

**Mercury Pollution in Aquatic Ecosystems**



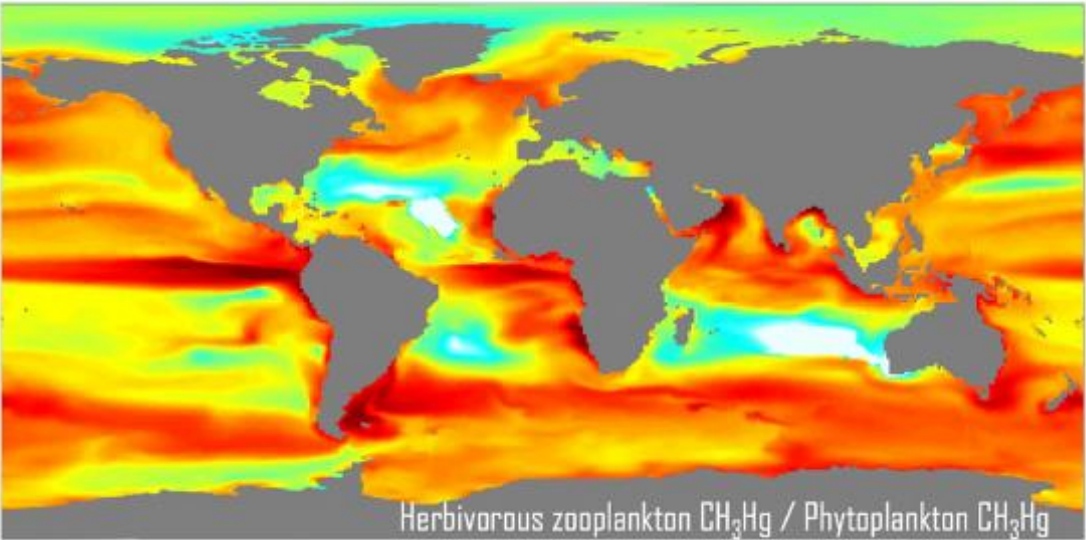
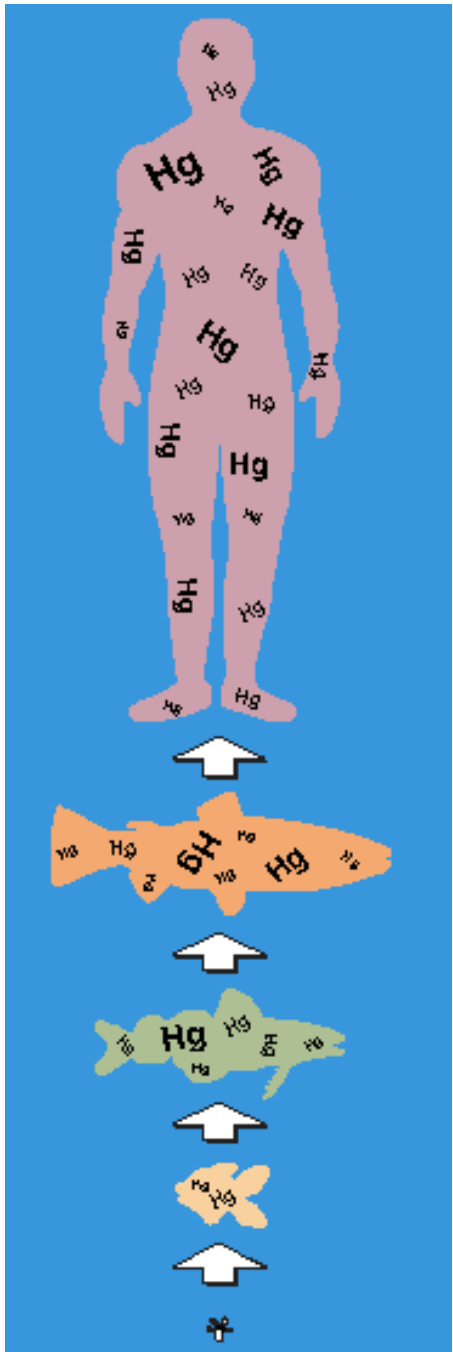
**Karen A. Merritt, PhD MPH**



# What do we know regarding the biomagnification process?

- Sulfate ( $\text{SO}_4^{2-}$ ) + low-to-no dissolved oxygen ( $\text{O}_2$ ) increases activity of sulfate-reducing **bacteria** (SRB);
- SRB in the presence of inorganic mercury ( $\text{Hg}^{2+}$ ) generate methyl mercury ( $\text{CH}_3\text{Hg}^+$ ) as an accident/**by-product of respiration**;
- Methyl mercury is **retained in biological tissue** more significantly than inorganic mercury because of the additional  $-\text{CH}_3$  (methyl) group;
- **Bioaccumulation** of methyl mercury occurs because the depuration (loss) rate of methyl mercury from biological tissue is much lower/slower than the loss rate of inorganic mercury;
- **Biomagnification** happens through the **trophic transfer** of bioaccumulated methyl mercury from small prey species to larger prey (or predator) species to largest predator species (including humans)



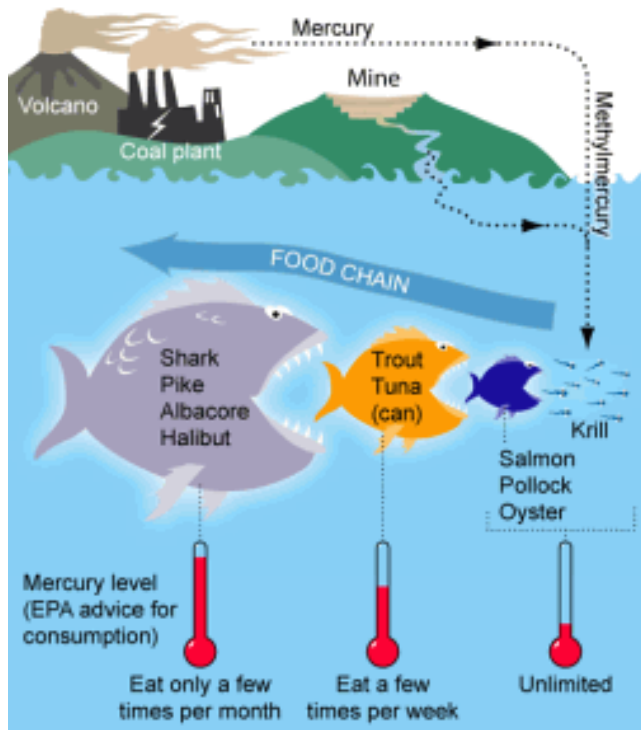
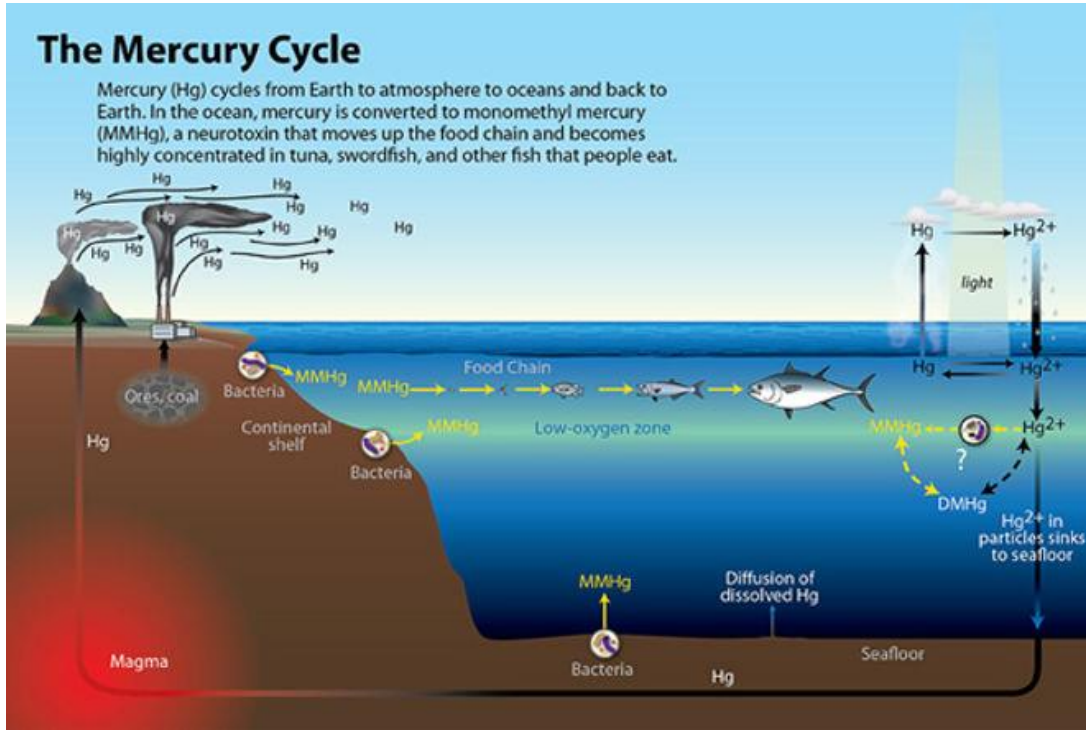


**A Global Model for Methylmercury Formation and Uptake at the Base of Marine Food Webs**

Yanxu Zhang<sup>1,2</sup>, Anne L. Soerensen<sup>3,4</sup>, Amina T. Scharup<sup>5,6,7</sup>, and Elsie M. Sunderland<sup>2,3</sup>

<sup>1</sup>Joint International Research Laboratory of Atmospheric and Earth System Sciences, School of Atmospheric Sciences, Nanjing University, Nanjing, China, <sup>2</sup>Harvard John A. Paulson School of Engineering & Applied Sciences, Harvard University, Cambridge, MA, USA, <sup>3</sup>Department of Environmental Health, Harvard T.H. Chan School of Public Health, Harvard University, Boston, MA, USA, <sup>4</sup>Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, Sweden, <sup>5</sup>Scripps Institution of Oceanography, La Jolla, CA, USA

