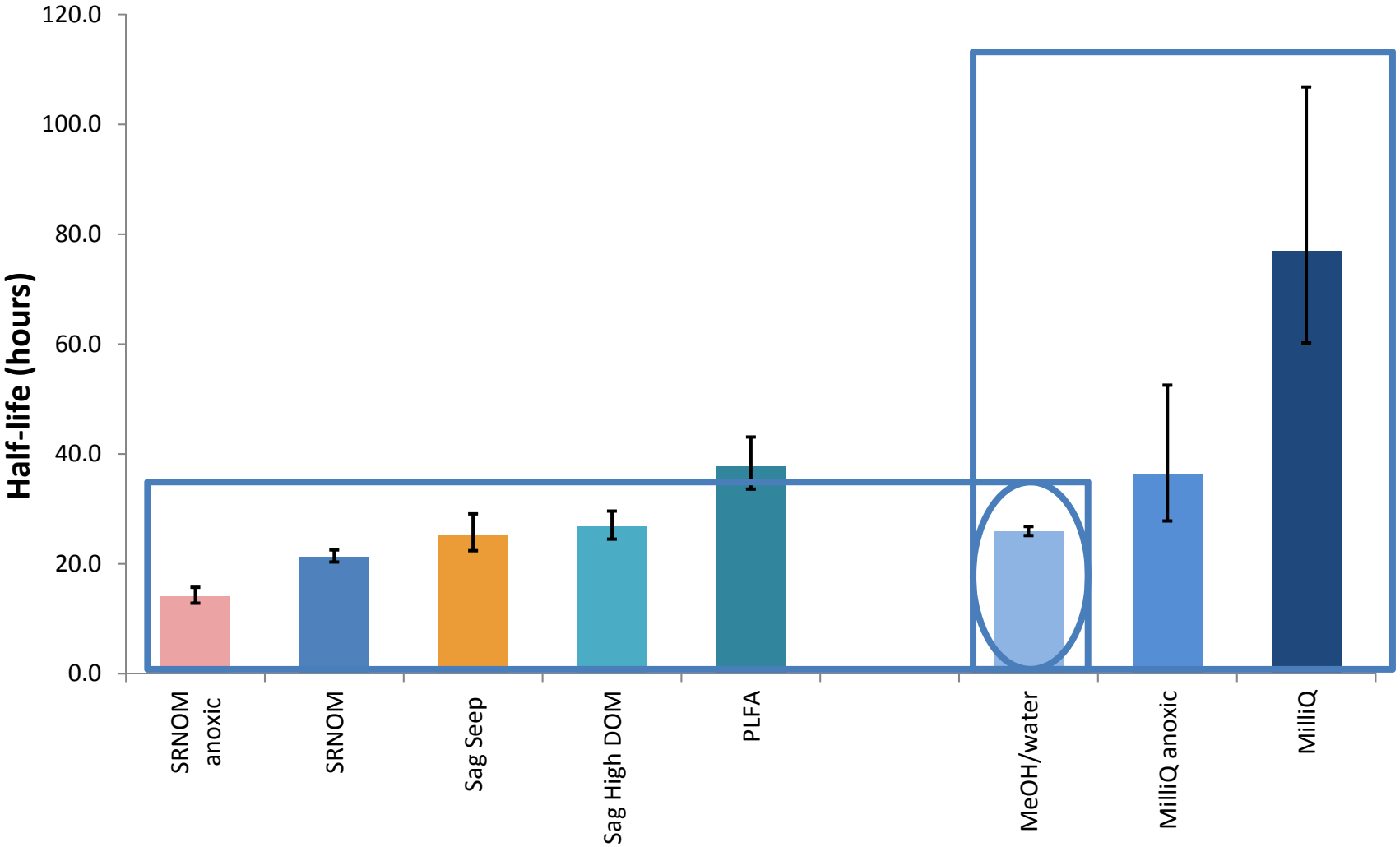
PLFA



MilliQ



Organic Solvent Effects



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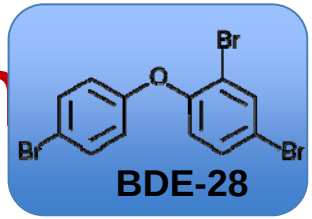
