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Faculty of Arts and Sciences
DEPARTMENT OF EARTH AND PLANETARY SCIENCES

HARVARD T.H. CHAN SCHOOL OF PUBLIC HEALTH
Powerful ideas for a healthier world

Impacts of Global Change on Cycling and Bioaccumulation of Anthropogenic Pollutants

GES 12, ETH Zurich 2022

Elsie M. Sunderland

July 25, 2022

Biogeochemistry of Global Contaminants HARVARD

HARVARD John A. Paulson School of Engineering and Applied Sciences

Human activities are transforming the global environment

Environmental Releases

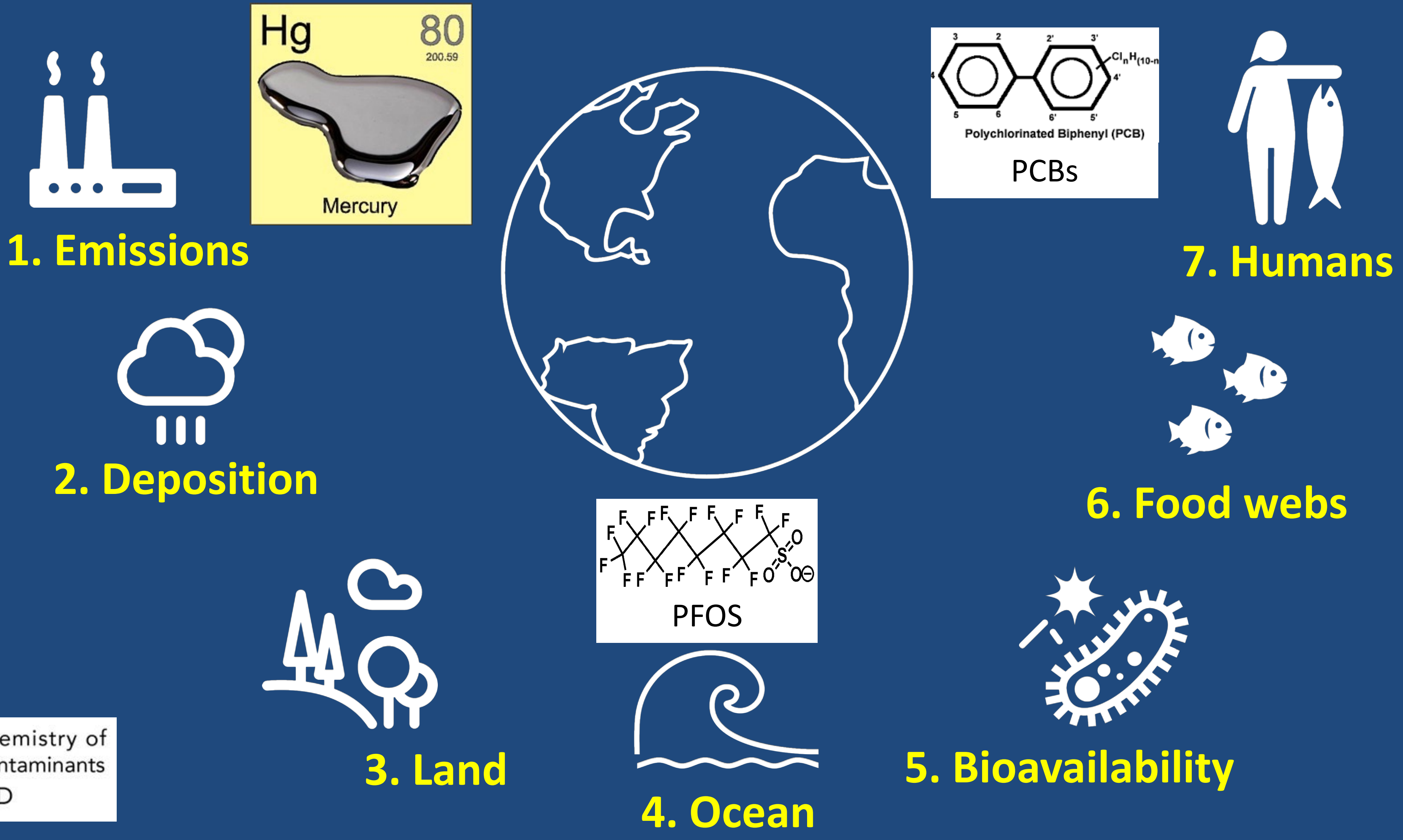
More than carbon

Fossil fuel feedstocks provide a cheap source of the parent chemicals to most synthetic organic substances

- 1-in-6 children suffer from a neurodevelopmental abnormality, mostly of unknown causes.
- Epidemiological studies note alarming rises in allergy, atopy, asthma, diabetes, obesity, autism spectrum disorders, etc. that are not linked to lifestyle changes.

http://braindrain.dk

Linking global contaminant releases to health in an era of environmental change



Biogeochemistry of Global Contaminants
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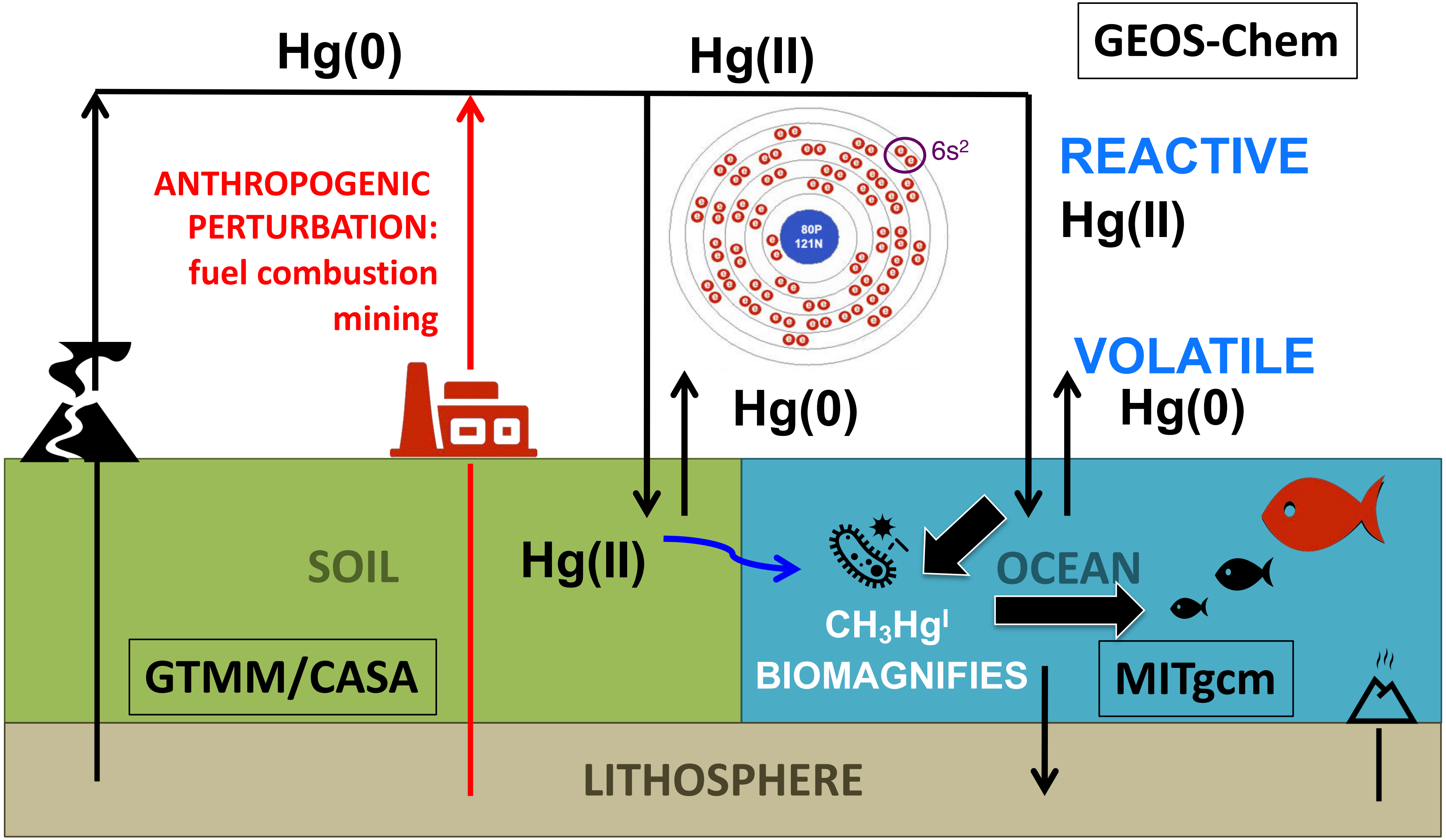
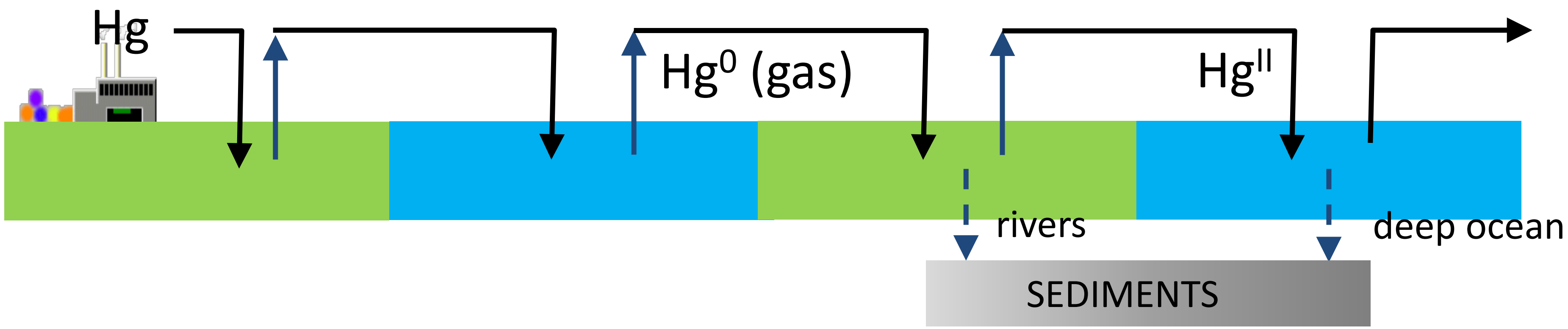
Research Questions

- Which physical/chemical properties are most important for the lifetime of persistent pollutants in the ocean?
- How will their distribution be affected by changes in ocean circulation and sea-ice cover?
- How are climate-driven changes affecting concentrations in food webs?

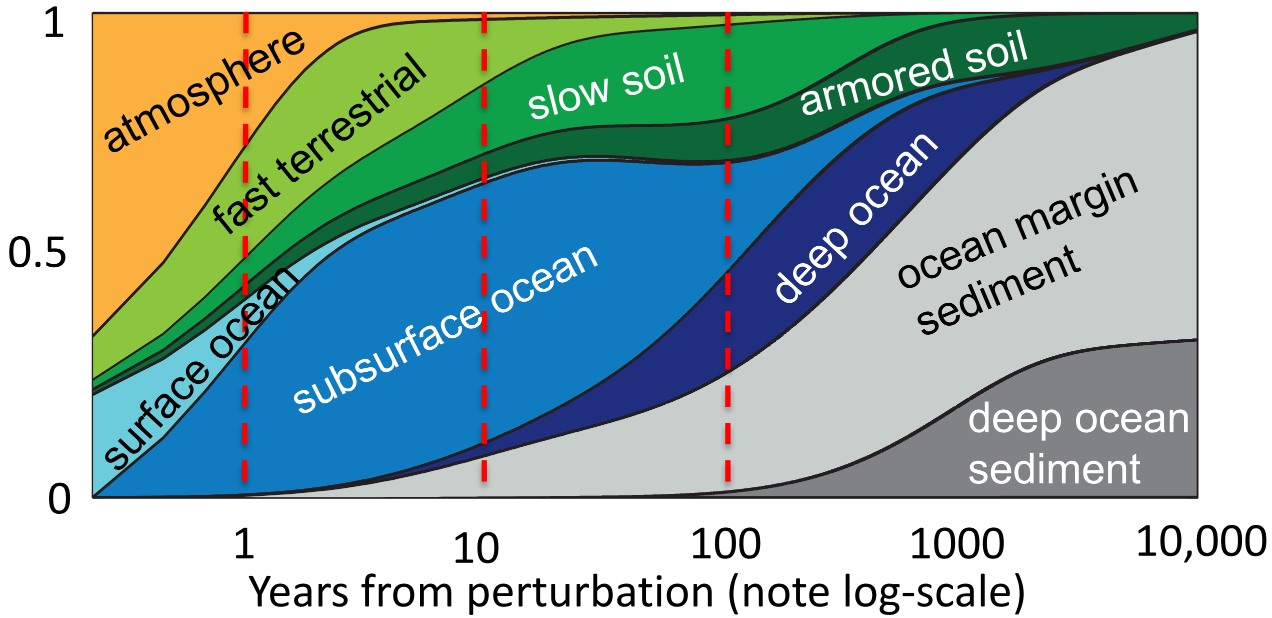
Global biogeochemical Hg cycle



Volatility is very important: Grasshopper effect extends Hg lifetime in surface reservoirs



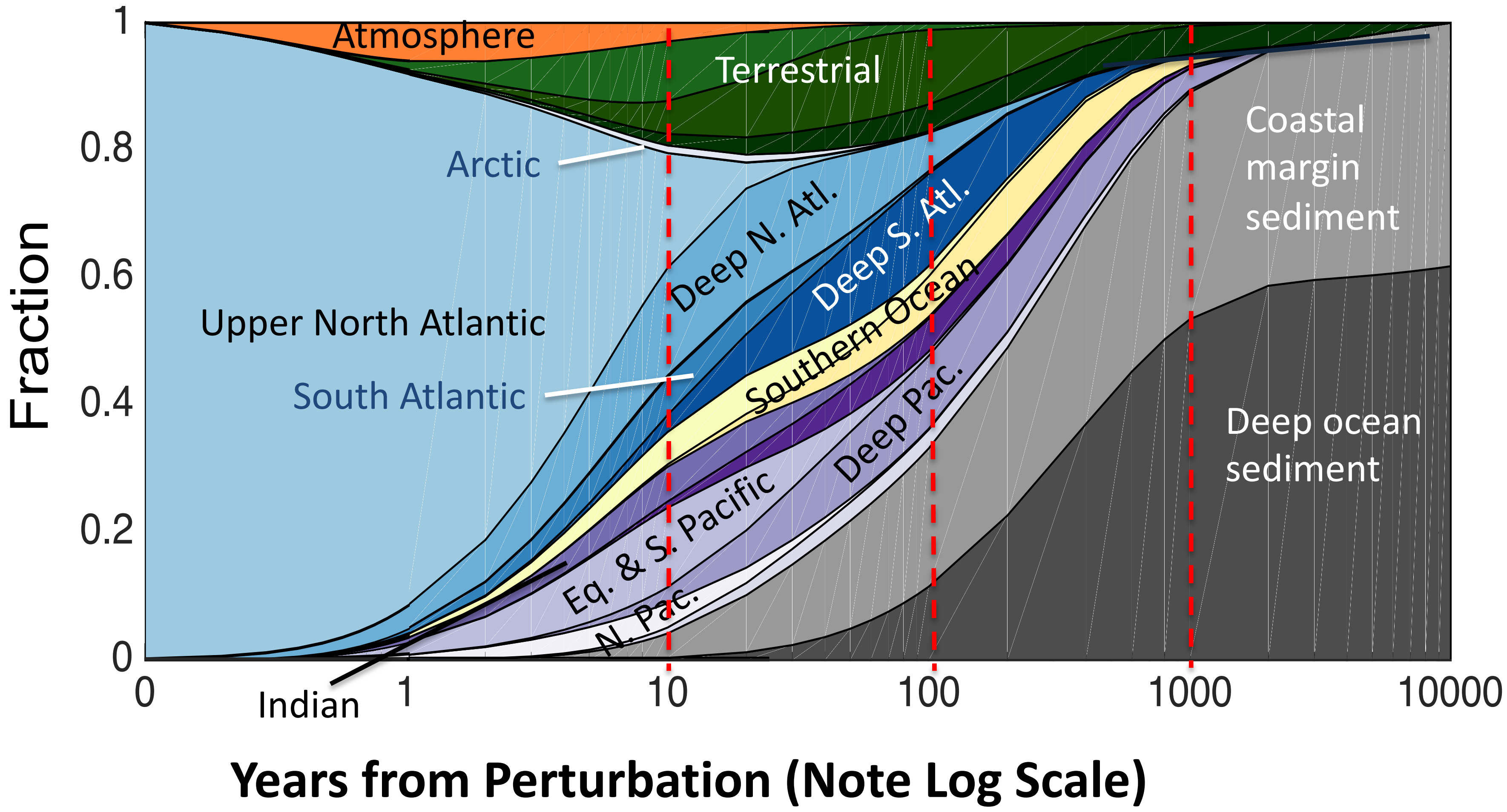
Fate of a unit pulse of Hg to the atmosphere (eigenanalysis)