**Abstract** Monomethylmercury ( $\text{CH}_3\text{Hg}$ ) is the only form of mercury ( $\text{Hg}$ ) known to biomagnify in food webs. Here we investigate factors driving methylated mercury [ $\text{MeHg} = \text{CH}_3\text{Hg} + (\text{CH}_3)_2\text{Hg}$ ] production and degradation across the global ocean and uptake and trophic transfer at the base of marine food webs. We develop a new global 3-D simulation of  $\text{MeHg}$  in seawater and phyto/zoo plankton within the Massachusetts Institute of Technology general circulation model. We find that high modeled  $\text{MeHg}$  concentrations in polar regions are driven by reduced demethylation due to lower solar radiation and colder temperatures. In the eastern tropical subsurface waters of the Atlantic and Pacific Oceans, the model results suggest that high  $\text{MeHg}$  concentrations are associated with enhanced microbial activity and atmospheric inputs of inorganic  $\text{Hg}$ . Global budget analysis indicates that upward advection/diffusion from subsurface ocean provides 17% of  $\text{MeHg}$  in the surface ocean. Modeled open ocean phytoplankton concentrations are relatively uniform because lowest modeled seawater  $\text{MeHg}$  concentrations occur in oligotrophic regions with the smallest size classes of phytoplankton, with relatively high uptake of  $\text{MeHg}$  and vice versa. Diatoms and synchococcus are the two most important phytoplankton categories for transferring  $\text{MeHg}$  from seawater to herbivorous zooplankton, contributing 35% and 25%, respectively. Modeled ratios of  $\text{MeHg}$  concentrations between herbivorous zooplankton and phytoplankton are 0.74–0.78 for picoplankton (i.e., no biomagnification) and 2.6–4.5 for eukaryotic phytoplankton. The spatial distribution of the trophic magnification factor is largely determined by the zooplankton concentrations. Changing ocean biogeochemistry resulting from climate change is expected to have a significant impact on marine  $\text{MeHg}$  formation and bioaccumulation.



Think about **risk profiles** for different locations in terms of:

- **Physical factors** – what is the burial rate of contamination based on the geological background (i.e., how much sediment is available for burying contamination quickly to a depth below the biological mixed depth or biologically active zone?); how do hydrodynamics impact stable burial?
- **Chemical factors** – what factors are present that can create the conditions in which SRB are active? Factors of concern are those that contribute sulfate ( $\text{SO}_4^{2-}$ ) and biochemical oxygen demand (BOD) such that significant  $\text{O}_2$  consumption occurs. Factors can be anthropogenic but aren't always.
- **Biological factors** – what are the species of concern and what do trophic transfer pathways look like? For human health concerns, what are the frequency and frameworks for consumption (i.e., recreational and infrequent vs frequent and culturally or socio-economically significant)?

# PHYSICAL

Sufficient sedimentation  
and low erosion potential  
to allow for stable burial

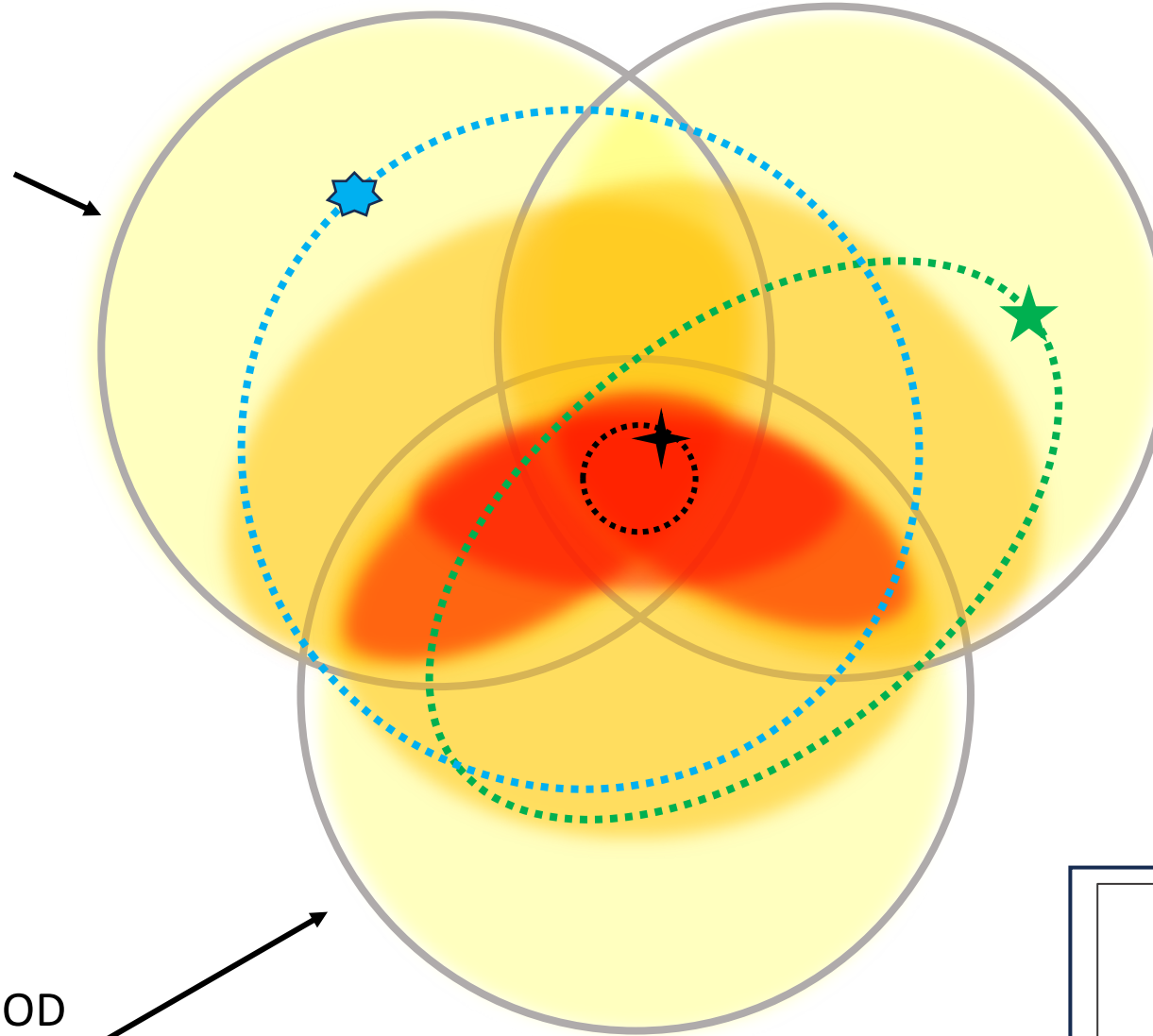
- ★ = Wabigoon River, ON
- ★ = Penobscot River, ME
- ★ =

# CHEMICAL

Factors that contribute BOD  
and sulfate ( $\text{SO}_4^{2-}$ ) and result  
in  $\text{O}_2$  consumption

# BIOLOGICAL

Multi-trophic level  
food chains with a top  
predator species that  
is frequently  
consumed



Think of this overview of  
risk profiles as describing  
orbits around a worst-case  
ecological and human  
health scenario

# Site Comparison

## Penobscot River Estuary, Maine

- Glaciated terrain and low sed. rates ( $\sim 0.5$  cm/yr)
- Lobster as a TL2 species; in terms of frequency, consumption is not culturally significant; TL4 specie is American eel – may be an ecological concern, but not an acute HH concern.
- Biogeochemical concerns due to wood waste – elevated % methylation on marshes; most concerning trophic transfer pathway to marsh species is via terrestrial food web for migratory songbirds.
- Surface sediment concentrations  $< 10$  mg/kg in vicinity of site and  $< 1$  mg/kg across majority of the estuary.
- No acute, severe or obvious human health concerns; species of greatest consumption are lobster and ducks, both of which have consumption restrictions in place via licensing structure/programs.

## Wabigoon River, Ontario

- Glaciated terrain and very low sed. rates ( $\sim 0.3$  cm /yr)
- Walleye and Northern pike as TL4 species; consumption is culturally significant
- Mill effluent renders the river suboxic/anoxic in summer; stratification of an in-river lake contributes to  $> 2$  ug/g in walleye.
- Surface sediment mercury concentrations exceed 50 mg/kg in vicinity of mill and are elevated consistently  $> 1$  mg/kg for a distance of  $\sim 40$  miles downstream.
- Human health impacts are acute, severe and with multi-generational manifestation; fish are consumed whether or not a consumption restriction is in place.



# Grassy Narrows ANA Community – This is Living Downstream



**Health in Grassy Narrows 'significantly worse' than other First Nations: report**





# Grassy Narrows ANA Community

## Research

A Section 508-conformant HTML version of this article is available at <https://doi.org/10.1289/EHP11301>.

## The Contribution across Three Generations of Mercury Exposure to Attempted Suicide among Children and Youth in Grassy Narrows First Nation, Canada: An Intergenerational Analysis

Donna Mergler,<sup>1</sup> Aline Philibert,<sup>1</sup> Myriam Fillion,<sup>2,1</sup> and Judy Da Silva<sup>3</sup>



## Mercury exposure and premature mortality in the Grassy Narrows First Nation community: a retrospective longitudinal study

Aline Philibert, Myriam Fillion, Donna Mergler

### Summary

**Background** Little is known about the influence of toxic exposures on reduced life expectancy in First Nations people in Canada. The Grassy Narrows First Nation community have lived with the consequences of one of the worst environmental disasters in Canadian history. In the early 1960s, 10 000 kg of mercury (Hg) was released into their aquatic ecosystem. Although Hg concentration in fish, their dietary staple, decreased over time, it remains high. We aimed to examine whether elevated Hg exposure over time contributes to premature mortality (younger than 60 years) in this community.