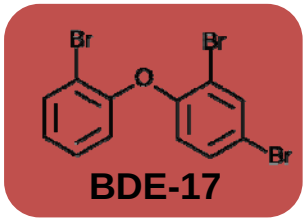
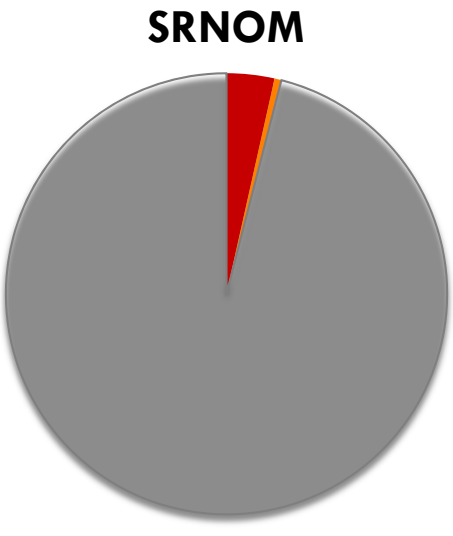
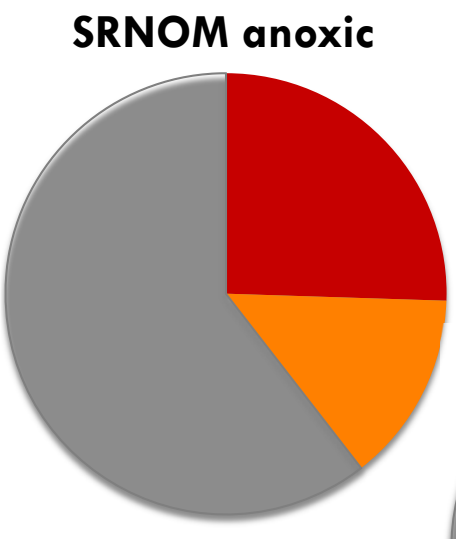
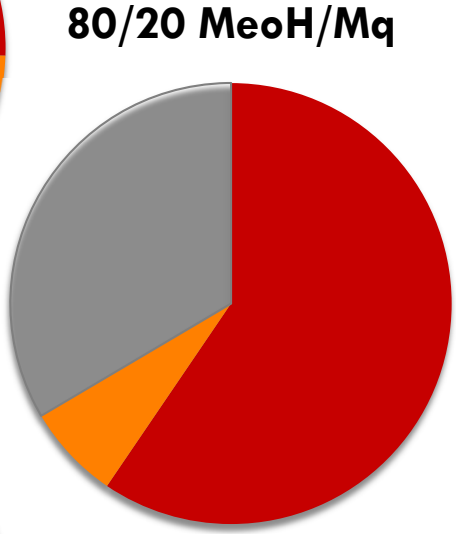
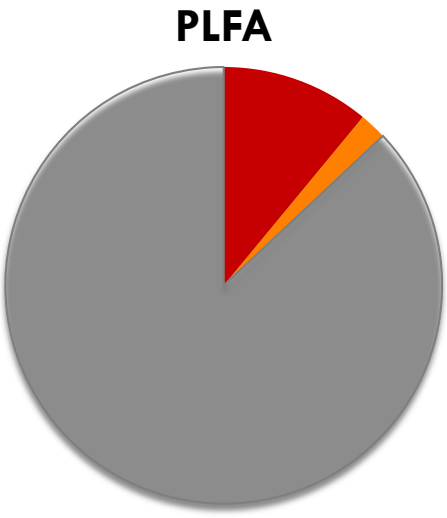