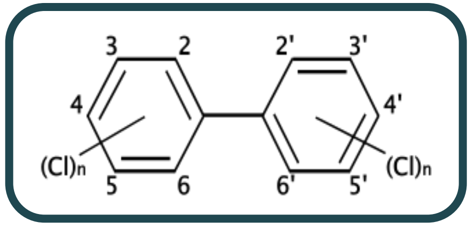
Amos et al., 2013; 2014; 2015

First-order lifetimes (τ) of Hg in upper 1000 m
<10 years for most ocean basins

Fate of unit Hg pulse to upper 1000m of North Atlantic



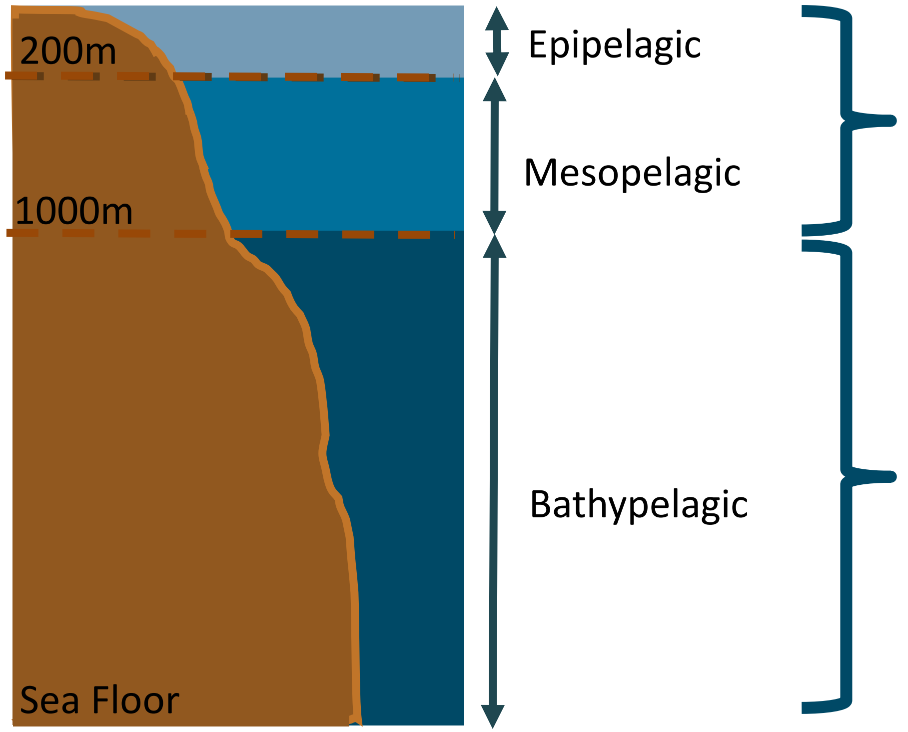
Stronger affinity of PCBs for particles than Hg leads to more rapid accumulation in the deep ocean

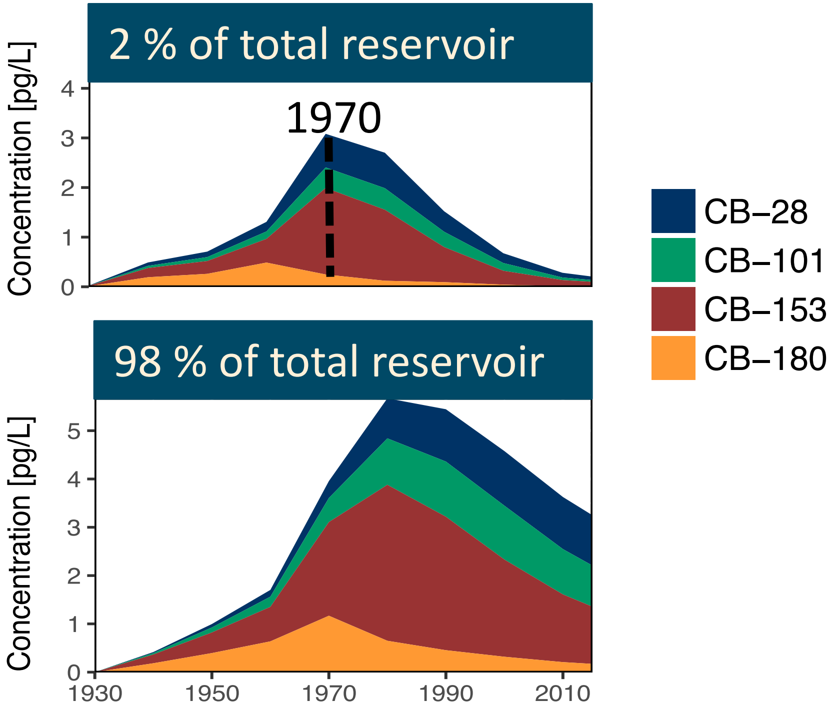


- 209 congeners; carcinogenic, neurotoxic
- Extremely hydrophobic
- Strong affinity for particles
- Variable volatility depending on MW

Log K_{oc} CB 153: 5.8-8.3

Log K_d Hg: ~4-6





Wagner et al., 2019

Relative enrichment of volatile congeners in the Arctic sustaining biological concentrations 30 years after ban