**Methods** We did longitudinal and case-control analyses with data for individuals of the Grassy Narrows First Nation community. In 2019, the community obtained their historical Hg biomarker data from a government surveillance programme, which was then shared with the authors. A matched-pair approach allowed us to compare longitudinal hair Hg concentration between cases (individuals who died aged younger than 60 years) and controls (individuals who lived beyond 60 years). Matching criteria included year of birth (allowing 2 years either side), sex, and a minimum of four hair Hg concentration measures, of which at least two were in the same year. Analyses included change-point detection, interrupted time series, mixed models, and Cox survival models.

**Findings** We analysed data collected between Jan 1, 1970, and Jan 31, 1997, for 657 individuals (319 women and 338 men, born between 1884 and 1991) for whom we assembled a retrospective database of yearly measures of hair Hg concentration (n=3603). Hair Hg concentration decreased over time. A subgroup of 222 individuals (107 women and 115 men) reached or could have reached 60 years old by August, 2019. There was an increased risk of dying at a younger age among those with at least one hair Hg measure of 15 µg/g or more (adjusted hazard ratio 1.55, 95% CI 1.11–2.16; p=0.0088). Among the deceased individuals (n=154), longevity decreased by 1 year with every 6.25 µg/g (4.35–14.29) increase in hair Hg concentration. Analyses of 36 matched pairs showed that hair Hg concentration of those who died aged younger than 60 years was 4.7 µg/g higher (3.4–5.9) than controls.

**Interpretation** The consistent findings between our different analyses support an association between long-term Hg exposure from freshwater fish consumption and premature mortality in this First Nation community. There is a need to do risk-benefit analyses of freshwater fish consumption in environmentally contaminated regions.



Lancet Planet Health 2020; 4: e141–48

This online publication has been corrected. The corrected version first appeared at [thelancet.com/planetary-health](https://www.thelancet.com/planetary-health) on May 11, 2020, and further corrections have been made on July 15, 2020

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CANADA

## Ontario knew about Grassy Narrows mercury site for decades, but kept it secret

Toronto Star  
November 11, 2017

A confidential 2016 report says provincial officials were told in the 1990s that the site of a paper mill near Grassy Narrows First Nation was contaminated with mercury — and that the poison is likely still present.



# Walleye (1970 – 2017)

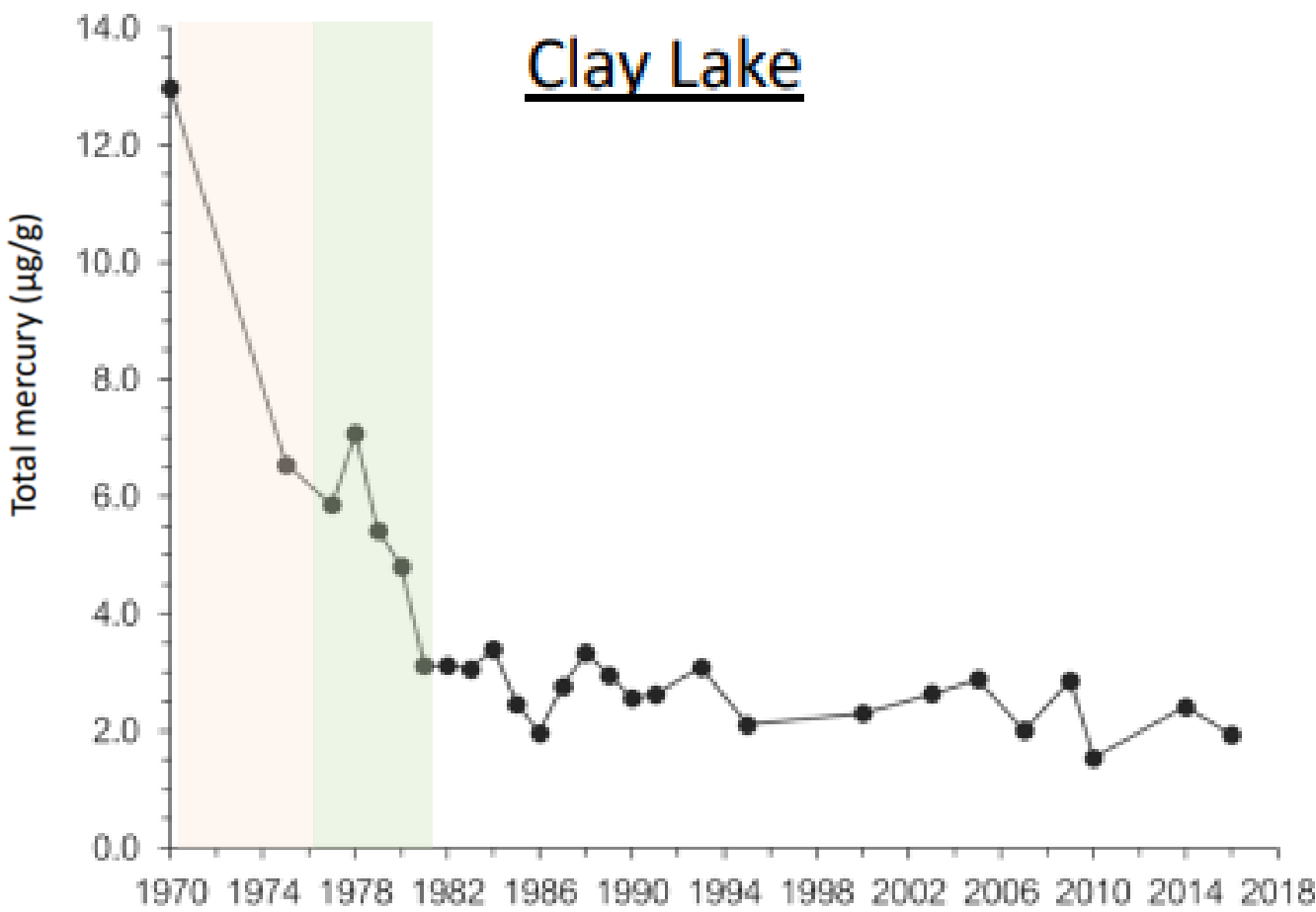


TABLE 7.1. Annual mercury discharges from the chlor-alkali plant, Great Lakes Forest Products Limited, Dryden.

Year	Mercury Loss (kg)
1962-69	1100
1970	350
1971	9.1
1972	2.3
1973	2.1
1974	1.7
1975	2.0
1976	1.2
1977	1.7

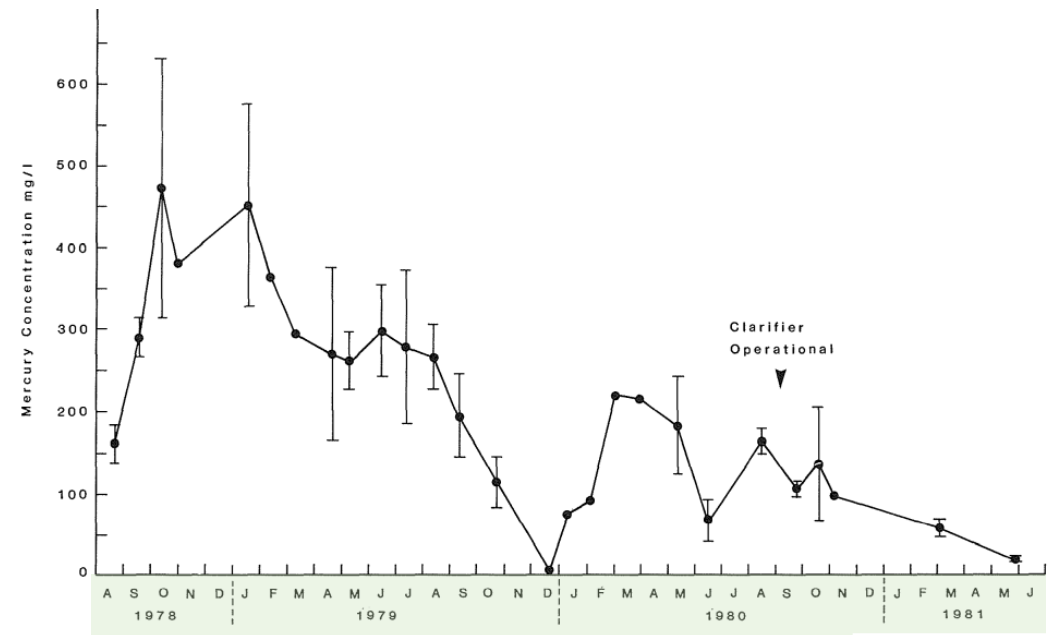


Figure 7.1 Mean monthly mercury concentrations of mill effluent, August, 197

# Waste from mill worsening mercury contamination in river near Grassy Narrows: study



Industrial discharge from a paper mill in northern Ontario is exacerbating mercury contamination in a river system near a First Nation that has been plagued with mercury poisoning for decades, a new study suggests. Grassy Narrows Chief Rudy Turtle holds a sign as he marches with supporters through downtown Toronto in a 2019 handout photo.