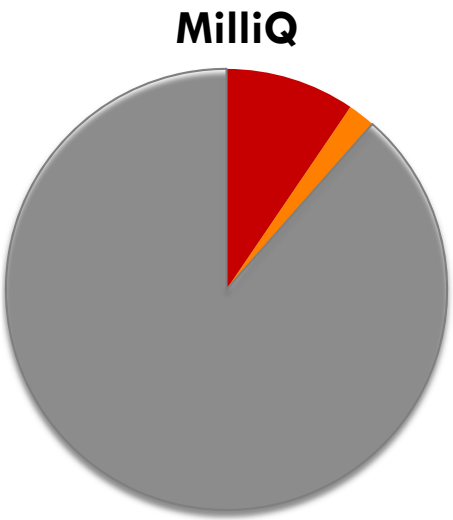


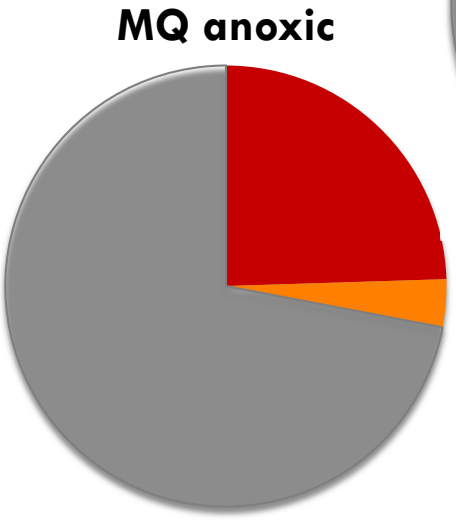




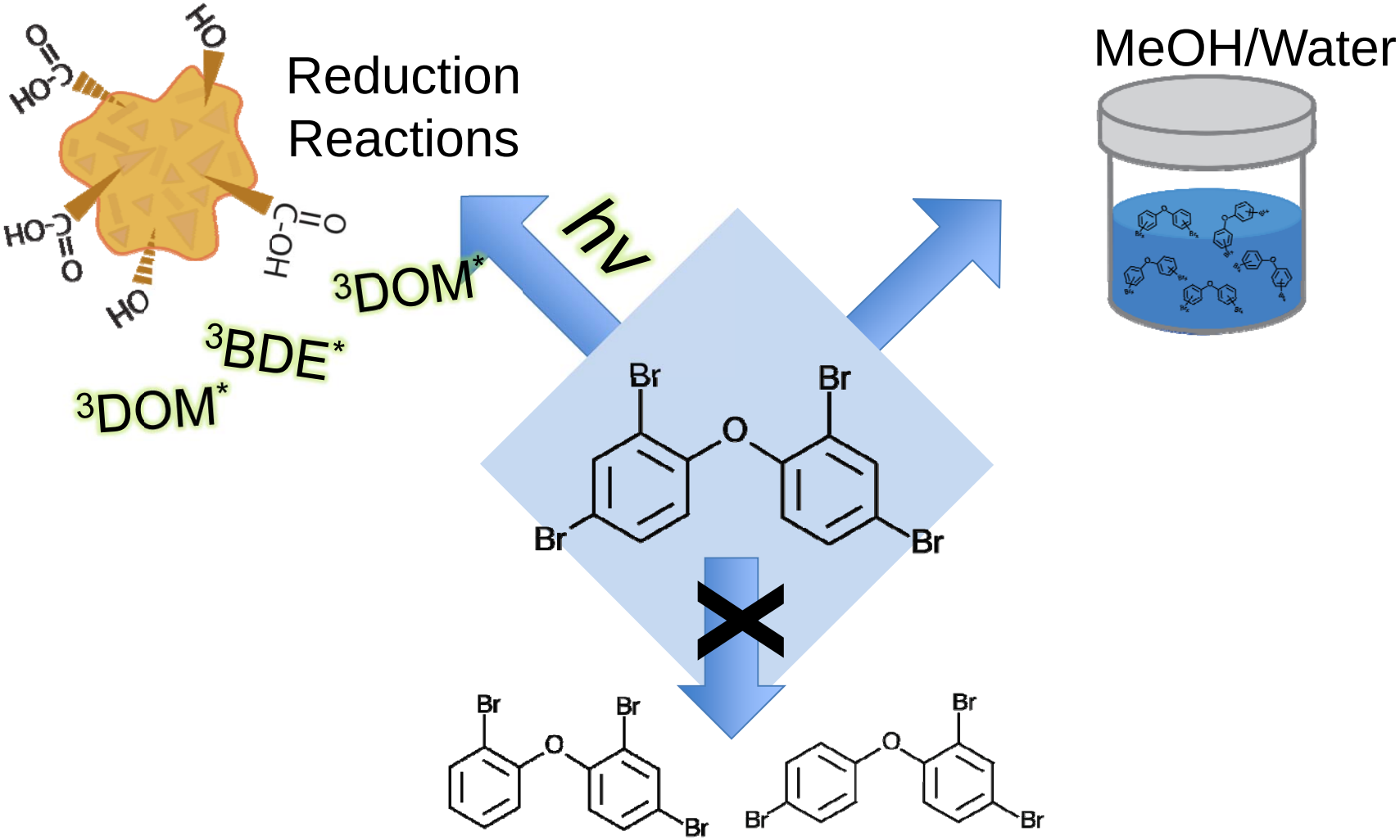




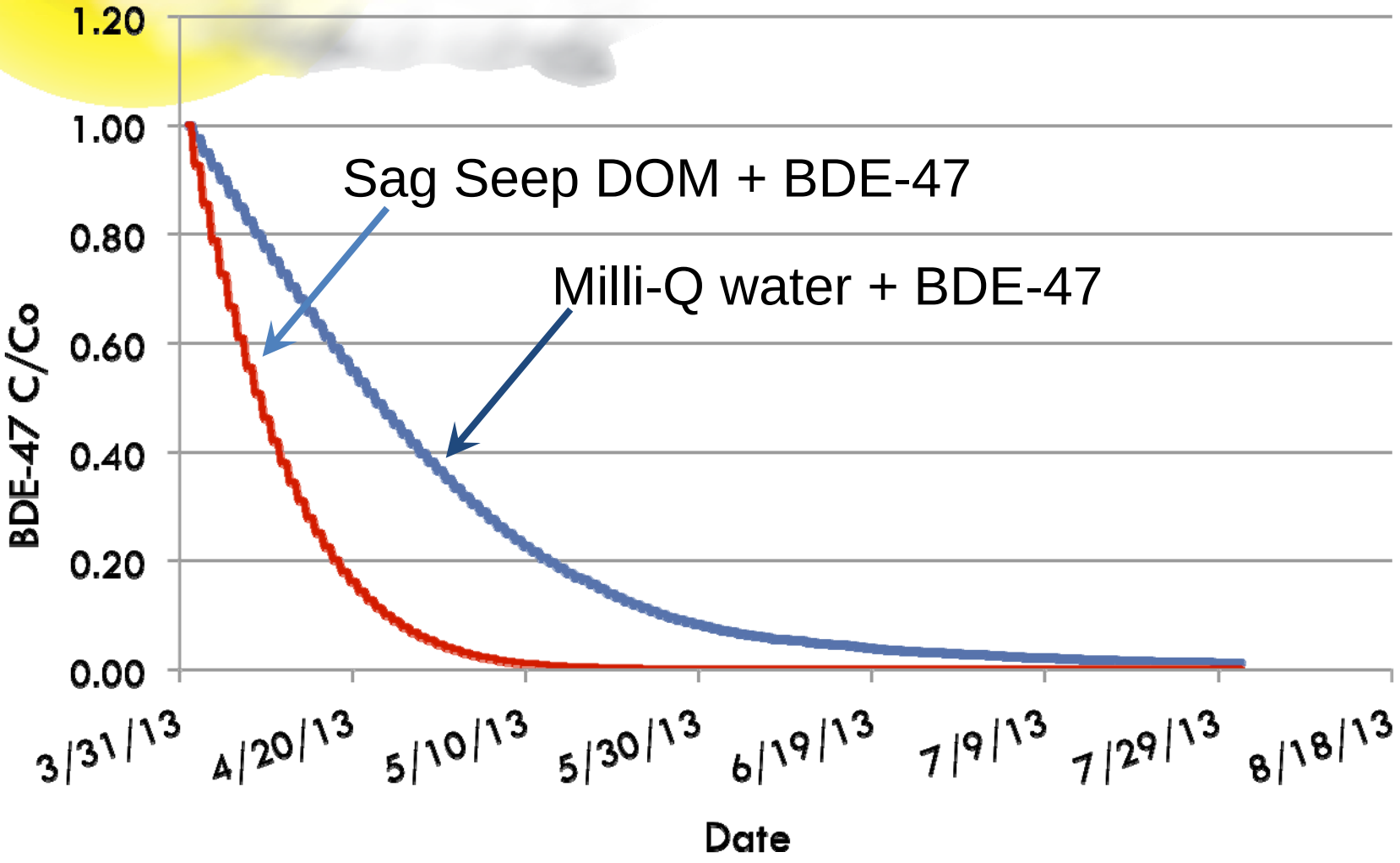




Conclusions 2



Arctic Photolysis model



Questions?

http://www.alaska-in-pictures.com/bow-lake-sunrise-banff-national-park-8189-pictures.htm