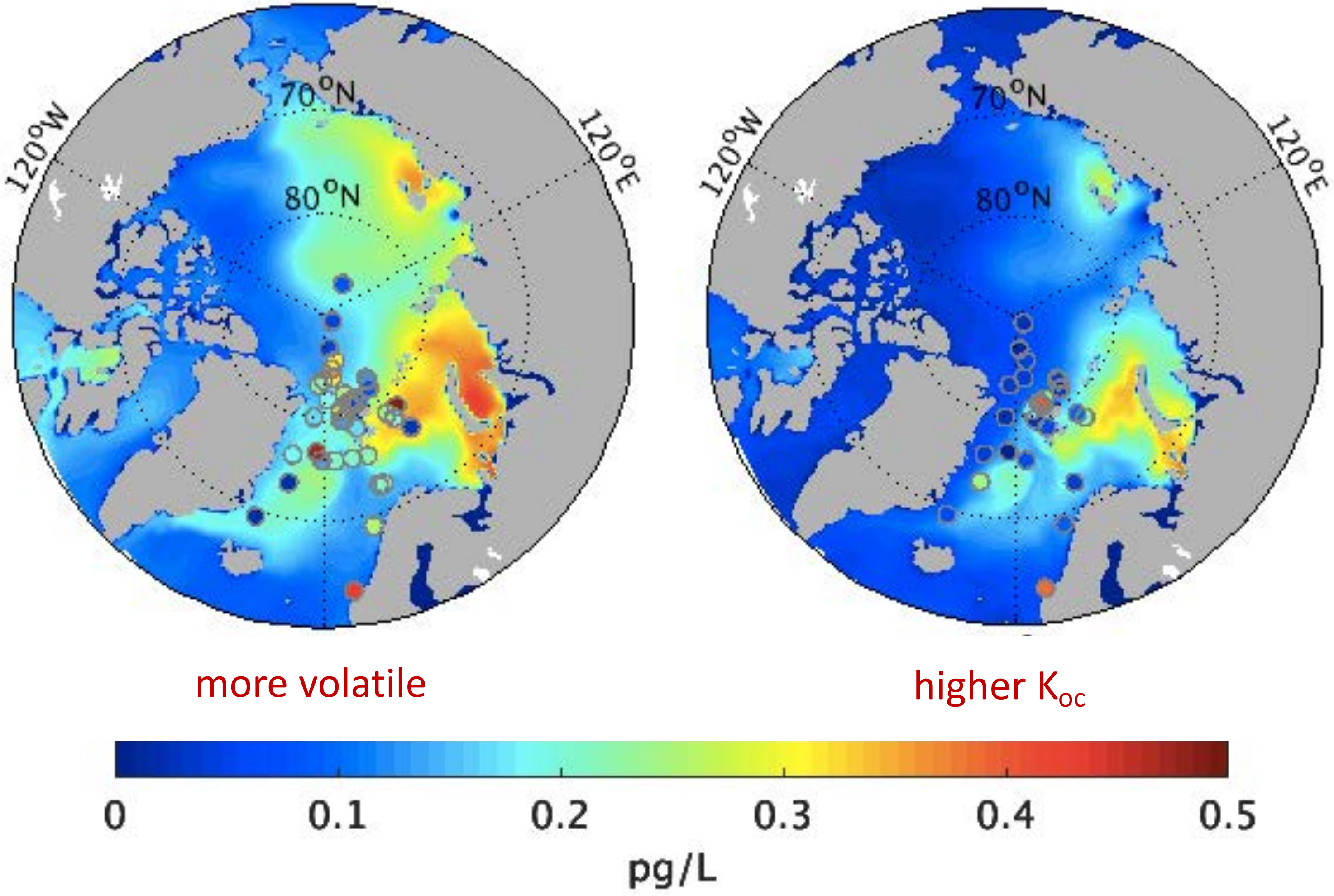
24% of ocean inputs

↓

59% of concentration

CB-28

CB-153



61% of ocean inputs

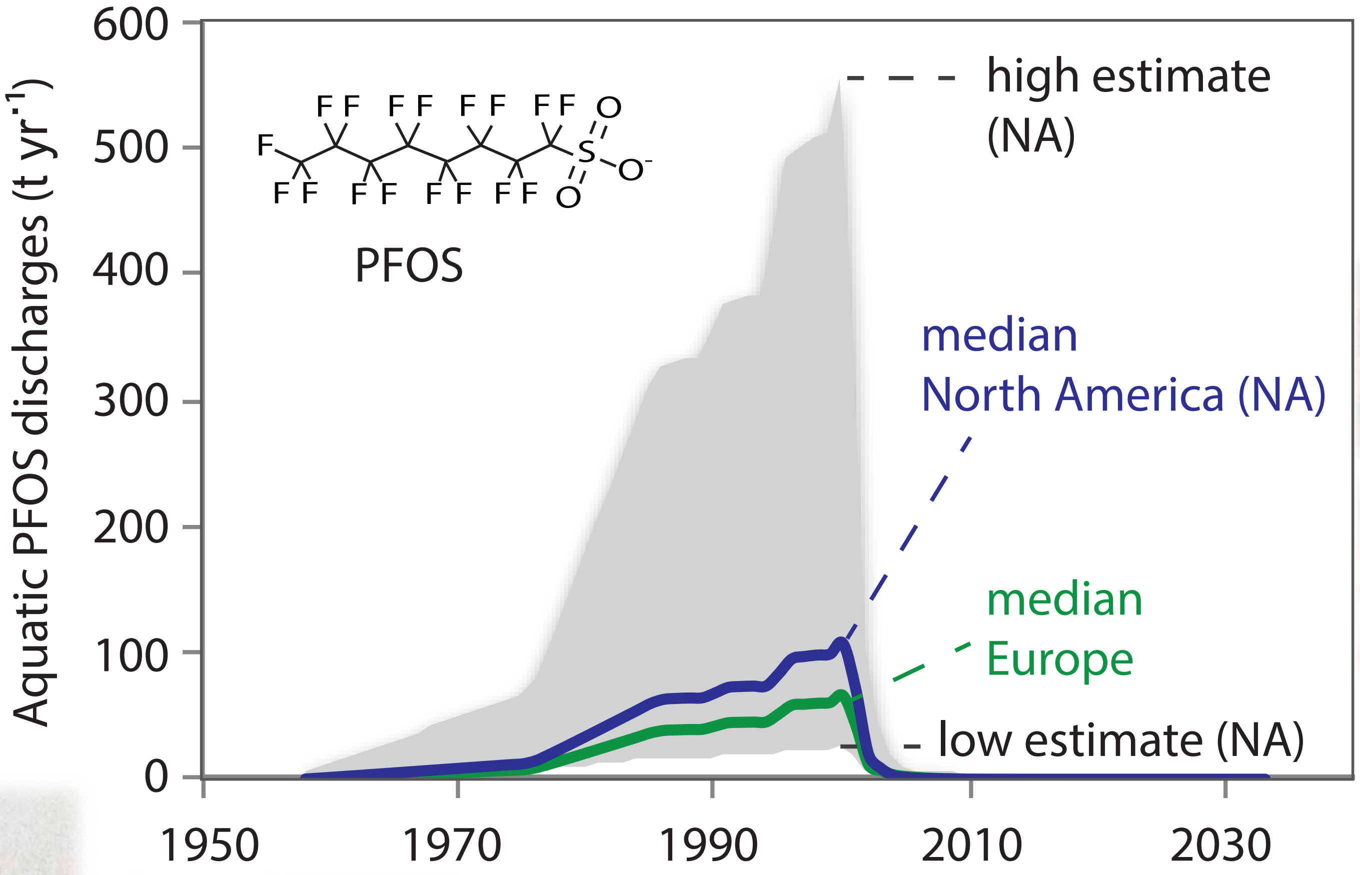
↓

33% of concentration

Wagner et al., 2019

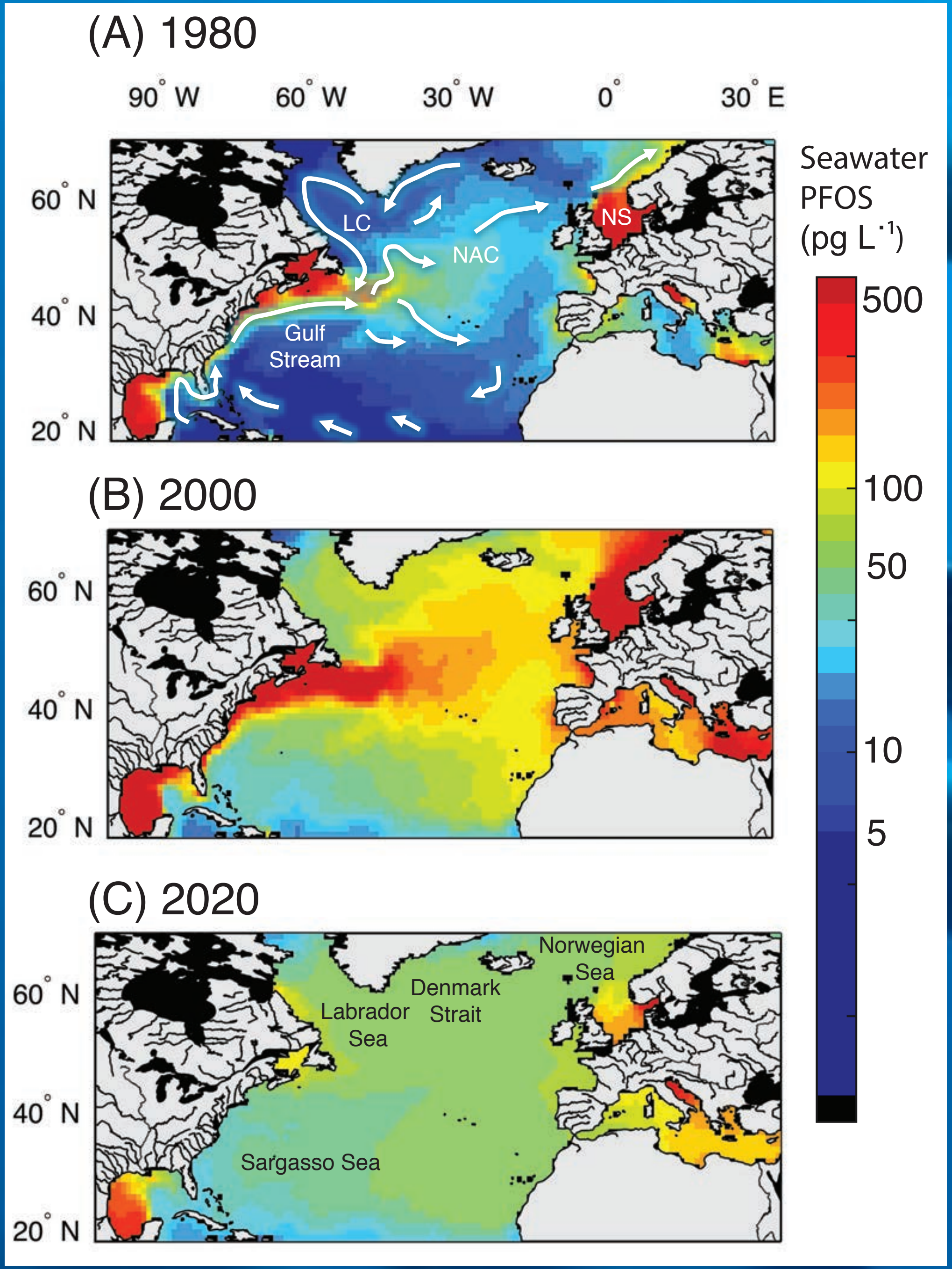
Parent chemical to perfluorooctane sulfonate (PFOS) phased out by 3M between 2000-2002

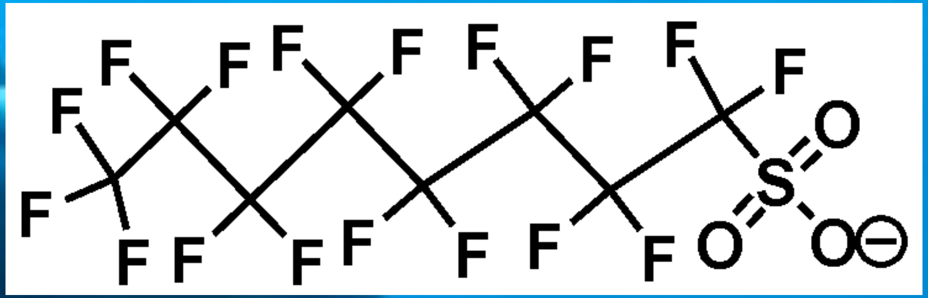
Riverine discharges to the North Atlantic Ocean



PFOS
Log K_{oc} = 2.6
pK_a = -3

Zhang et al., 2017



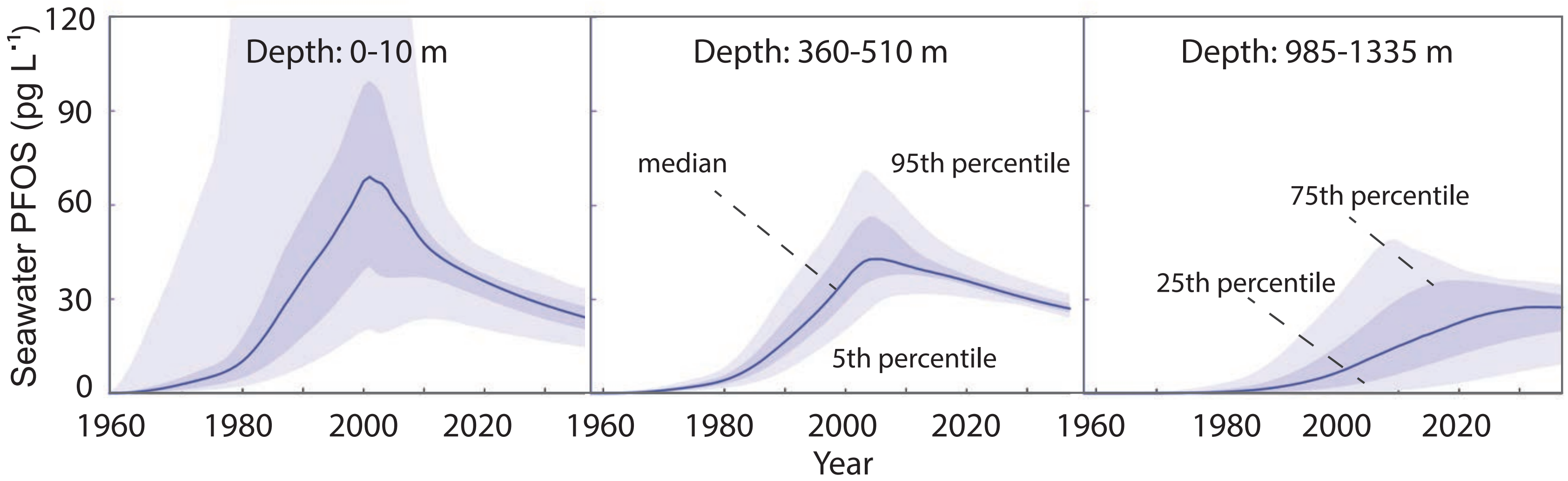


Modeled PFOS in North Atlantic seawater (10 m)

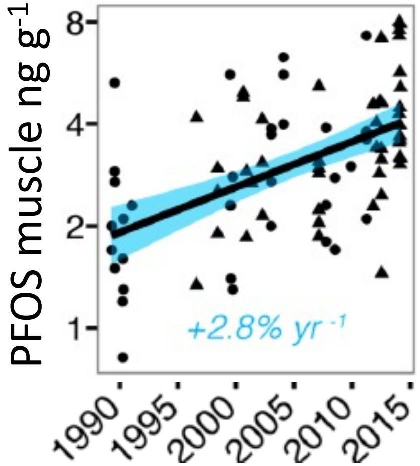
X. Zhang et al., 2017

Overturning of the North Atlantic results in rapid declines in concentrations in the surface ocean

Variable concentrations and response times depending on depth



Organisms with deep foraging preferences (e.g., pilot whales) will respond most slowly



Juvenile males 9-12 years
~700 m foraging depth

Zhang et al., 2017
Dassuncao et al., 2017

Research Questions

- Which physical/chemical properties are most important for the lifetime of different pollutants in the ocean?
- How will their distribution be affected by changes in ocean circulation and sea-ice cover?
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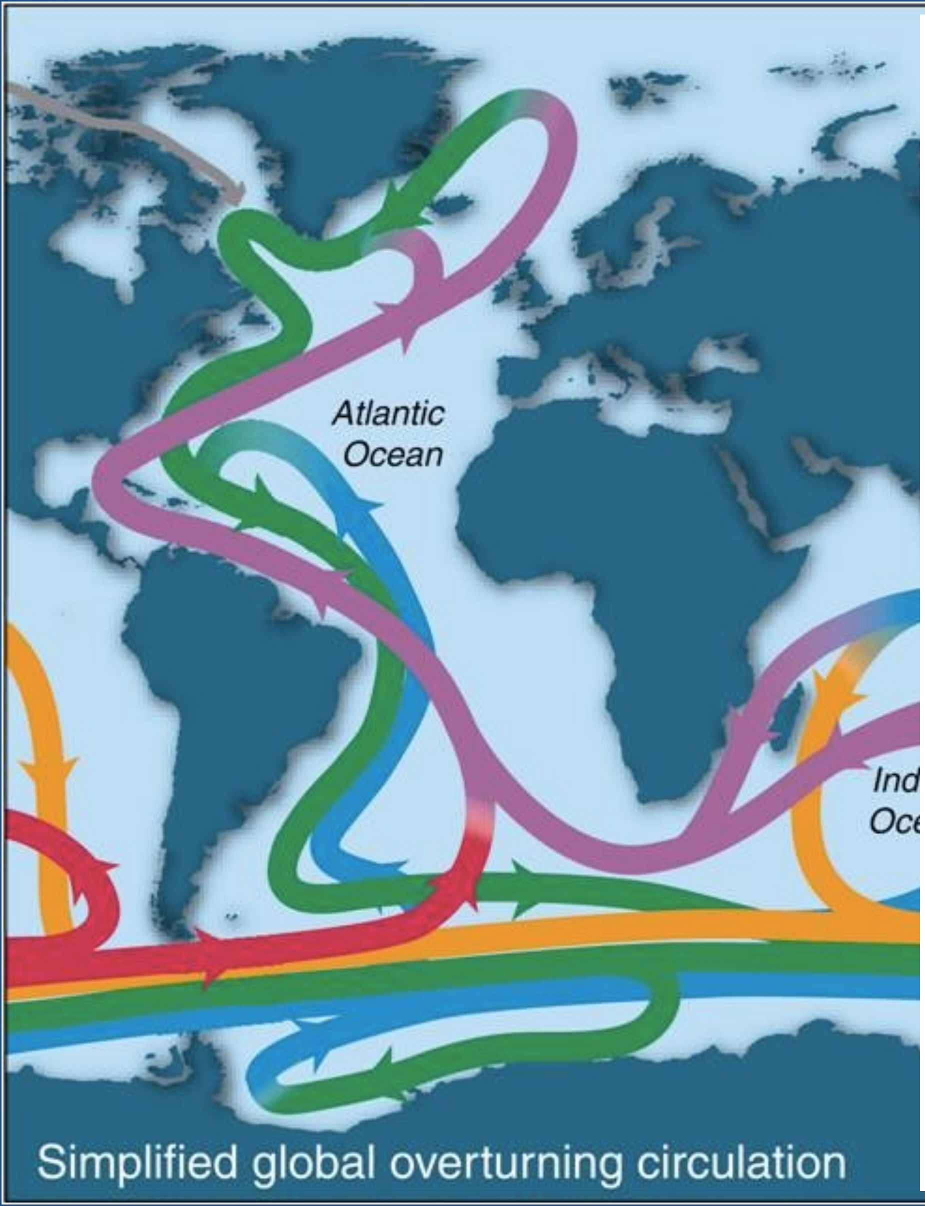
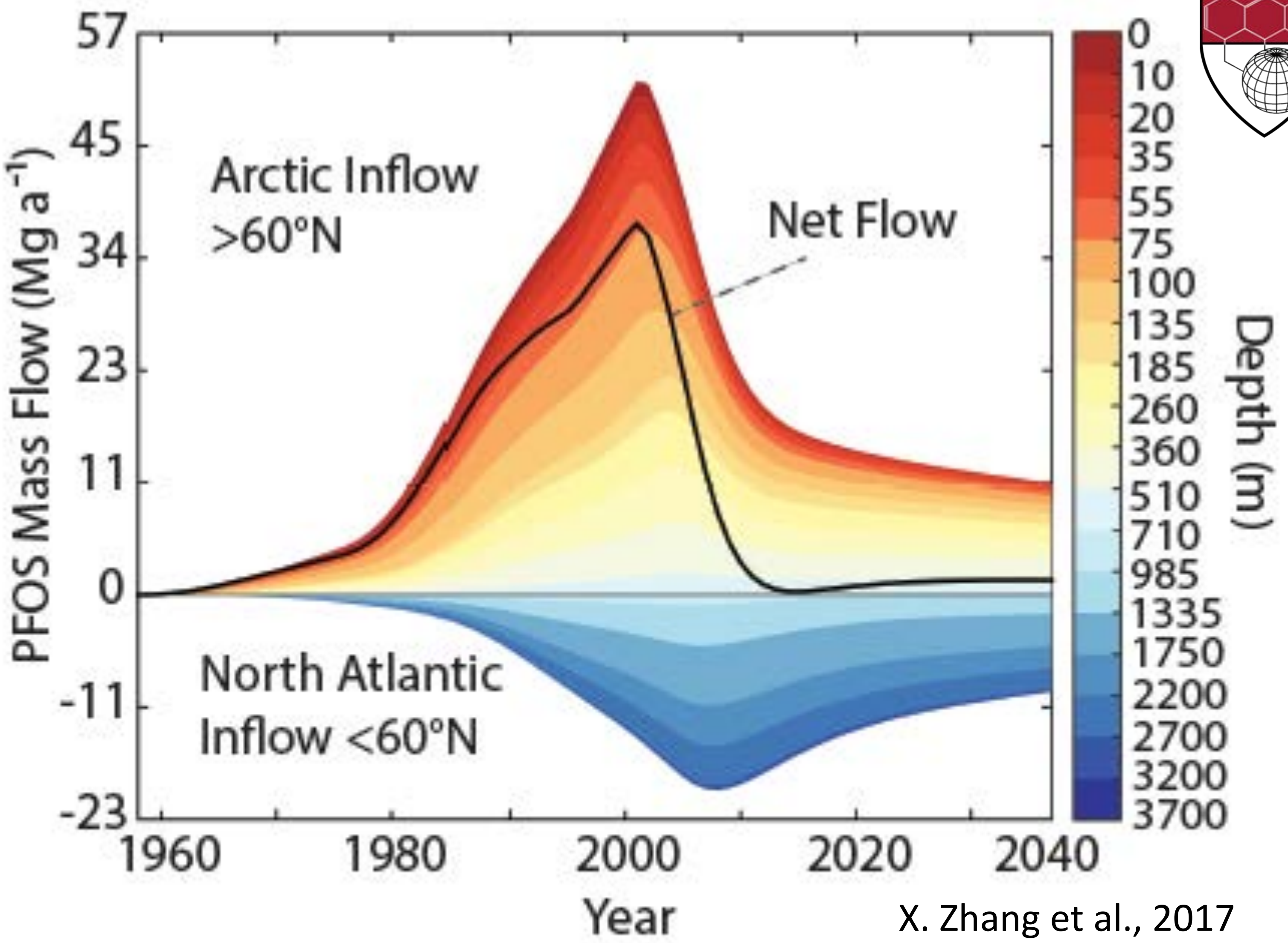
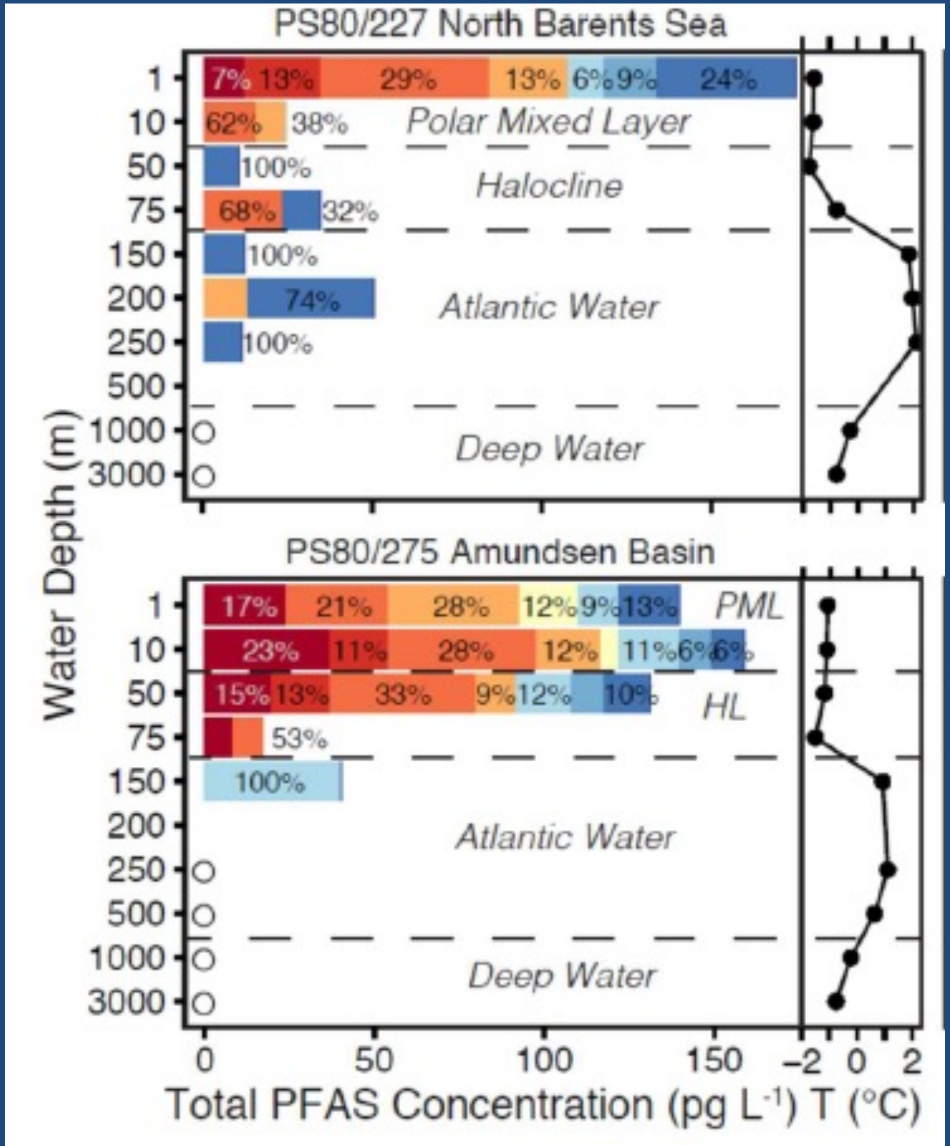
For chemicals like PFOS with weak sorption to organic carbon
Weakened AMOC = >>>bioaccumulative contaminants to the Arctic