## Grassy Narrows chief calls out Ottawa for 'ridiculous' delays to mercury treatment centre construction

Trudeau said 'money is not the objection' to building the centre during 2019 election debate

 [Brett Forester](#) · CBC News · Posted: Feb 16, 2024 12:42 PM EST | Last Updated: February 16



Rudy Turtle, chief of Grassy Narrows First Nation, addresses a rally against mining proposals on First Nations territory in Toronto in July 2023. (Evan Mitsui/CBC)

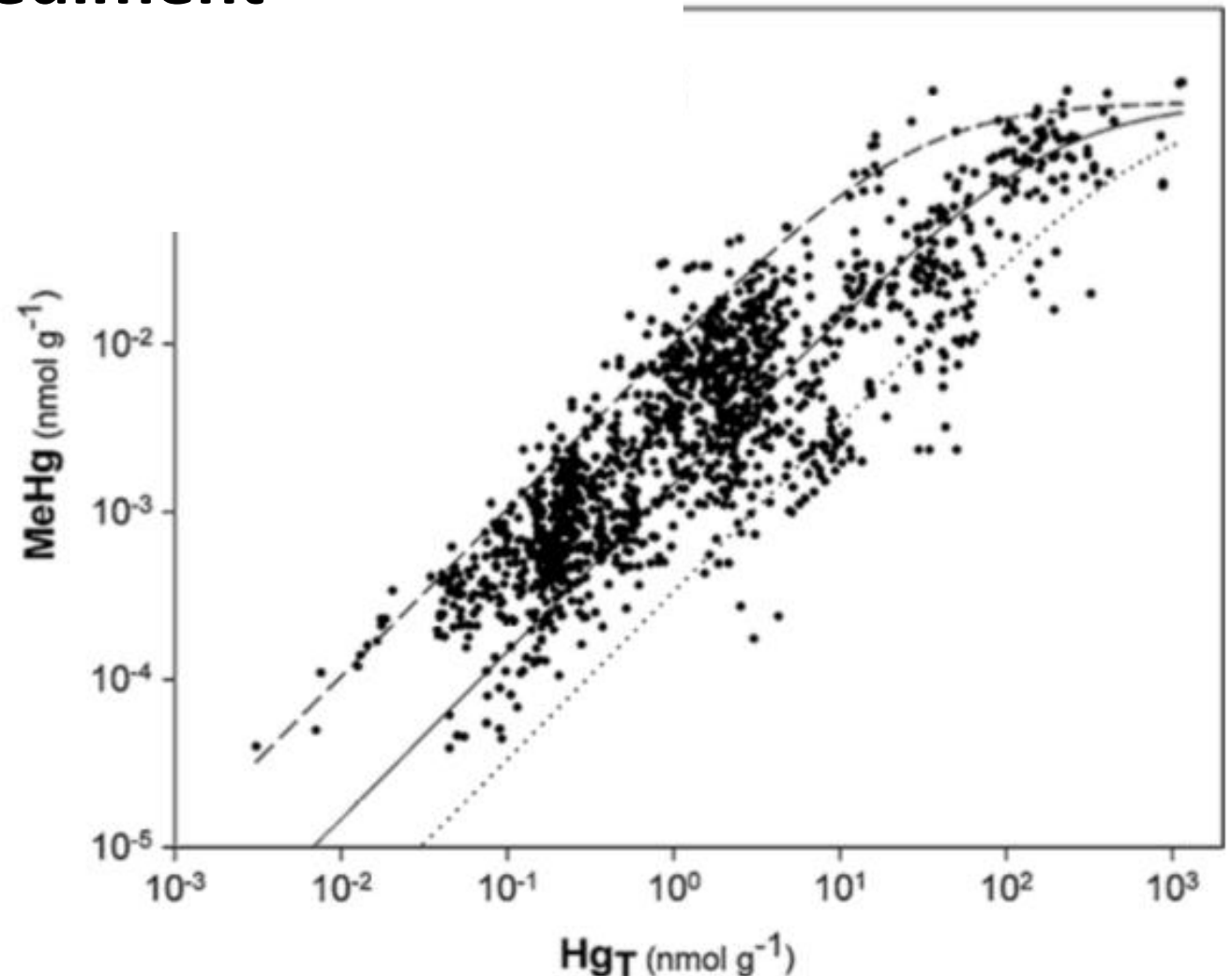




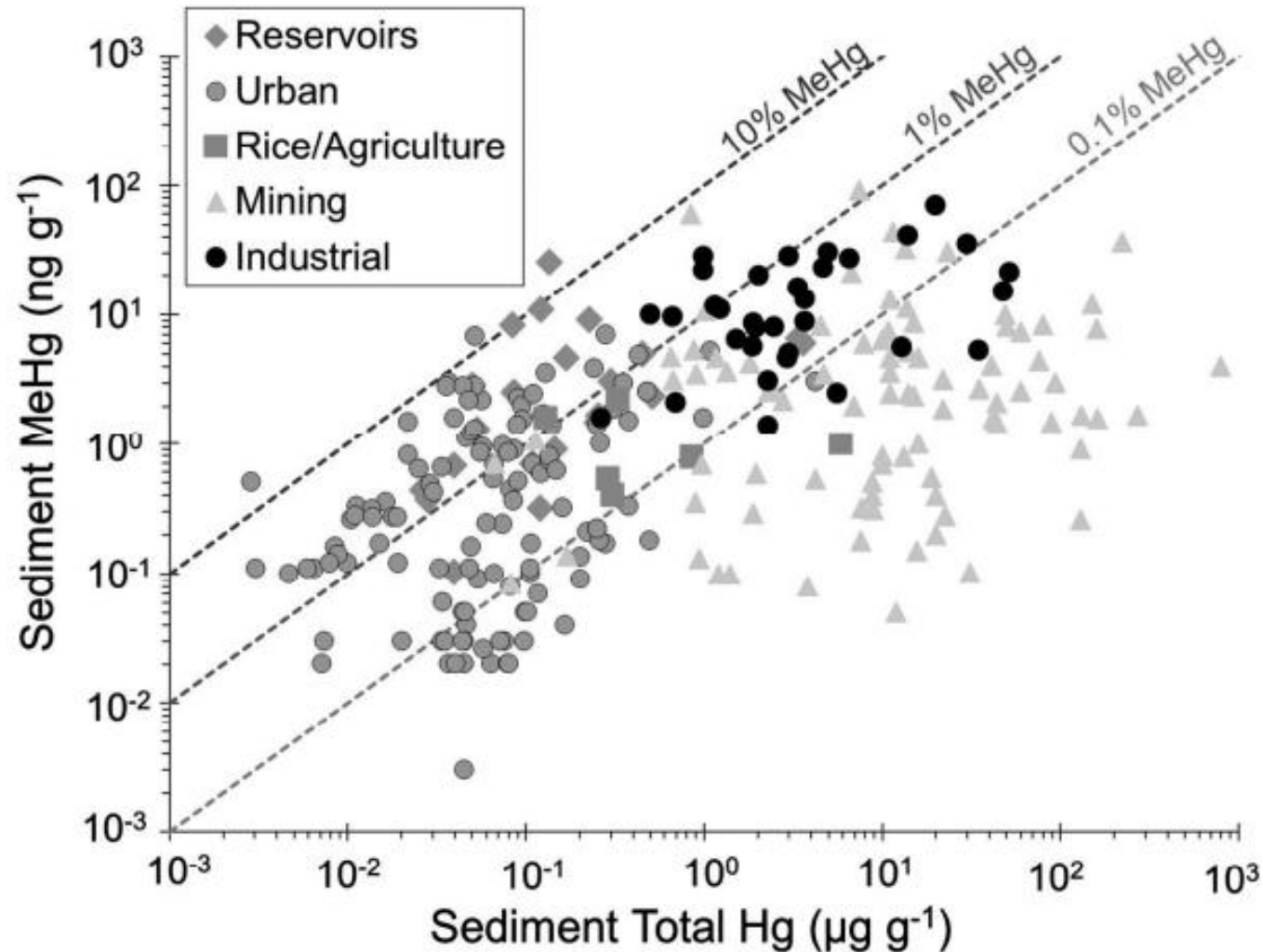
# Relationship between total mercury ( $\text{Hg}_T$ ) and methyl mercury (MeHg) in **sediment**

- 1400 data pairs
- Salinity continuum
- Range in organic carbon concentration and quality
- Range in level of contamination
- Variable sources

Note that the relationship in this graph is descriptive of sampling conditions; it is not predictive of remedial response (meaning: we should be careful of trying to over-specify the extent to which decreasing  $\text{Hg}_T$  necessarily results in predictable declines in MeHg).



# How Do These Data Distribute by Source/Type of Environment?



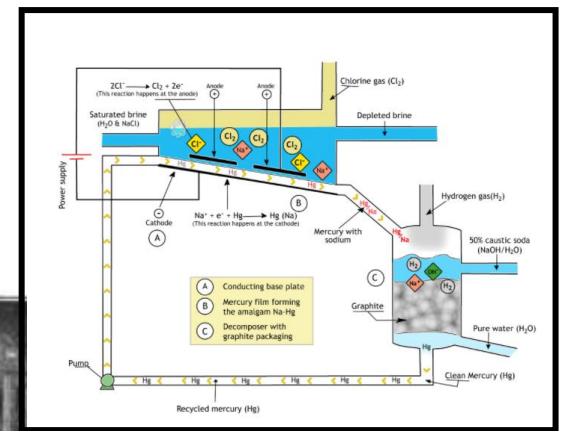
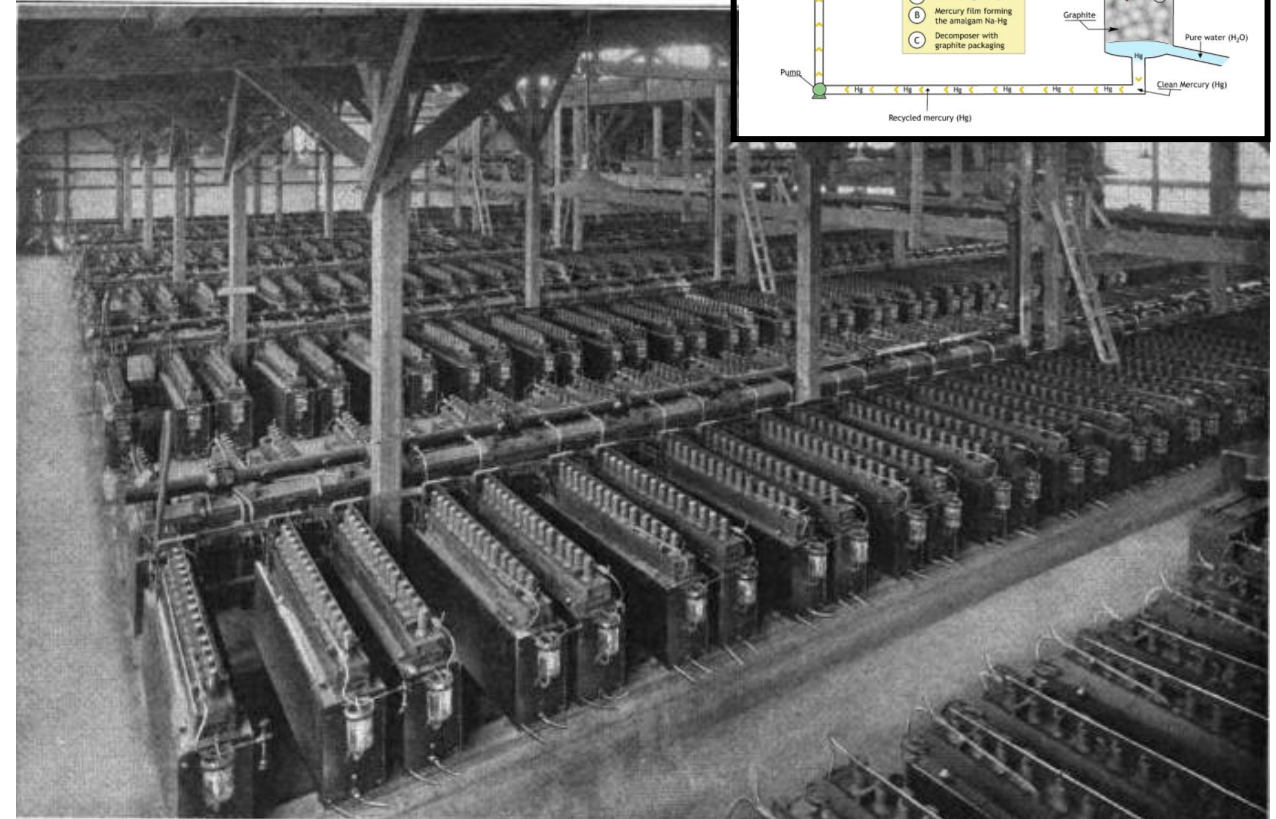
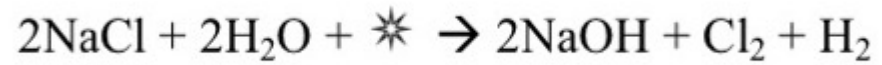
Note that the relationships in this graph are descriptive of sampling conditions; they are not predictive of remedial response (meaning: we should be careful of trying to over-specify the extent to which decreasing  $\text{Hg}_T$  necessarily results in predictable declines in MeHg).







# Mercury cell chlor-alkali process



Facility operations commonly released ~ 10 tons of mercury into adjacent waters (plus unquantified volumes into the atmosphere)



## Locations of Former or Current Mercury Cell Chlor-Alkali Facilities

Acme, NC	Algeria-1
Ashtabula, OH	Algeria-2
Augusta, GA	Angola-1
Bellingham Bay, WA	Libya-1
Berlin, NH	Morocco-1
Brunswick, GA	
Calvert City, KY	Bohus, Sweden
Charleston, TN	Stenungsund, Sweden
Deer Park, TX	Skoghall, Sweden
Delaware City, DE	Domsjö, Sweden
East St. Louis, IL	Koepmanholmen, Sweden
Lake Charles, LA	Sweden-6
Lavaca Bay, TX	Sarpsborg, Norway
Lemoyne, AL	Kokemäenjoki, Finland
Linden, NJ	Oulu, Finland
McIntosh, AL	Aetna, Finland
Midland, MI	Kuusankoski, Finland
Mobile, AL	Pallanza Bay, Italy
Moundsville, WV	Priolo, Italy
Muscle Shoals, AL	Augusta Bay, Italy
New Castle, DE	Montova, Italy
New Martinsville, WV	Tavazzano, Italy
Niagara Falls, NY (x2)	Gela, Italy
<b>Orrington, ME</b>	Saline di Volterra Italy
Port Edwards, WI	Rosignano Solvay, Italy
St. Gabriel, LA	Brescia, Italy
Syracuse, NY	Bussi, Italy
	Pieve Vergonte, Italy
Dalhousie, NB	Volterra, Italy
Saguenay, Quebec	Toreviscosa, Italy
Beauharnois, Quebec	Porto Marghera/Venice, Italy
Marathon, ON	Ravenna, Italy
Cornwall, ON	Hallein, Austria
Samia, ON	Brückl, Austria
Dryden, ON	Vieux-Thann, France
Ontario - 5	Tavaux, France
Port Abercrombie, NS	St. Auban, France
Squamish, BC	Jarrie, France
	Loos, France
Coatzacoalcas-Minatitlán, Mexico	Lavéra, France
García Nuevo León, Mexico	Jemeppe, Belgium
Santa Clara, Mexico	Antwerp, Belgium
Sagua la Grande, Cuba	Tessenderlo, Belgium
Cartagena, Colombia	Linne Herten, Netherlands
Colombia -2	Hengelo, Netherlands
Botafogo River estuary, Brazil	Slovenia -1
Ribeira Bay, Brazil	Slovenia -2
Santos- Cubatão, Brazil	Bosnia - 1
Acari-São João de Meriti River, Brazil	Serbia -1
Cinco Saltos / Upper Negro River, Argentina	Montenegro -1
Bahia Blanca, Argentina	Switzerland-1
Argentina -3	Fermoy, Ireland
Montevideo, Uruguay	Runcorn, UK
Peru-1	Sandbach, UK
Peru-2	Staveley, UK
	Fleetwood, UK

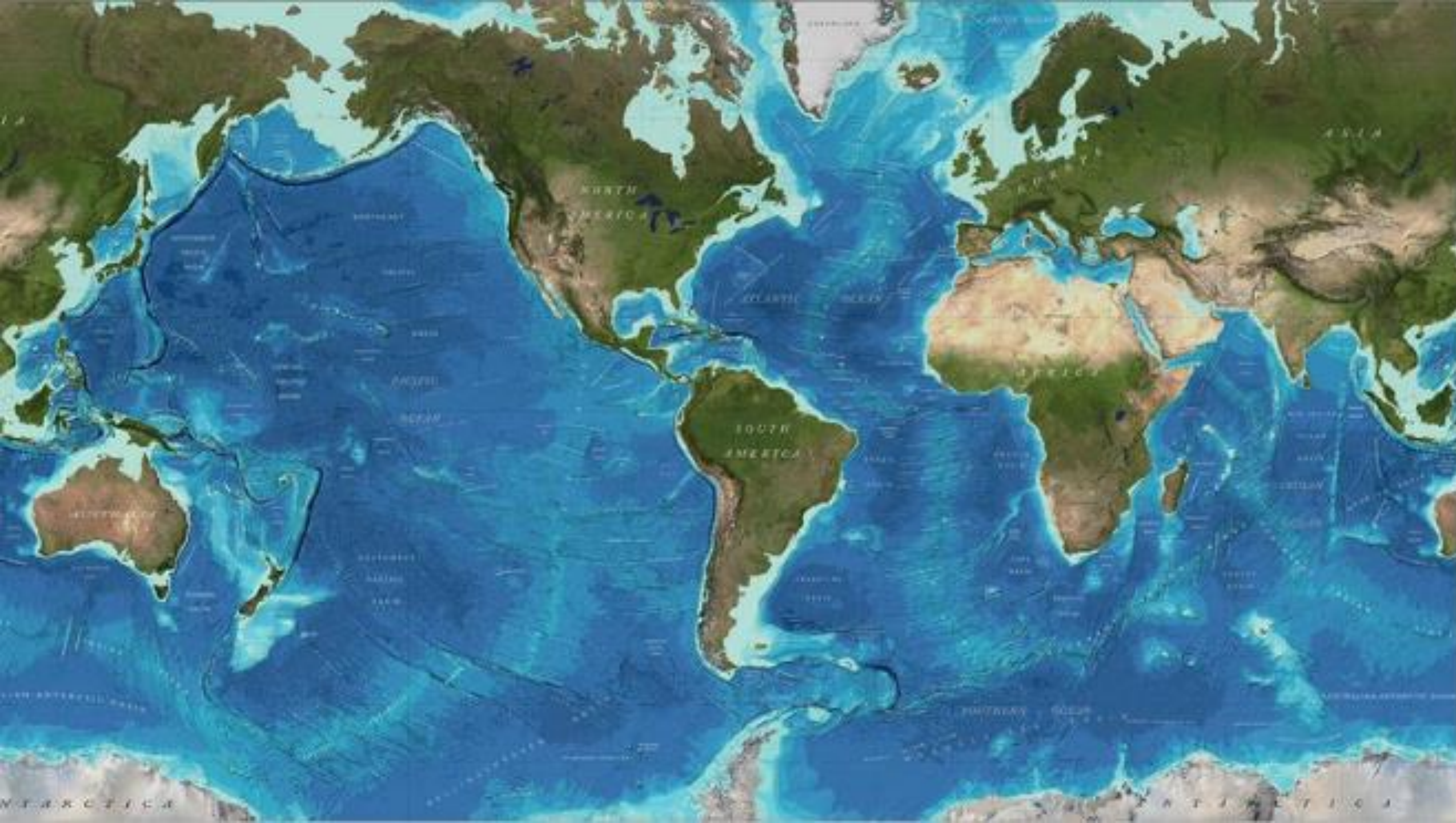
## Locations of Former or Current Mercury Cell Chlor-Alkali Facilities