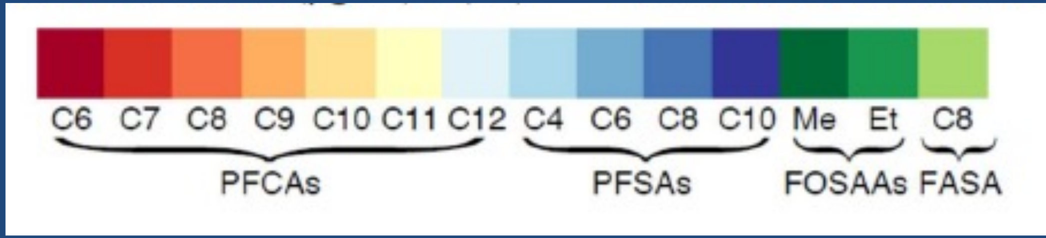


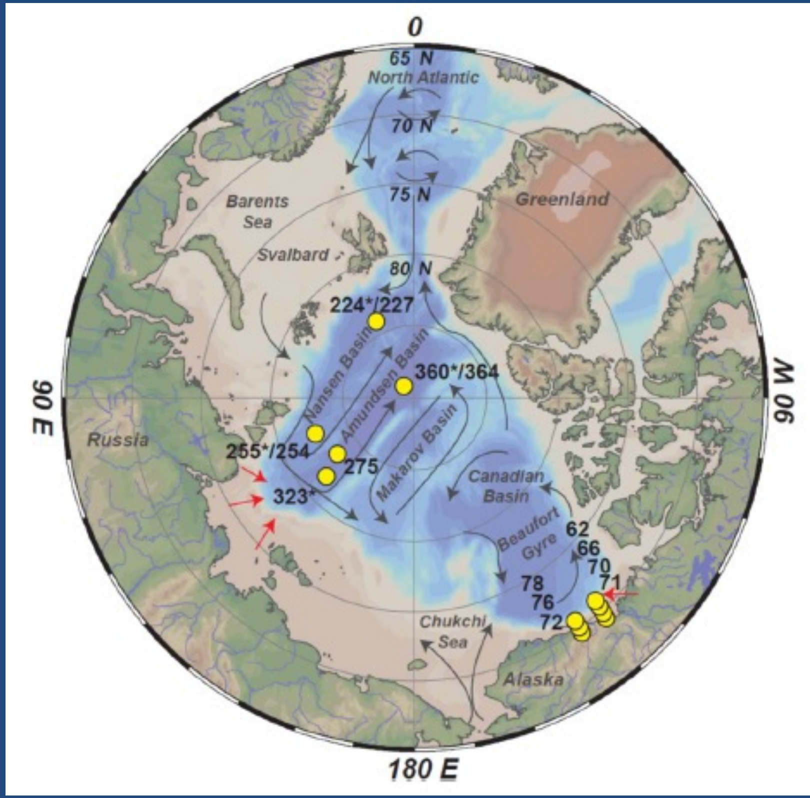


X. Zhang et al., 2017

Surfactant properties enriching concentrations at the surface of the Arctic Ocean?

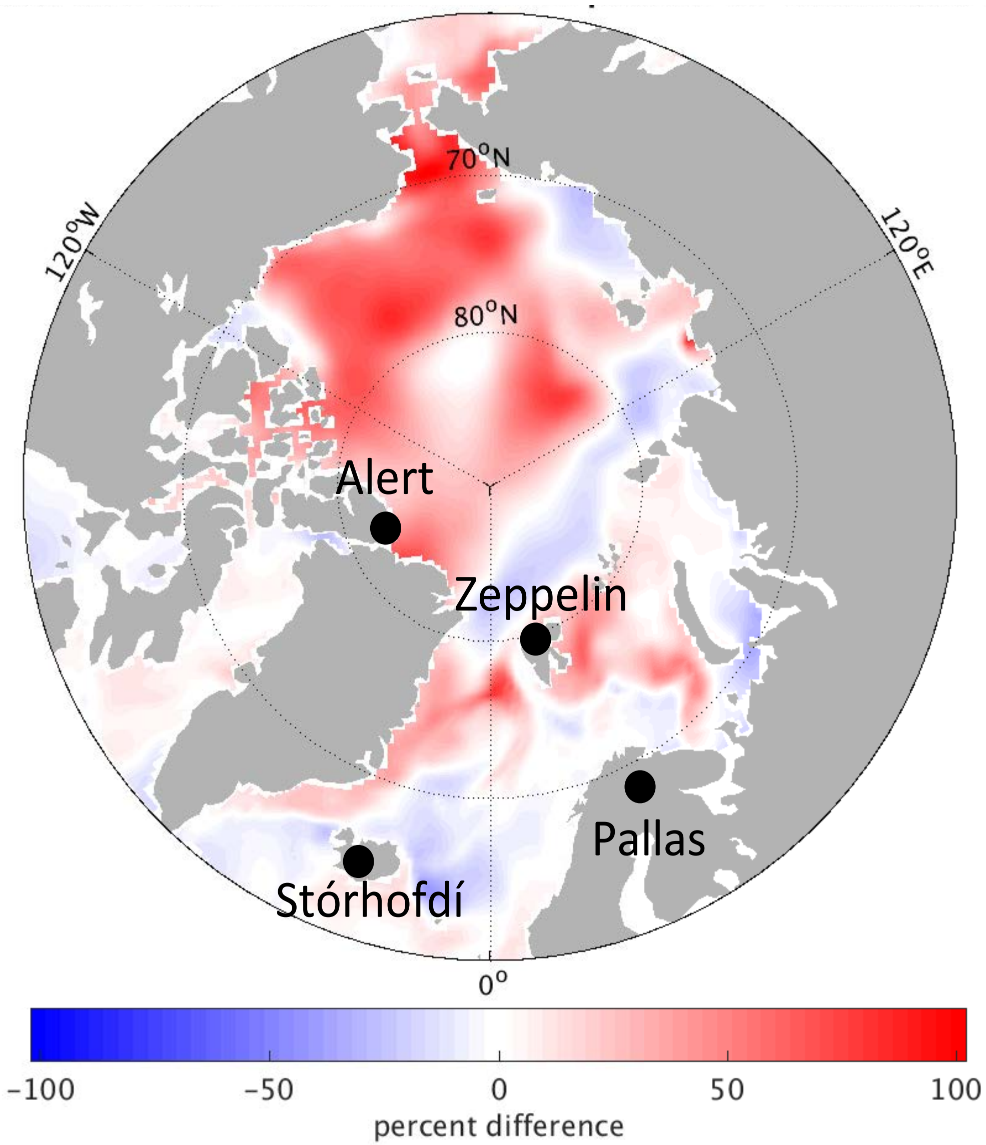






Leung et al., 2017

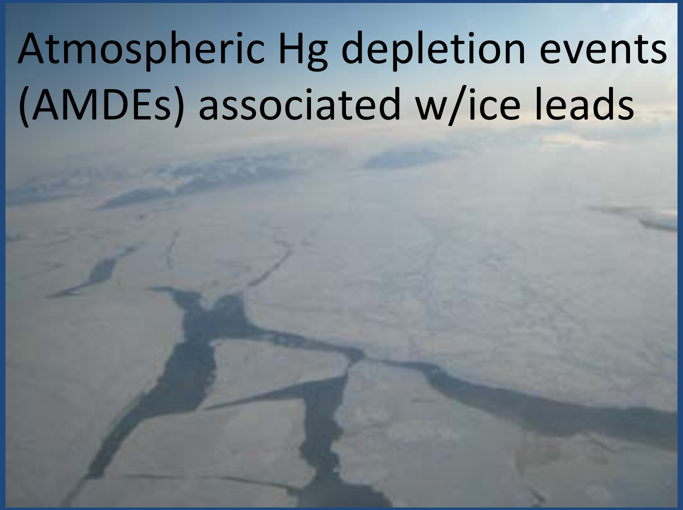
Sea-ice melt enhancing modeled concentrations of PCBs in some regions of the Arctic

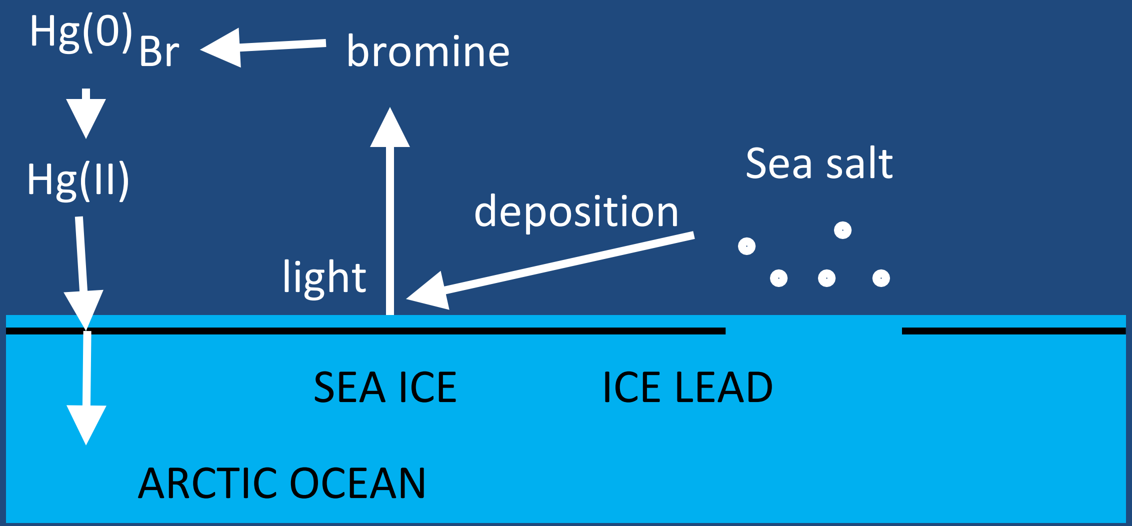


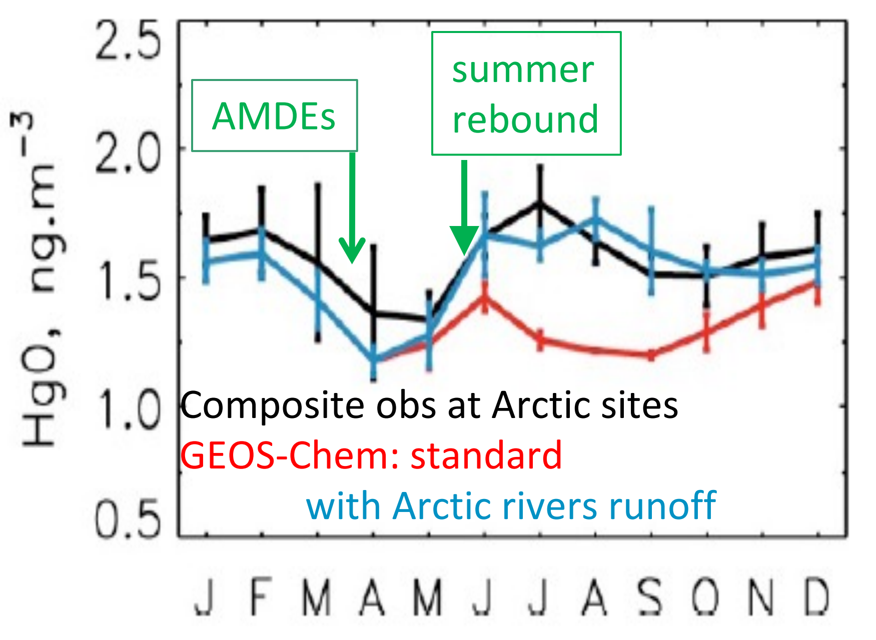
Difference between simulated concentrations of chlorinated biphenyl 153 (CB-153) with constant 1992-1996 meteorology and 1992 to 2015 meteorology