Ellesmere Port, UK	Komsomolsk-on-Amur, Russia
Torrelavega, Spain	Usolye-Sibirskoye, Russia
Vilaseca, Spain	Koryazhma, Russia
Huelva, Spain	
Flix, Spain	Yavan, Tajikistan
Jodar, Spain	Turkmenistan -1
Monzon, Spain	Sumgait, Azerbaijan
Hernani, Spain	Pavlodar, Kazakhstan
Sabinanigo/Huesca, Spain	Temirtau, Kazakhstan
Povoá de Santa Iria, Portugal	
Ria de Aveiro, Portugal	Bandar Imam, Iran
Thessaloniki, Greece	Kor River site, Iran (?)
Bitterfeld, GR	Iran -3
Burghausen, GR	Iran -4
Dormagen, GR	Iraq -1
Frankfurt, GR	Iraq -2
Gendorf, GR	Iraq -3
Gersthofen, GR	Israel-1
Ibbenbüren, GR	Syria-1
Knapsack, GR	United Arab Emirates-1
Krefeld-Uerdingen, GR	
Lampertheim, GR	Alroli, India
Leverkusen, GR	Mumbai, India
Ludwigshafen, GR	Ganjam, India
Lülsdorf, GR (x2)	Singrauli, India
Marl, GR (x2)	India -5
Marktredwitz, GR	India -6
Rheinfelden, GR	India -7
Schkopau, GR	Kala Shah Kaku, Pakistan
Schkopau, GR	Myanmar -1
Uerdingen, GR	Minamata Bay, Japan
Wilhelmshafen, GR	Niigata, Japan
Neratovice, Czech Republic	Omi, Japan
Ústí nad Labem, Czech Republic	Arai/Kosai, Japan
Pardubice, Czech Republic	Uto, Japan
Nováky, Slovakia	An Ning, China
Tarnów, Poland	Huludao, China
Bydgoszcz, Poland	Tianjin, China
Włocławek, Poland	Yongjing, China
Brzeg Dony, Poland (?)	Qingzhen, China
Varna, Bulgaria	Jilin City, China
Kazincbarcika, Hungary	China-7
Ramnicu Valcea, Romania	China-8
Vlora, Albania	Indonesia-1
Kyiv, Ukraine	Indonesia-2
Kalush, Ukraine (?)	Indonesia-3
	Indonesia-4
Kirovo-Chepetsk, Russia	Indonesia-5
Sterlitamak, Russia (possibly x2)	Philippines-1
Volgograd, Russia (possibly x2)	Hamhung, North Korea
Sayansk, Russia	North Korea-2
Ufa, Russia	
Dzerzhinsk, Russia	
Novodvinsk, Russia	
Chapaevsk, Russia	
Irkutsk, Russia	
	Chlor-Alkali Facility – identified
	Chlor-Alkali Facility– not confirmed
	Acetaldehyde Facility – identified

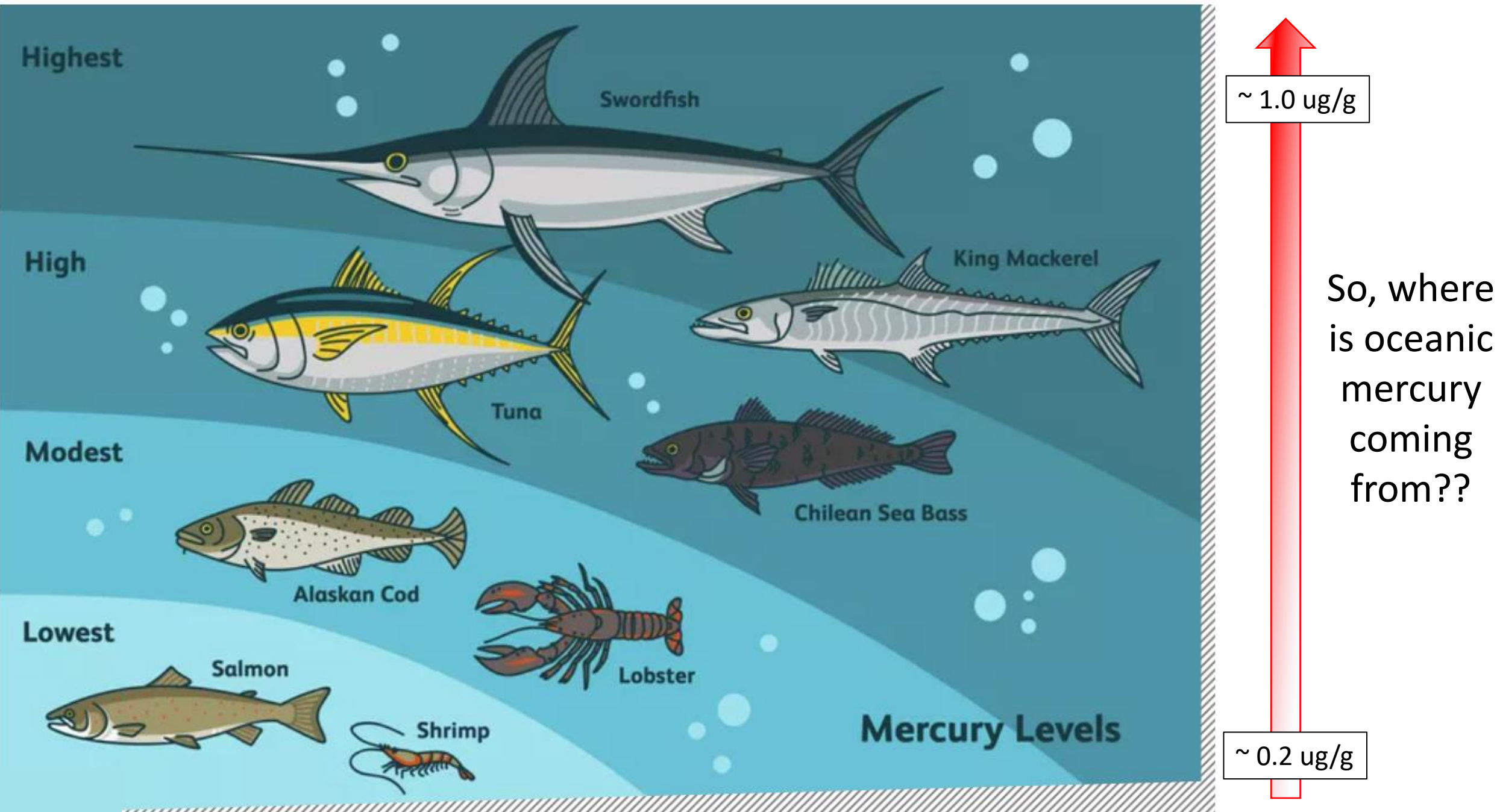
- The **Penobscot River** is the second largest river system in New England
- The estuary is:
  - ~20 miles long
  - 12 ft tidal range
- Seasonally variable discharge:
  - 5000 – 60,000 cfs
- Glaciated terrain and a long narrow river channel upgradient of Frankfort
- A mercury cell chlor-alkali facility operated in the estuary from 1967 – 2000
- Preceding history of wood products industry complicates remediation of the estuary and extends a recovery timeline to 70+ years





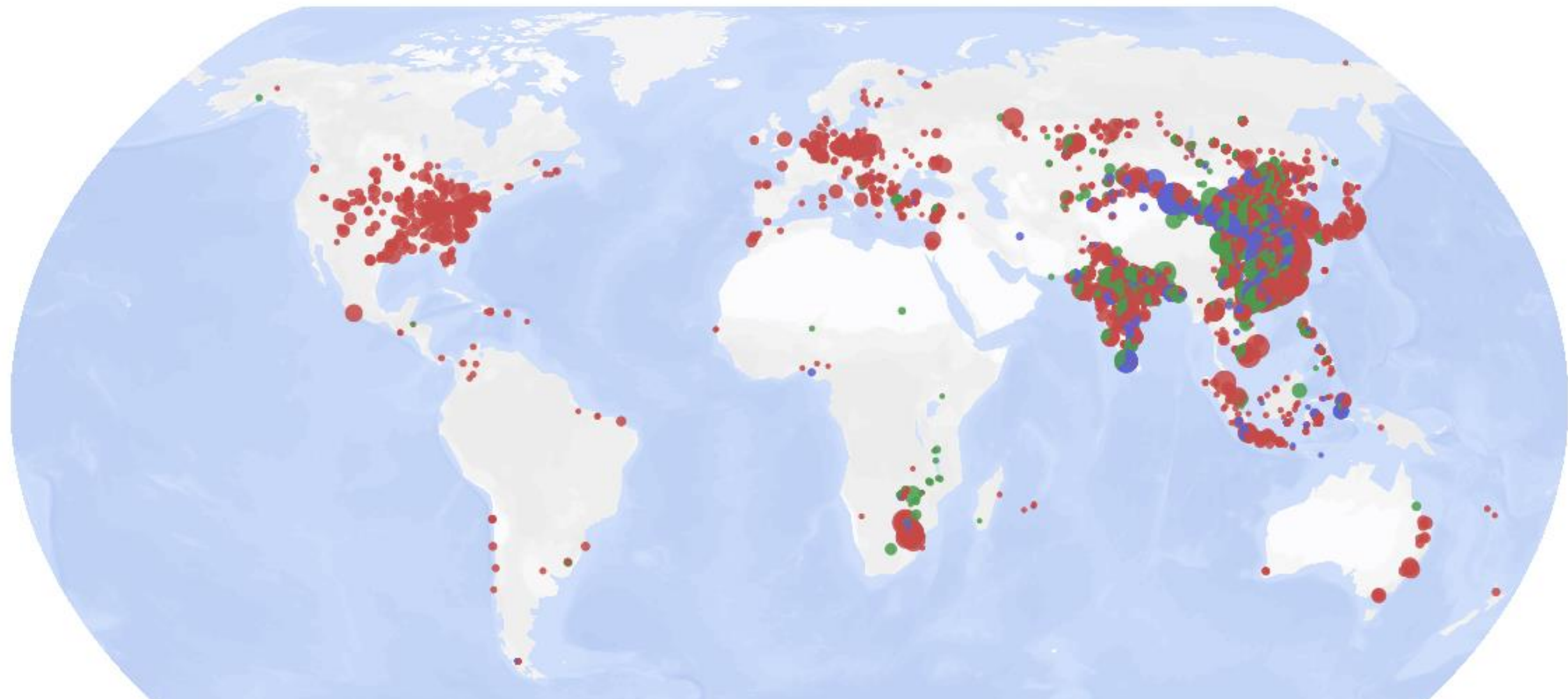










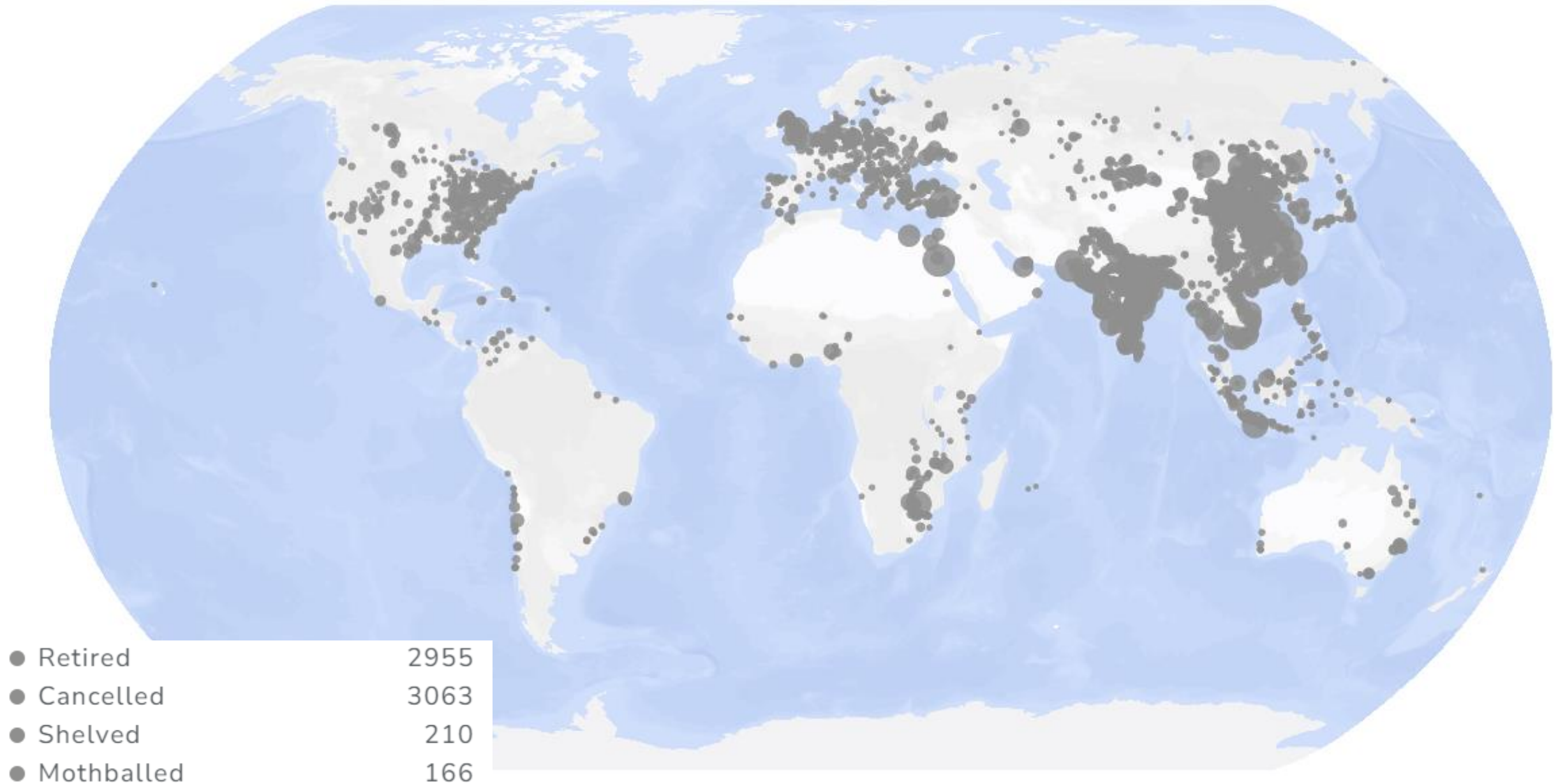


✓	Operating	6525
✓	Construction	421

●	Permitted	254
●	Pre-Permit	229
●	Announced	181



Also...is this what a **tipping point** looks like...?







And on a smaller (individually) but no less dangerous  
(individually AND globally) scale....



### Artisanal and Small-Scale Gold Mining (ASGM)



(gold mining is extraordinarily dangerous for those who  
have to feed their families this way....)





**Serra Pelada, Brazil**

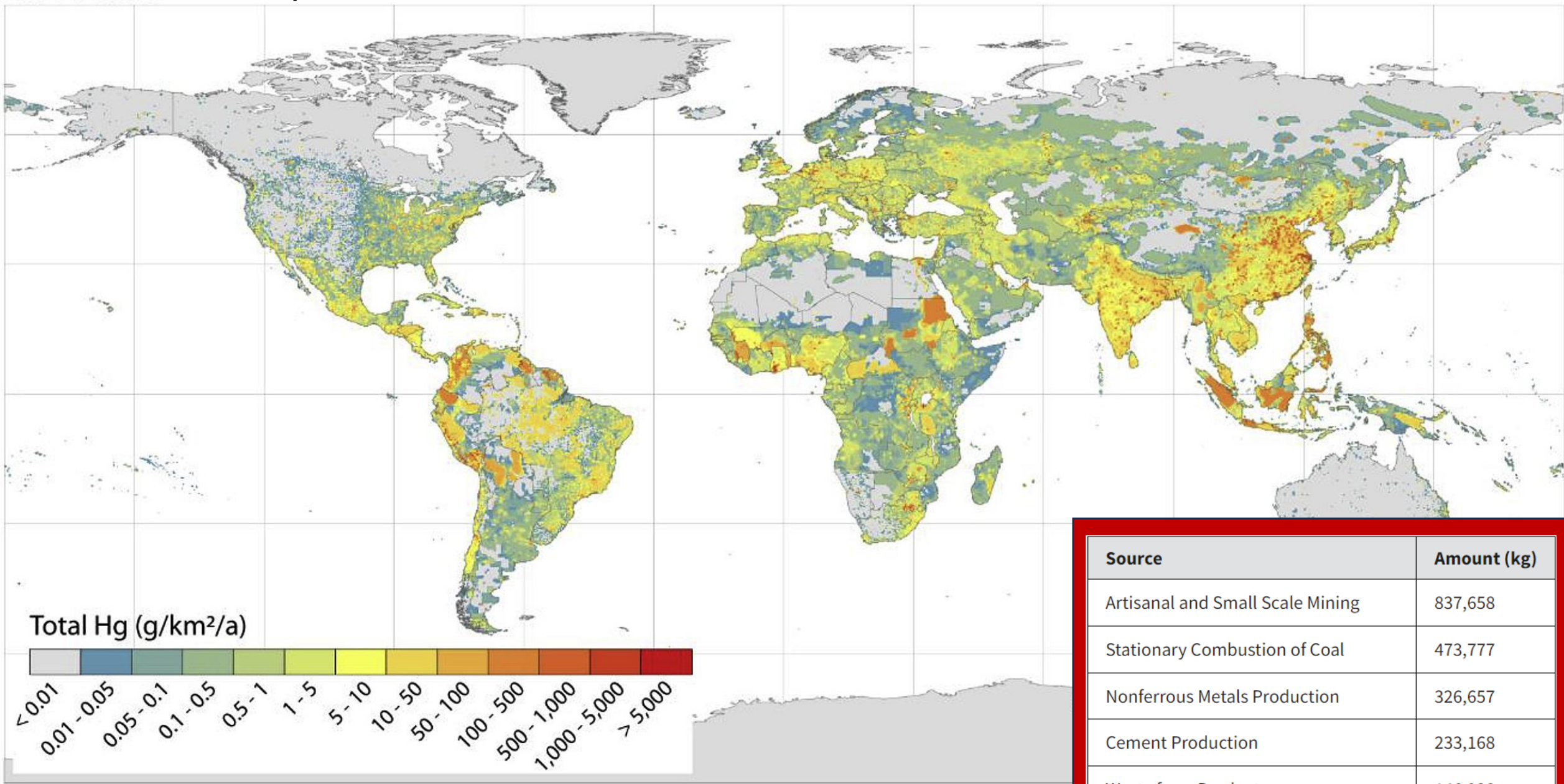
Photographer:  
Sebastiao Salgado  
(1944 - 2025)

1986 – 1989 | gold mine





# All sectors - Atmospheric emissions











## A global ocean inventory of anthropogenic mercury based on water column measurements

Carl H. Lamborg<sup>1</sup>, Chad R. Hammerschmidt<sup>2</sup>, Katlin L. Bowman<sup>2</sup>, Gretchen J. Swarr<sup>1</sup>, Kathleen M. Munson<sup>1</sup>, Daniel C. Ohnemus<sup>1</sup>, Phoebe J. Lam<sup>1</sup>, Lars-Eric Heimbürger<sup>3</sup>, Micha J. A. Rijkenberg<sup>4</sup> & Mak A. Saito<sup>1</sup>