Wagner et al., 2019

Our early work suggested declines in sea-ice cover increase losses of Hg from seawater







- Summer rebound in atmospheric observations can be explained by a large riverine source of Hg

- Changing river inputs and shrinking sea ice in future climate could greatly affect Hg levels in Arctic Ocean

- Modeling allows major oceanic sources to be constrained by atmospheric observations

Fisher et al., 2012; 2013

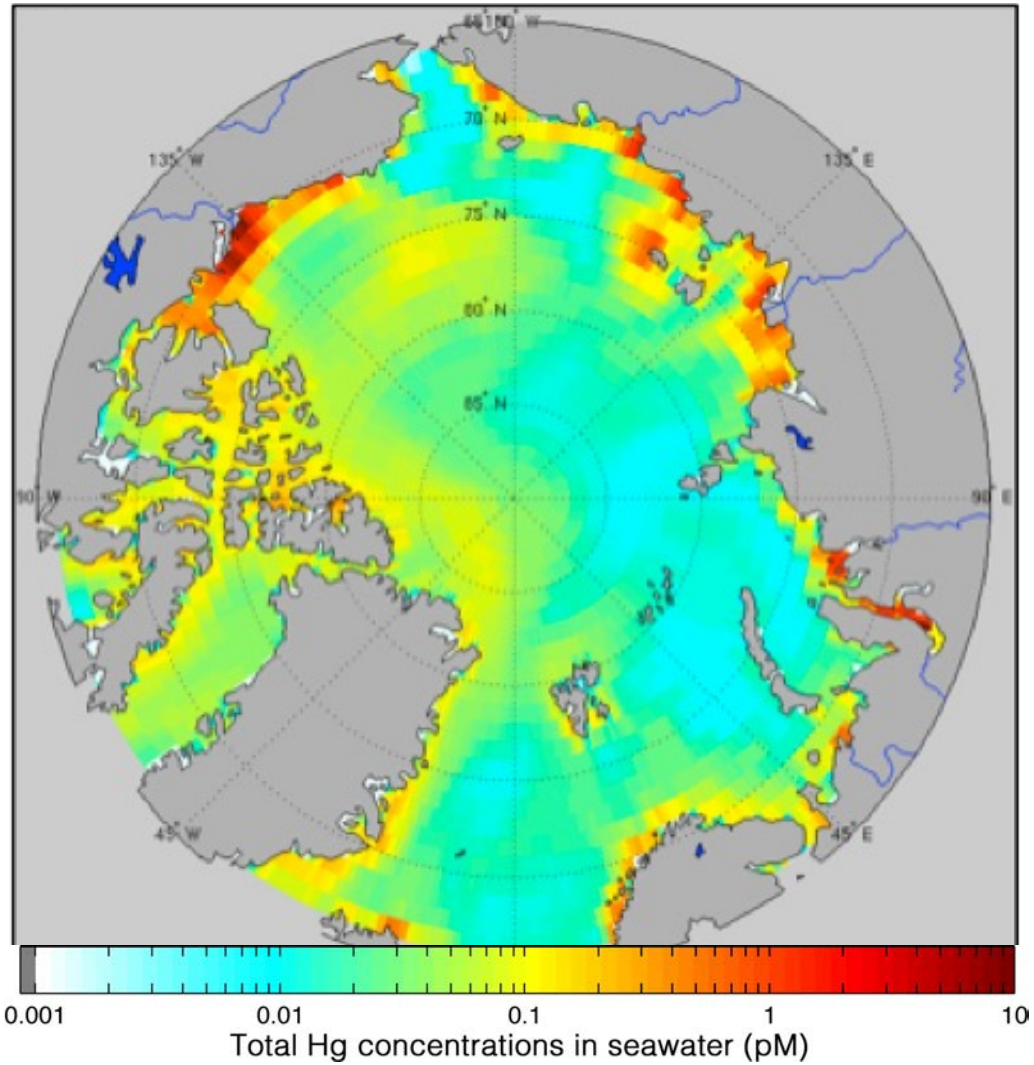
Arctic Ocean is a net Hg source to lower latitudes due to transformations of the terrestrial landscape

Warming 2 x Global Average

Melting Permafrost

Loss of Sea Ice

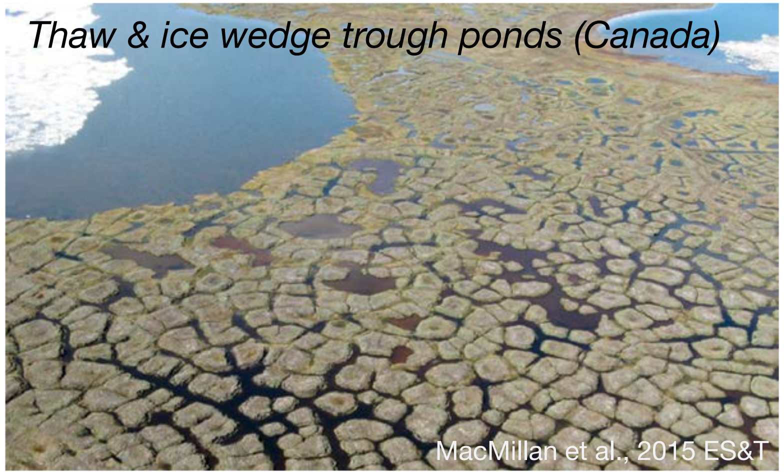
Modeled (MITgcm) Hg inputs to the Arctic Ocean from rivers



Vulnerable Human Populations

Fisher et al., 2012; 2013; Zhang et al., 2015; Soerensen et al., 2016, Sonke et al., 2019; Zolkos et al., 2022

Melting permafrost and wildfires in the Arctic expected to have large impacts on the global Hg cycle



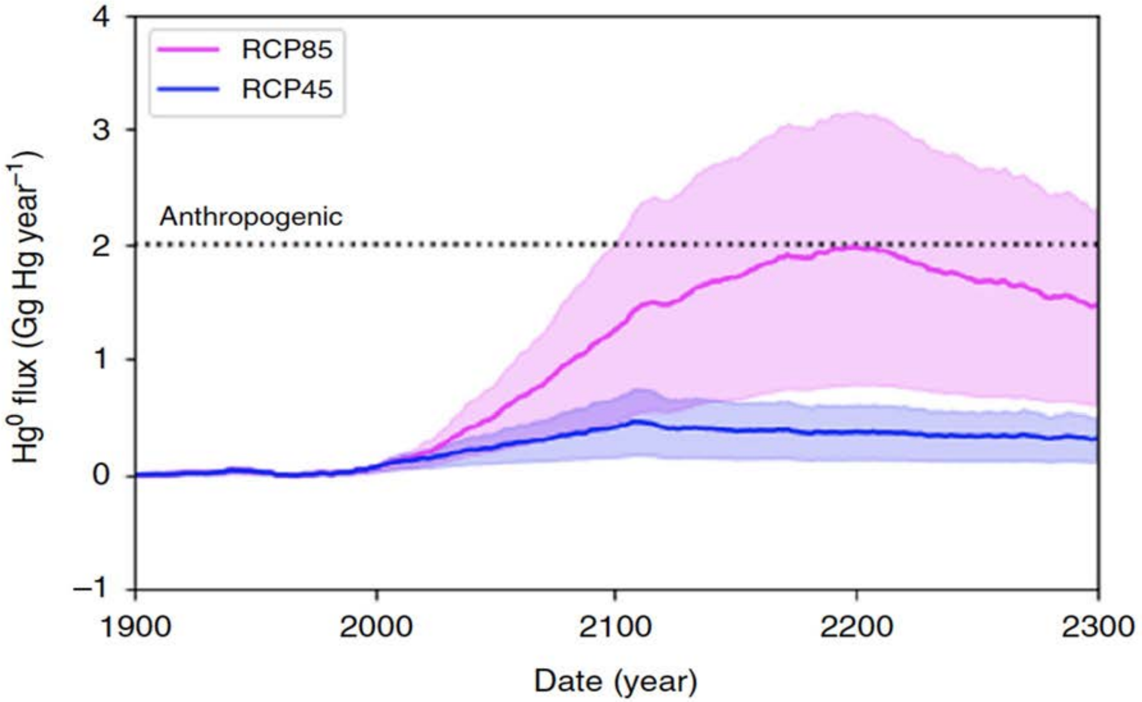


Fig. 2 Annual net elemental mercury (Hg^0) flux into the atmosphere. The net flux is Hg^0 evasion into the atmosphere minus Hg^0 deposition from the atmosphere, summed across all permafrost regions. The shaded areas represent uncertainty in the net Hg^0 flux and the dashed line represents current global anthropogenic emissions.

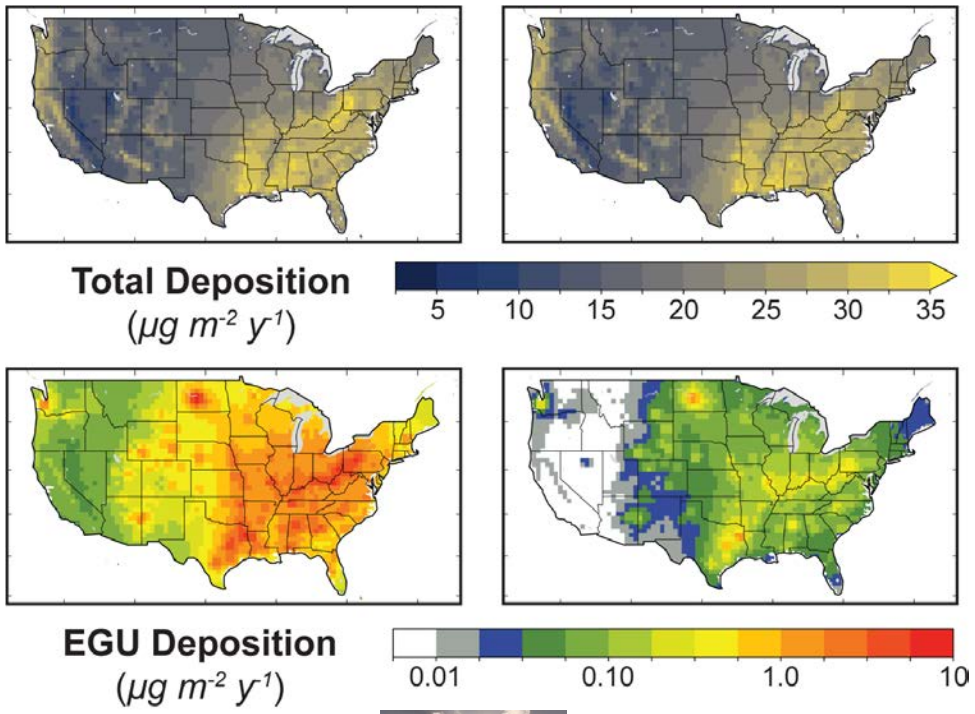
Schaefer et et al., 2020

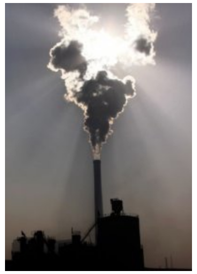
Research Questions

- Which physical/chemical properties are most important for the lifetime of different pollutants in the ocean?
- How will their distribution be affected by changes in ocean circulation and sea-ice cover?
- How are climate-driven changes affecting concentrations in food webs?

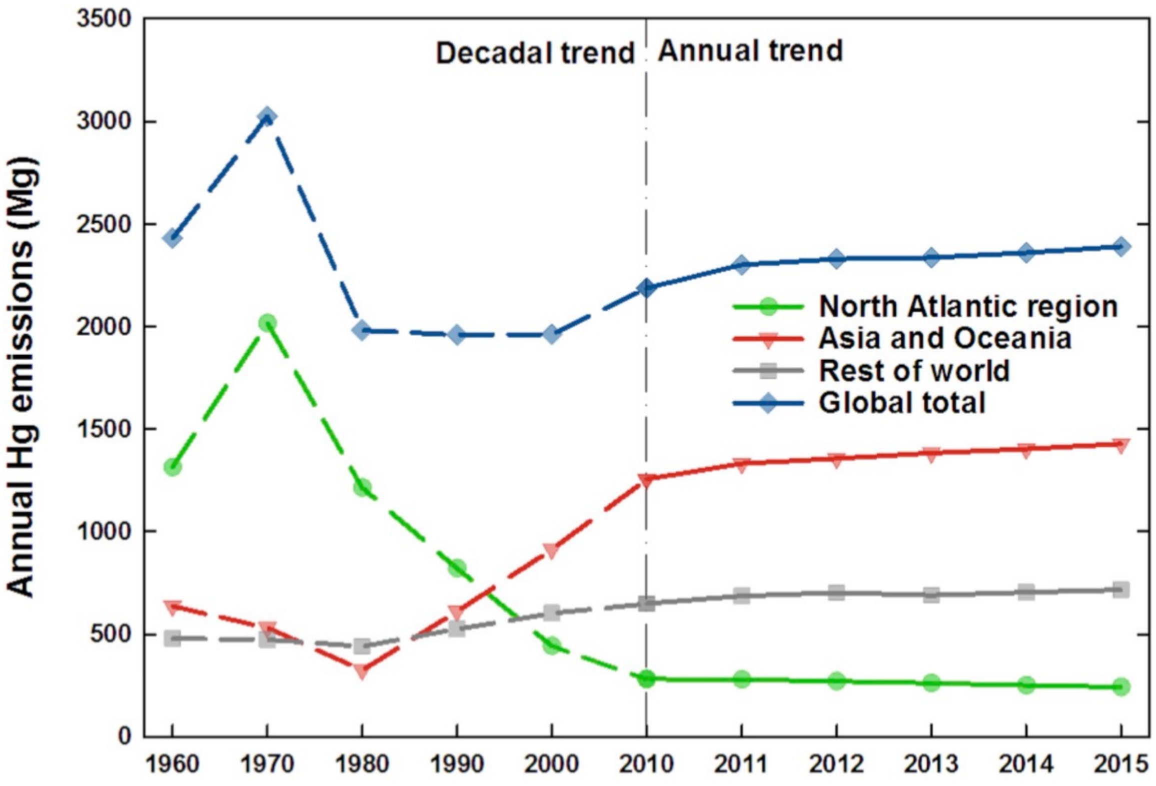
What does the future hold?

2010 **2020**





Global emissions roughly constant since 2010

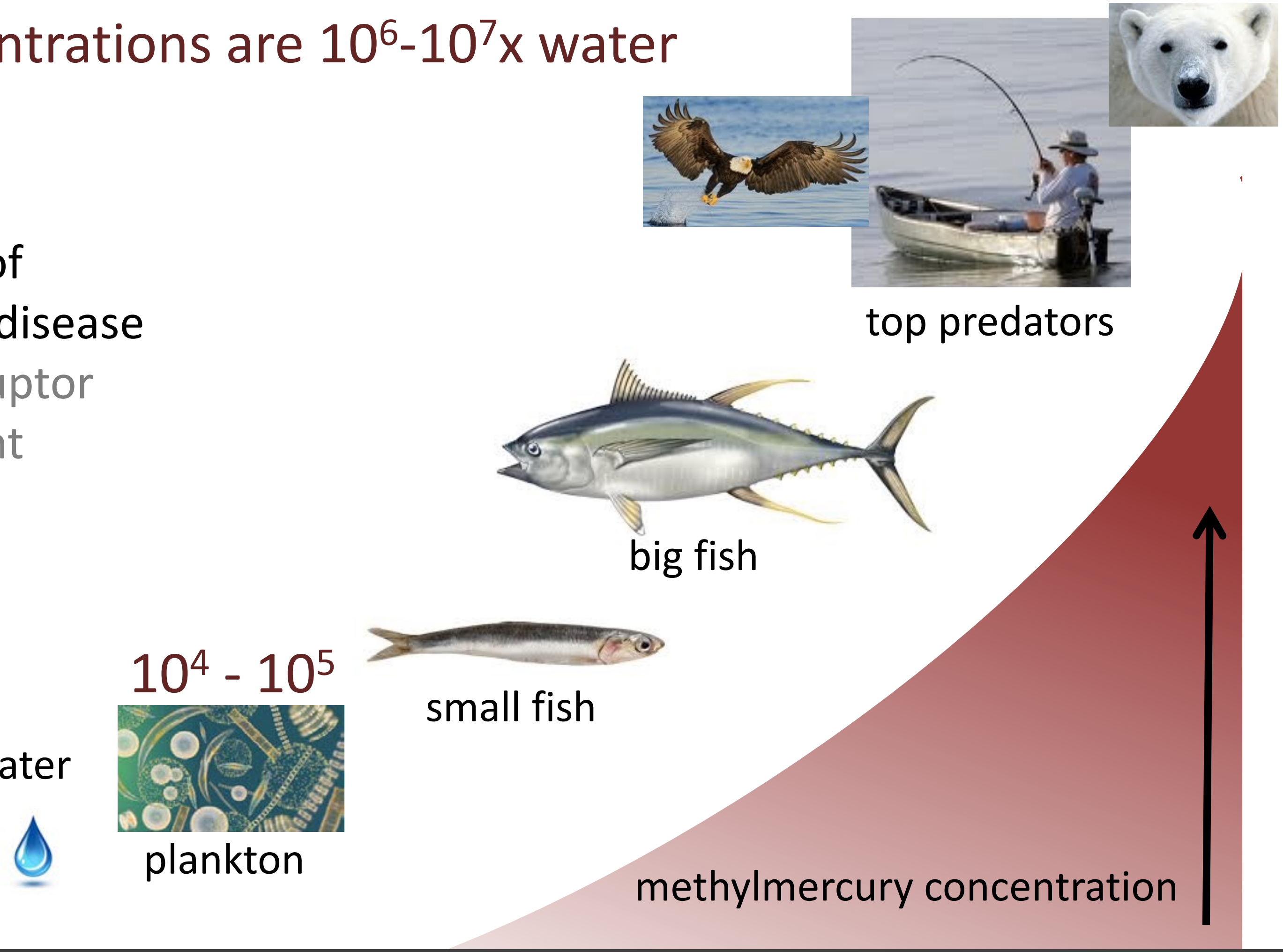


Streets et al. (2019)

Bioaccumulation results in magnification of chemical concentrations at each trophic level in a food web

Concentrations are 10^6-10^7x water

- Neurotoxicant
- Increased risk of cardiovascular disease
- Endocrine disruptor
- Immunotoxicant



CH_3Hg
methylmercury

Societal Costs of methymercury exposure in US > $64 B

(Sunderland et al., in prep.)

Seawater

VOLATILE

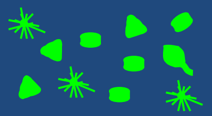
VOLATILE

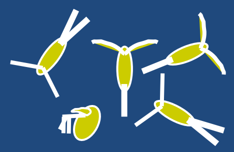
photo/biotic photo/biotic

$$Hg^0 \rightleftharpoons Hg^{II} \rightleftharpoons (CH_3)Hg^{I} \rightleftharpoons (CH_3)_2Hg^0$$

biotic

a/biotic





Elemental Mercury

Divalent Mercury

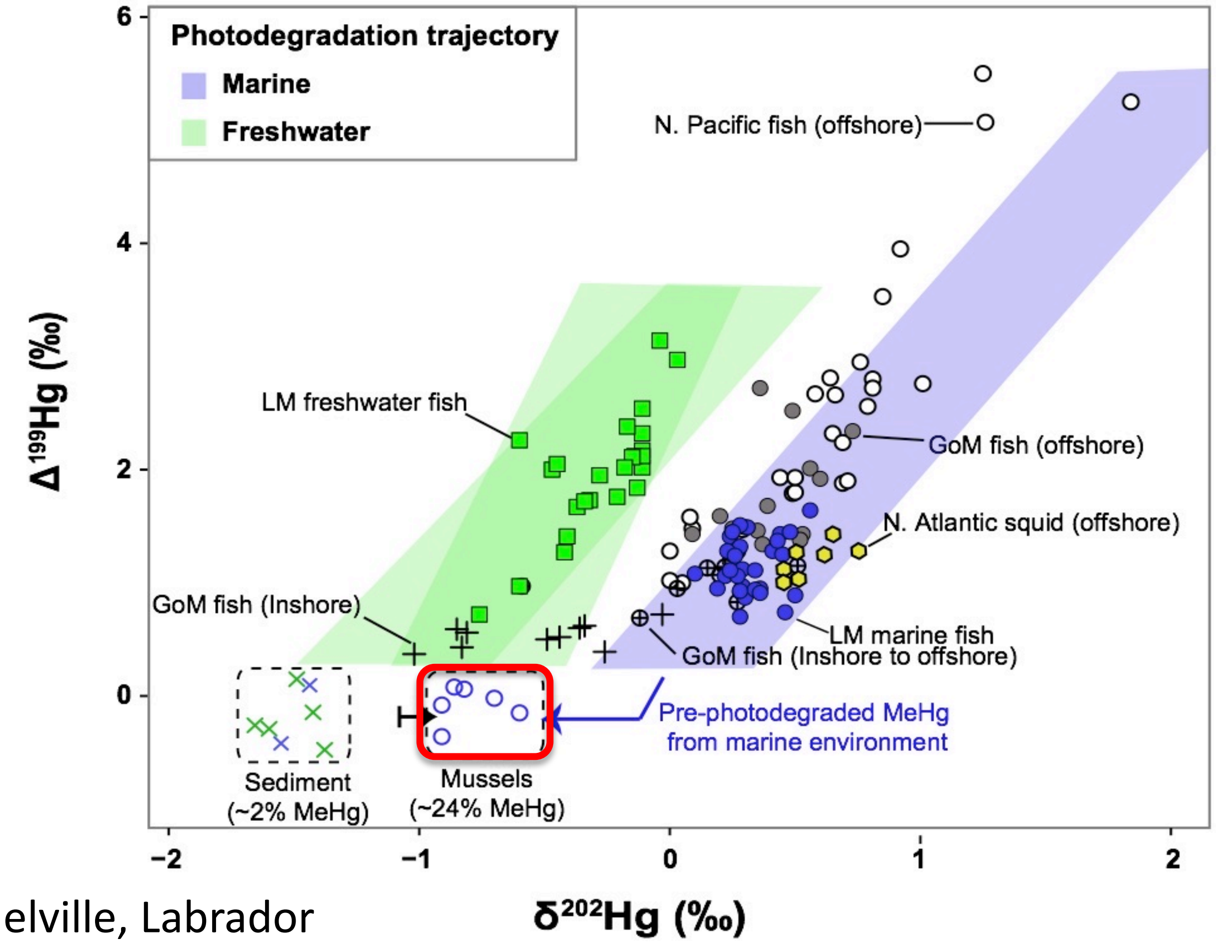
Monomethylmercury

Dimethylmercury

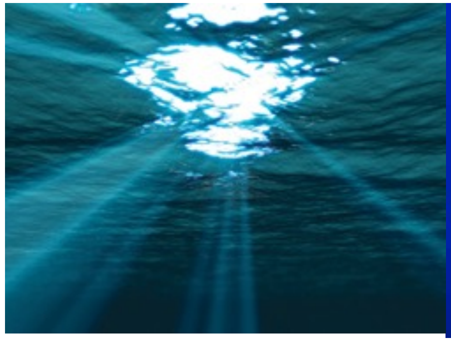
Common Hg isotopic signature in marine fish confirms water column origin of MeHg (rather than sediment)

Seven stable isotopes: ^{196}Hg (0.16%), **^{198}Hg** (10.0%), **^{199}Hg** (16.9%), **^{200}Hg** (23.1%), **^{201}Hg** (13.2%), **^{202}Hg** (29.7%), ^{204}Hg (6.8%).

Mass independent fractionation



Mass dependent fractionation



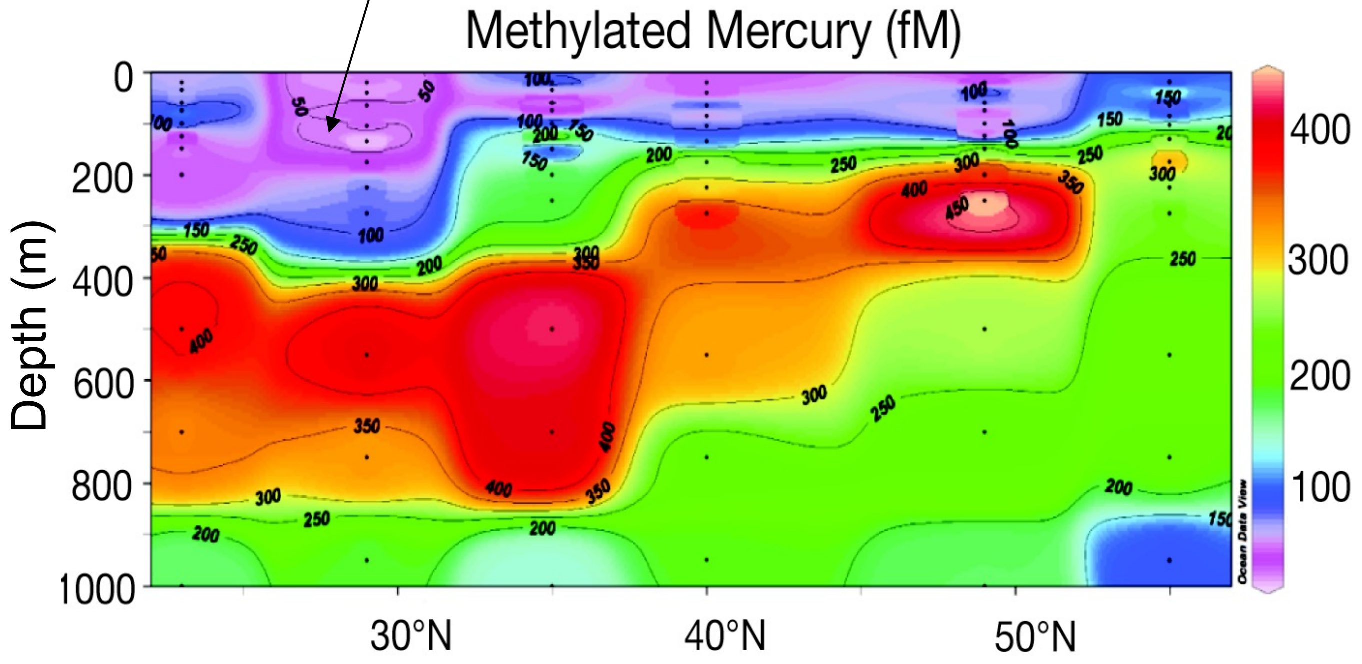
Li et al. (2016), Madigan et al. (2018)

LM = Lake Melville, Labrador
GoM = Gulf of Mexico

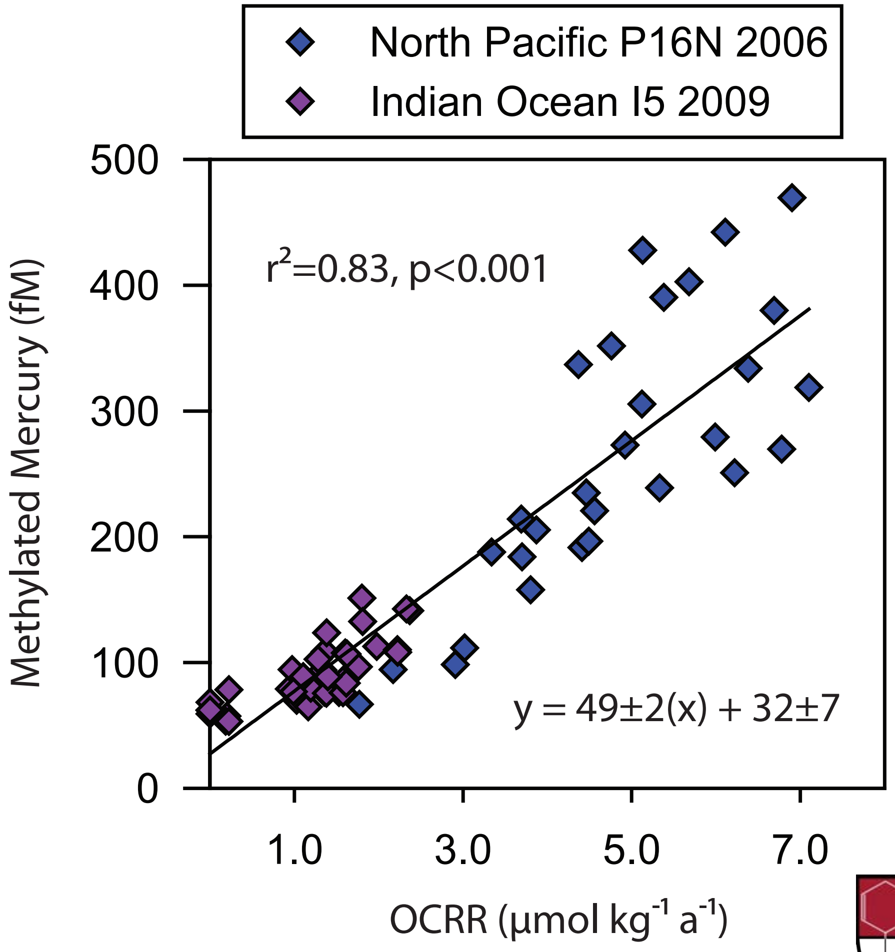
Peak methylated Hg (ΣMeHg) in subsurface ocean waters

NORTH PACIFIC OCEAN (P16N)

Low concentrations in surface waters



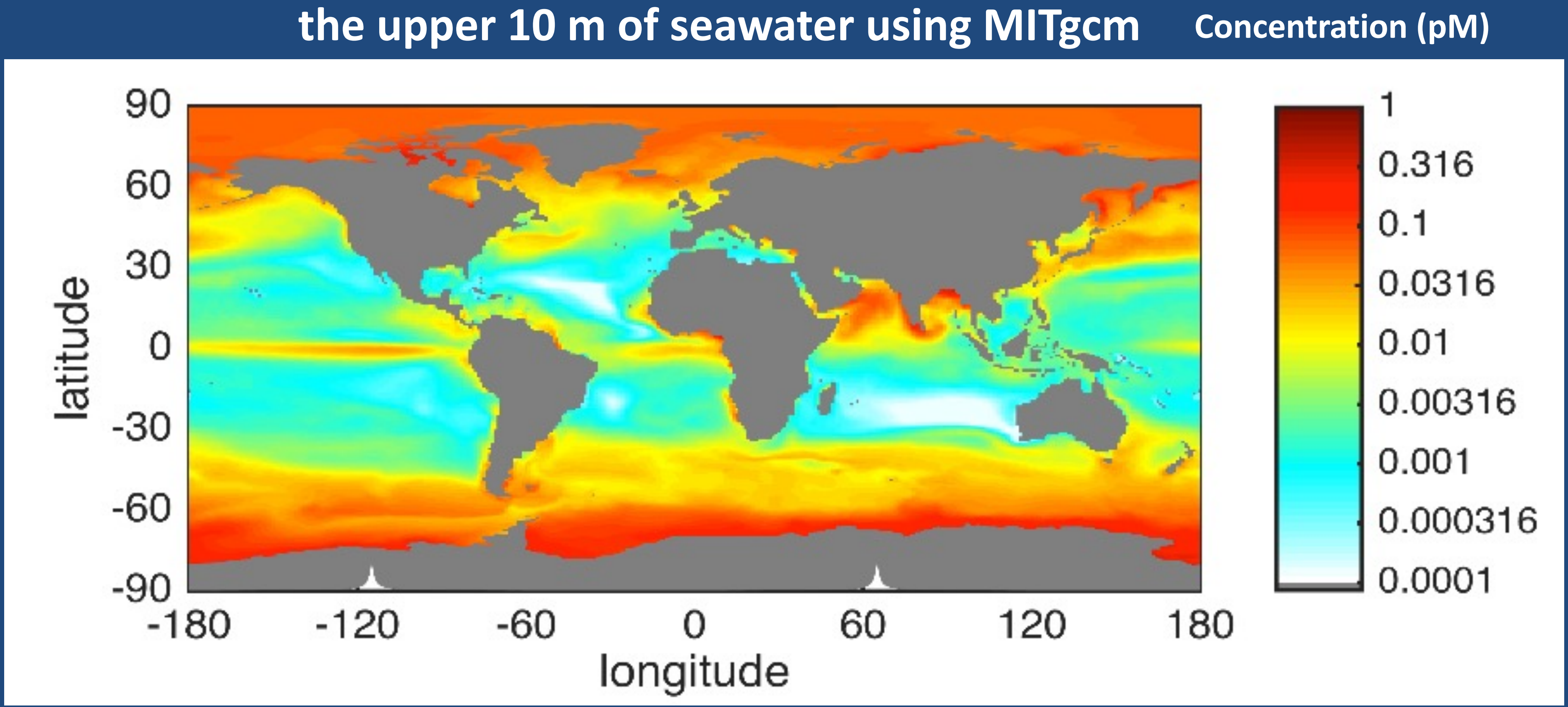
peak in bacterially active waters with active organic carbon remineralization



Sunderland et al., 2009, Cossa et al., 2009, many others since this time

Methylated Hg species highest in polar regions due to decreased light and cold temperatures

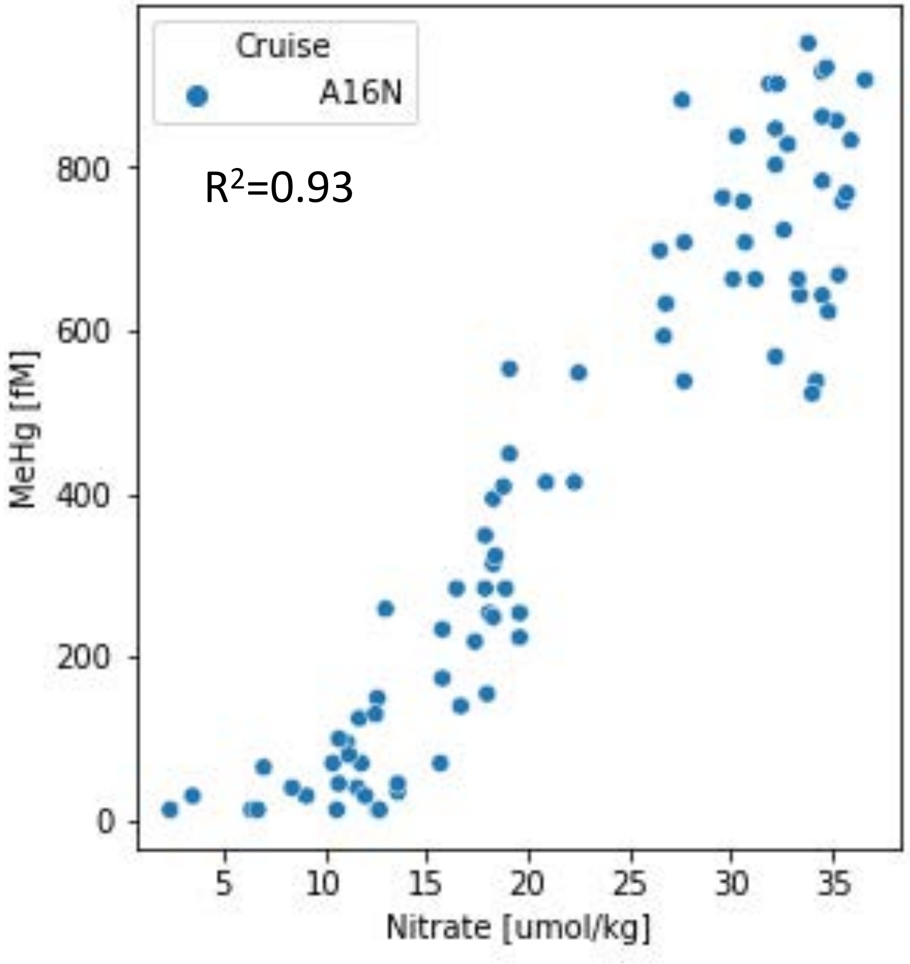
Modeled present-day methylated Hg concentration in the upper 10 m of seawater using MITgcm



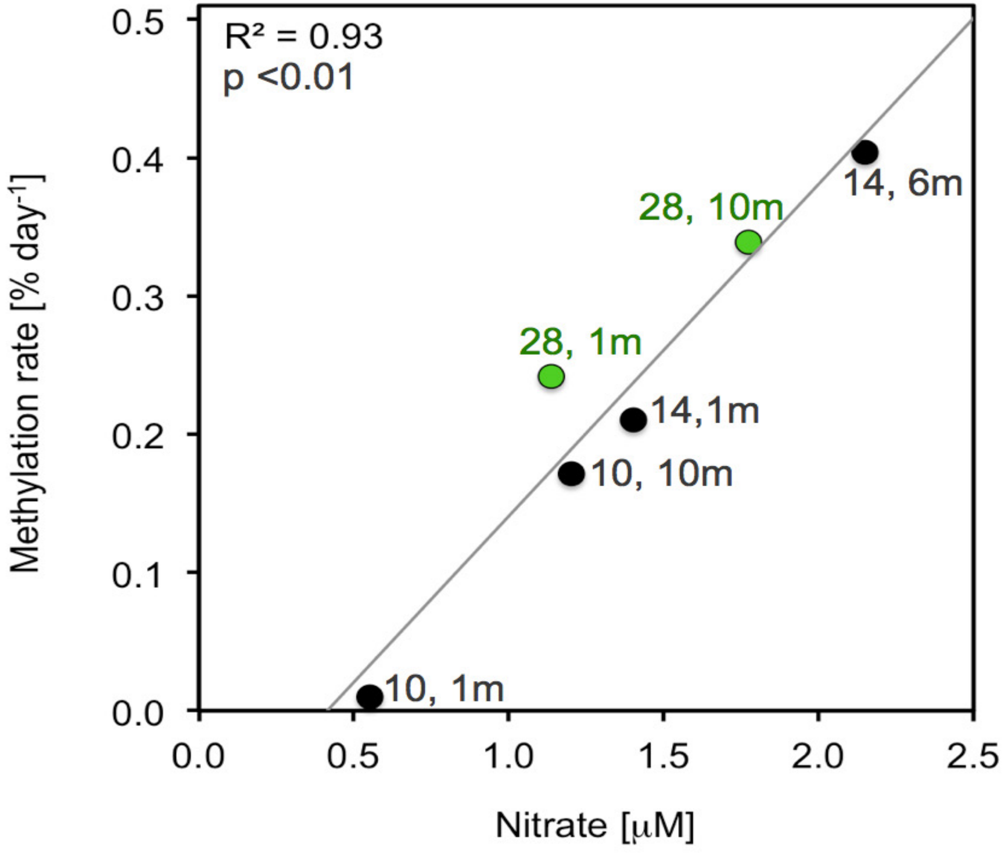
Zhang et al., 2020

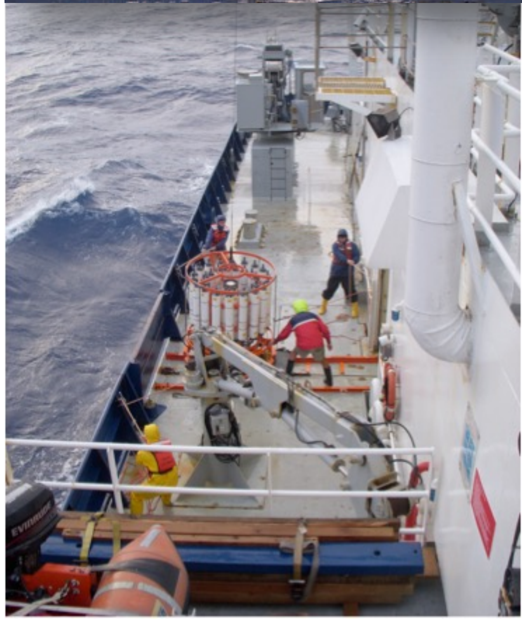
Strongest correlation in the Atlantic Ocean with nitrate concentrations

North Atlantic Ocean (A16N)
CLIVAR 2013 (unpublished)

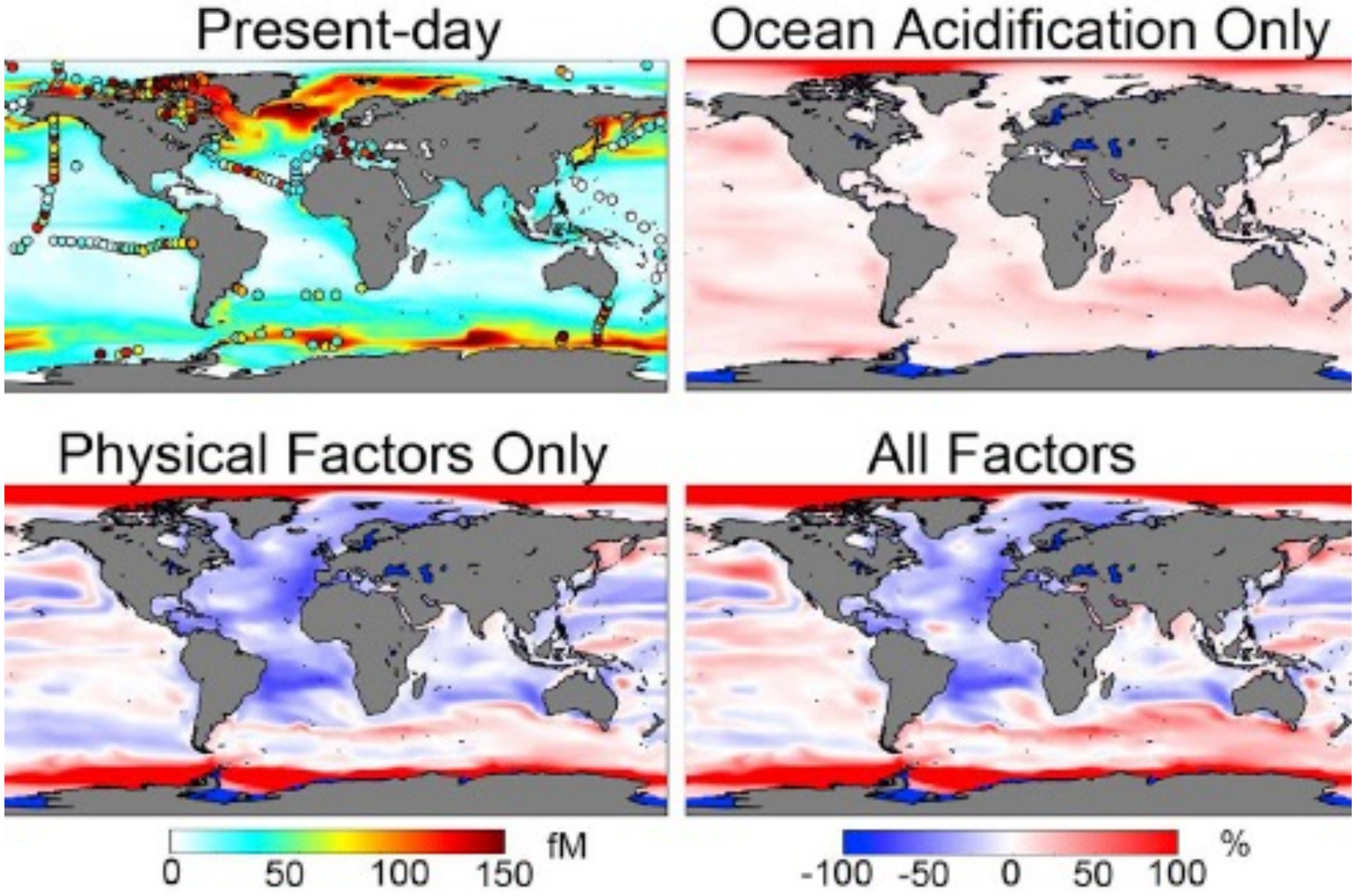


West Atlantic Fjord (Schartup et al., 2015)





Global modeling predicts changes in seawater MeHg as a function of shifts in circulation/ocean acidification

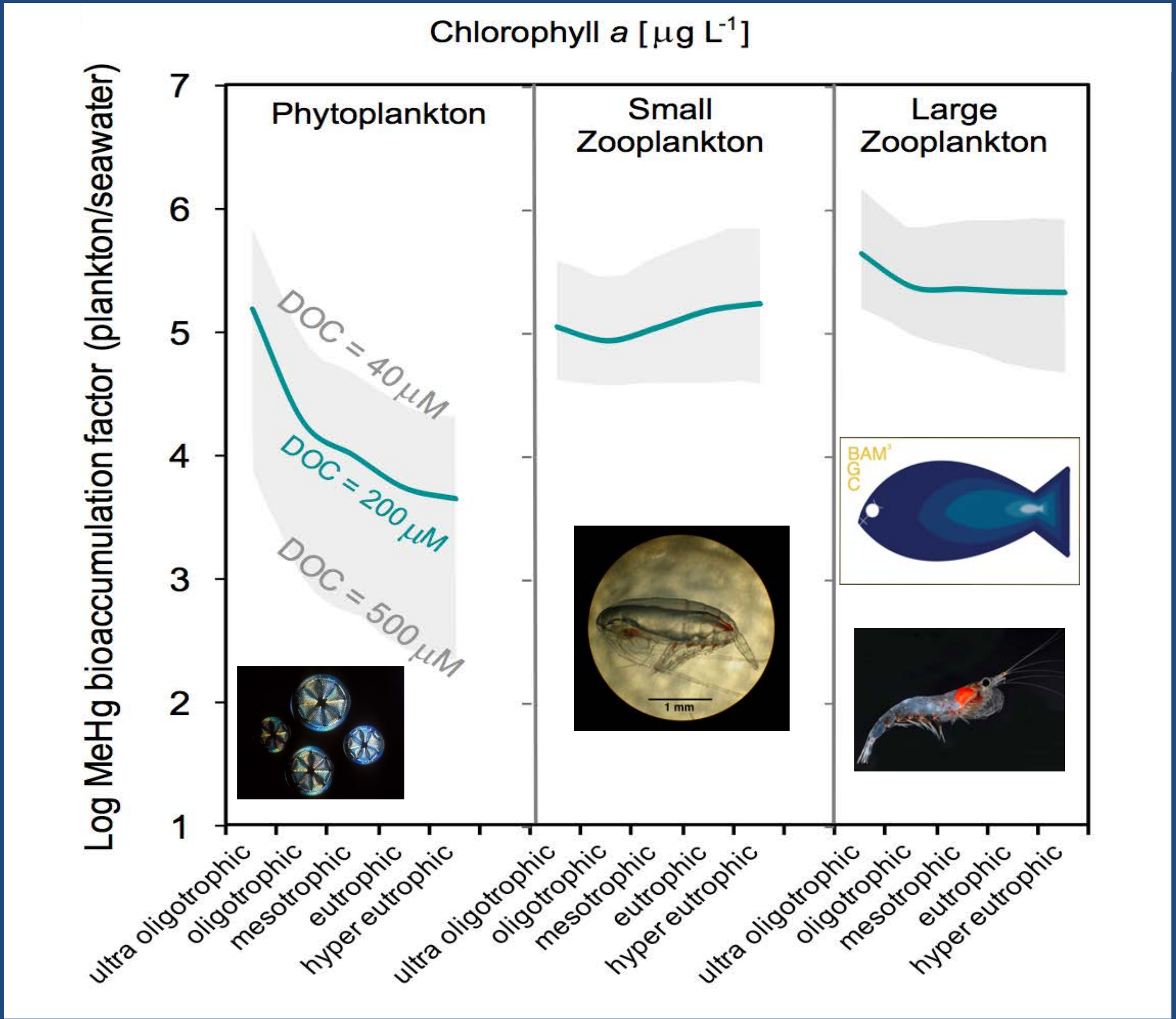


Simulations are under constrained due to limited understanding of the true drivers of MeHg formation in seawater

Zhang et al., 2021

Impacts of shifts in DOC and nutrients are dampened in zooplankton due to competing intake vs. growth

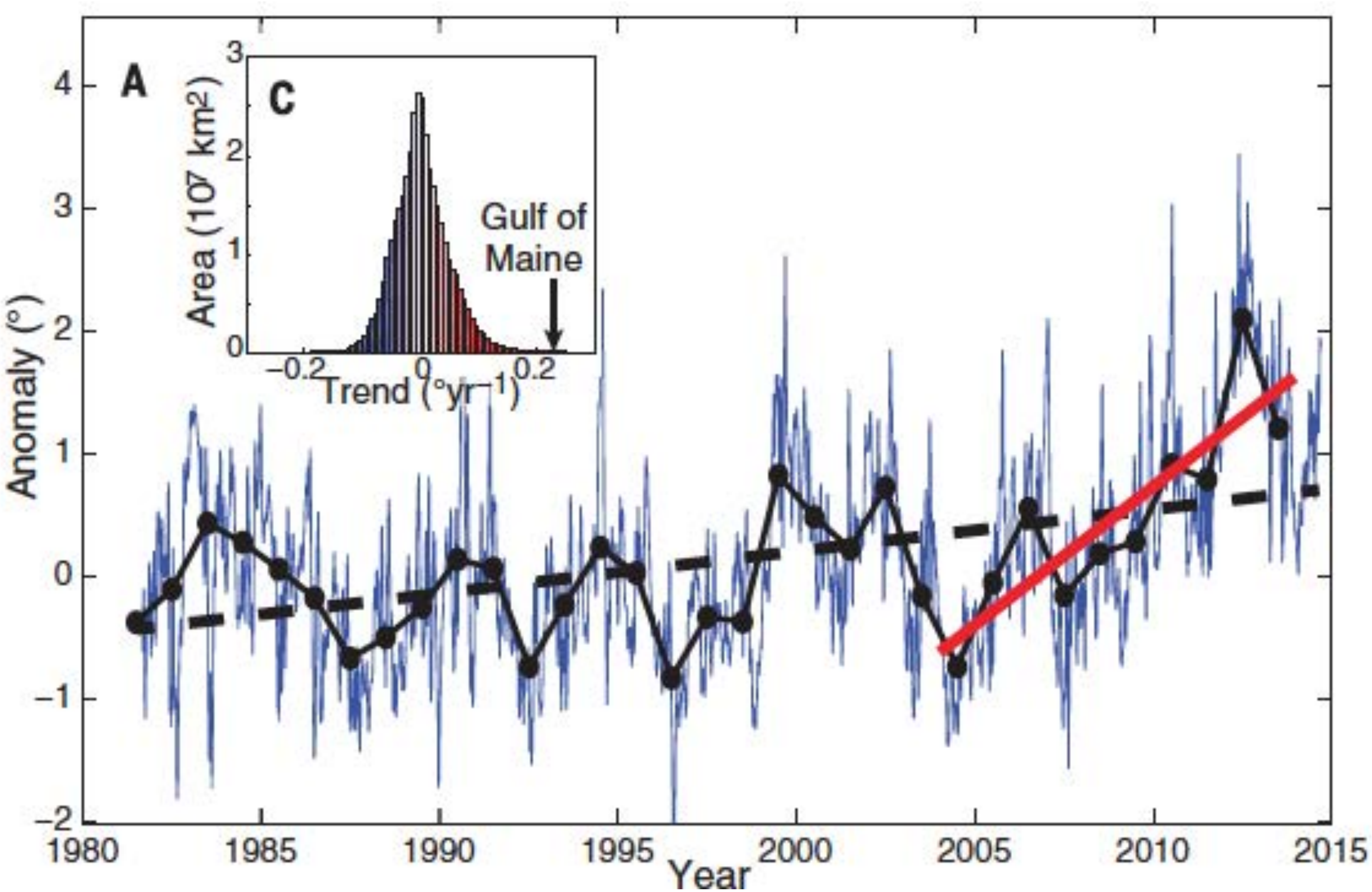
Log BAF (Plankton/Seawater)

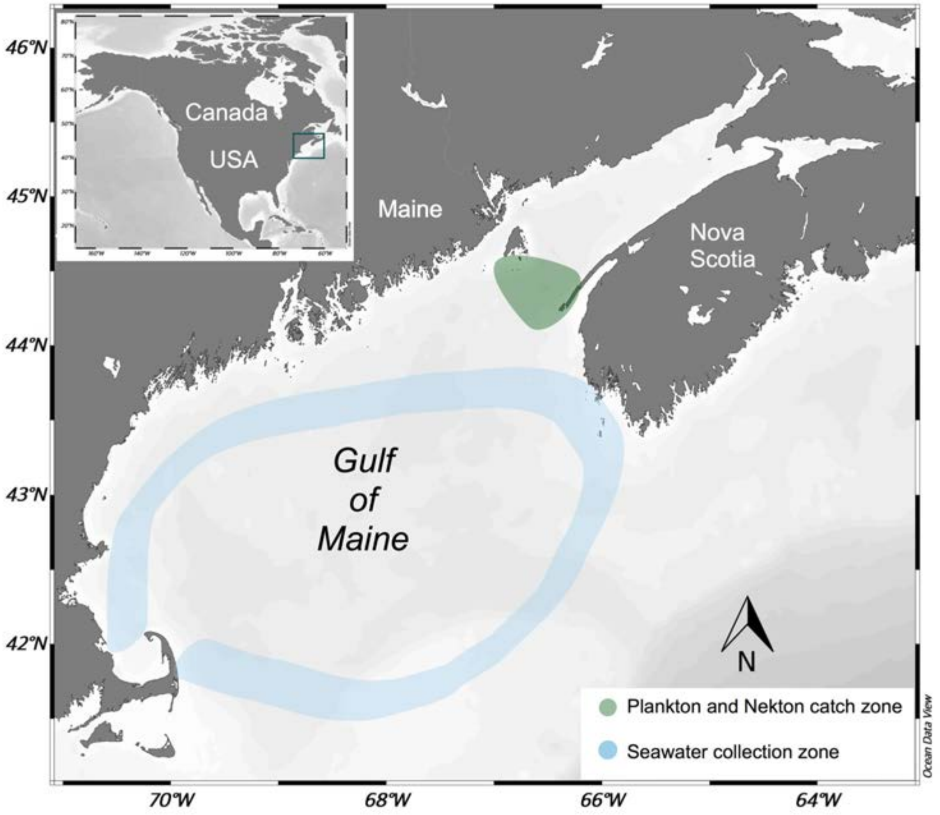


Schartup et al., 2018

Seawater warming affects fish metabolism and growth, MeHg elimination, prey availability, and species habitat

Unprecedented warming in the Gulf of Maine

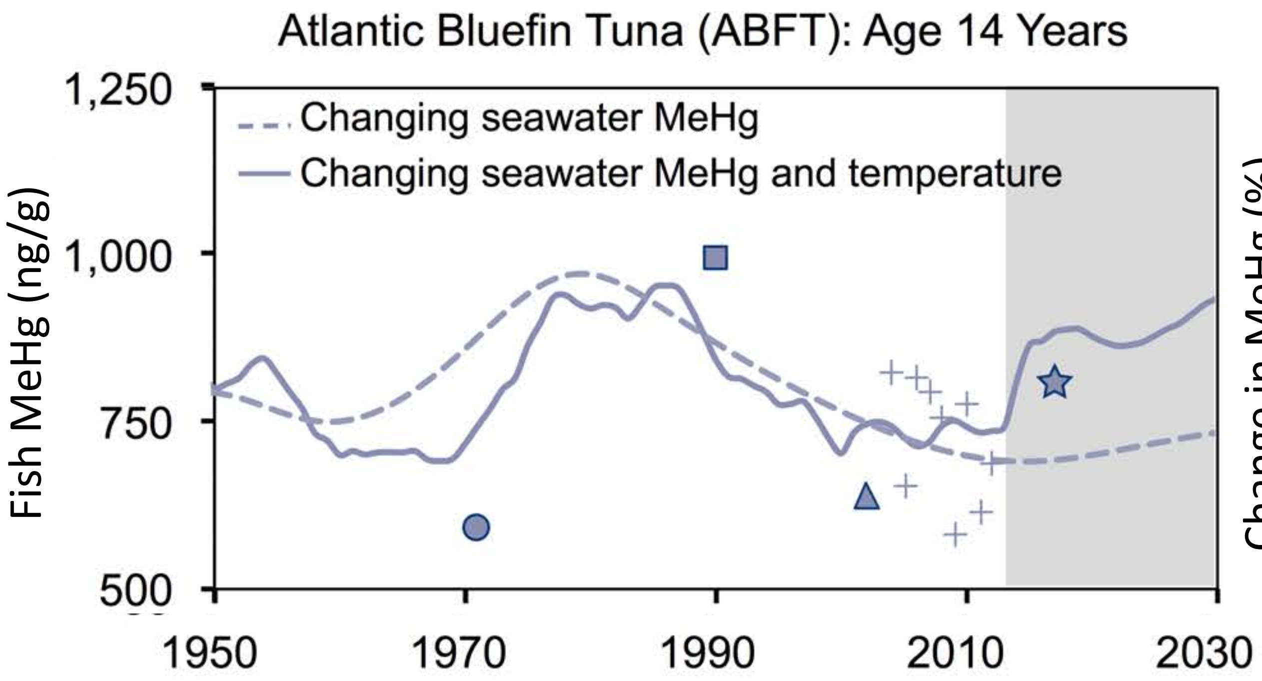


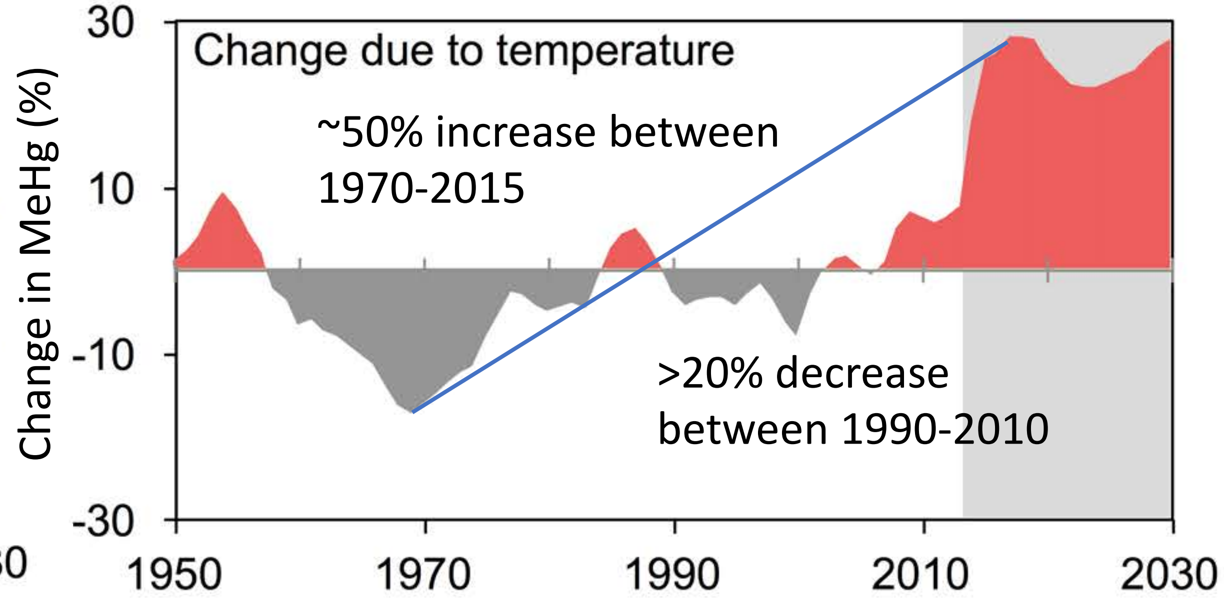


Pershing et al., 2015

Fluctuations in Hg concentrations in Atlantic bluefin tuna reflect changes in both seawater MeHg + ocean biogeochemistry

Seawater warming affects fish metabolism and growth, MeHg elimination, prey availability, and species habitat





Year ABFT Captured

Schartup et al., 2019

Summary

- Volatility extends the persistence of pollutants in surface environments but effectively lowers the concentrations of some pollutants in seawater over the short term
- Partitioning to solids is an effective removal mechanism and linked to aquatic productivity
- Ionogenic compounds like PFOS are especially sensitive to changes in ocean circulation
- In the Arctic, melting permafrost and future changes in freshwater discharges likely to enhance direct inputs of contaminants to the atmosphere and ocean
- Declines in sea-ice cover may lead to greater evasion and lower seawater concentrations of volatile compounds in the Arctic
- Seawater temperature increases can substantially amplify concentrations of bioaccumulative pollutants

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