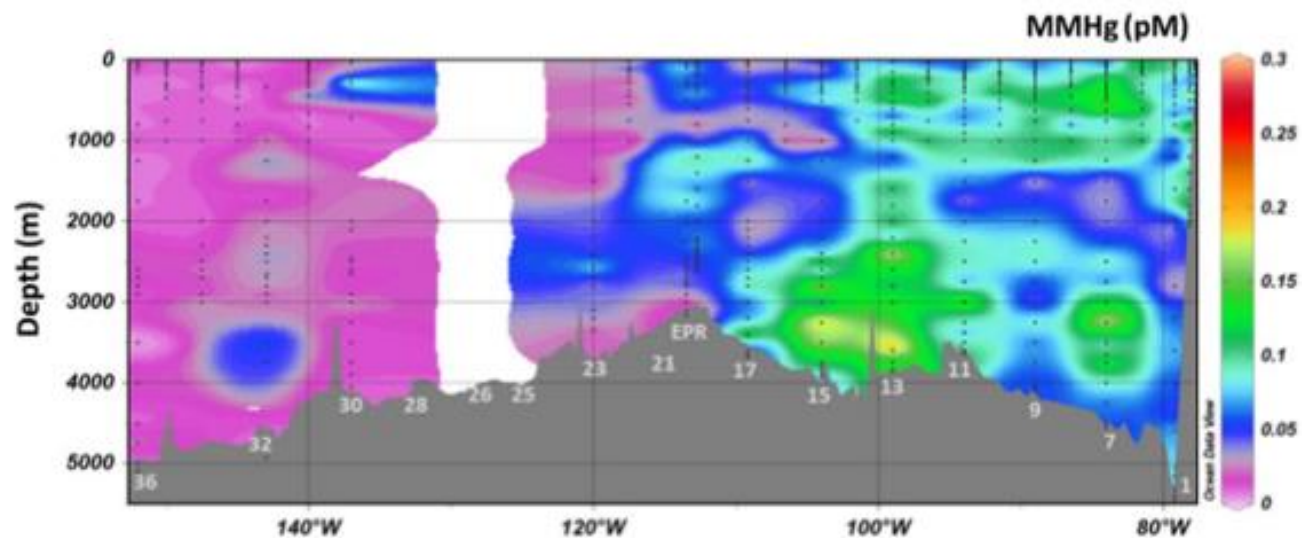
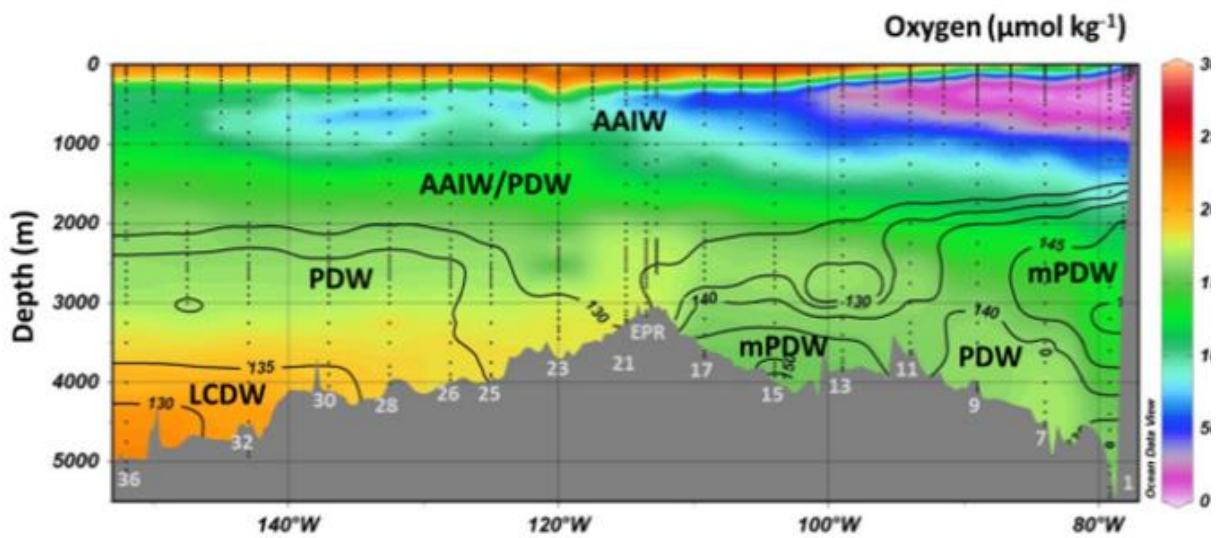
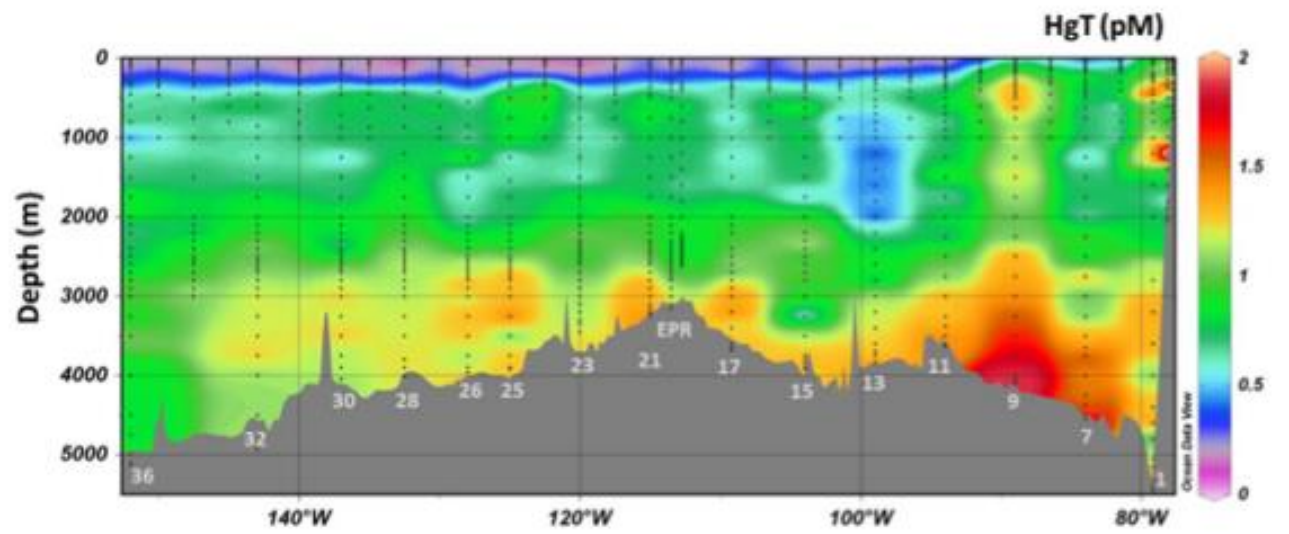
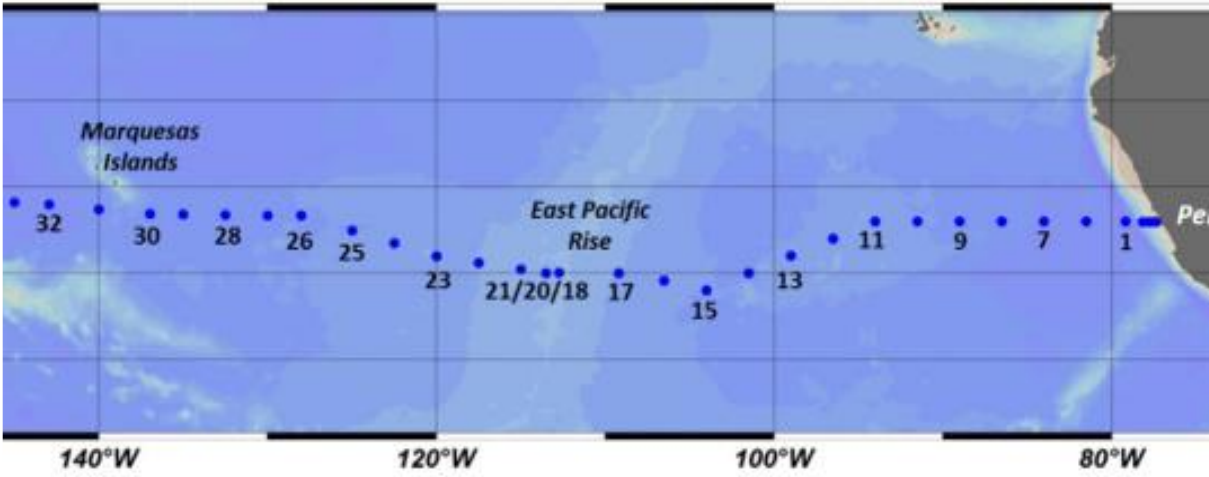
**Abstract** Monomethylmercury ( $\text{CH}_3\text{Hg}$ ) is the only form of mercury (Hg) known to biomagnify in food webs. Here we investigate factors driving methylated mercury [ $\text{MeHg} = \text{CH}_3\text{Hg} + (\text{CH}_3)_2\text{Hg}$ ] production and degradation across the global ocean and uptake and trophic transfer at the base of marine food webs. We develop a new global 3-D simulation of MeHg in seawater and phyto/zooplankton within the Massachusetts Institute of Technology general circulation model. We find that high modeled MeHg concentrations in polar regions are driven by reduced demethylation due to lower solar radiation and colder temperatures. In the eastern tropical subsurface waters of the Atlantic and Pacific Oceans, the model results suggest that high MeHg concentrations are associated with enhanced microbial activity and atmospheric inputs of inorganic Hg. Global budget analysis indicates that upward advection/diffusion from subsurface ocean provides 17% of MeHg in the surface ocean. Modeled open ocean phytoplankton concentrations are relatively uniform because lowest modeled seawater MeHg concentrations occur in oligotrophic regions with the smallest size classes of phytoplankton, with relatively high uptake of MeHg and vice versa. Diatoms and *synechococcus* are the two most important phytoplankton categories for transferring MeHg from seawater to herbivorous zooplankton, contributing 35% and 25%, respectively. Modeled ratios of MeHg concentrations between herbivorous zooplankton and phytoplankton are 0.74–0.78 for picoplankton (i.e., no biomagnification) and 2.6–4.5 for eukaryotic phytoplankton. The spatial distribution of the trophic magnification factor is largely determined by the zooplankton concentrations. Changing ocean biogeochemistry resulting from climate change is expected to have a significant impact on marine MeHg formation and bioaccumulation.

## Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16)

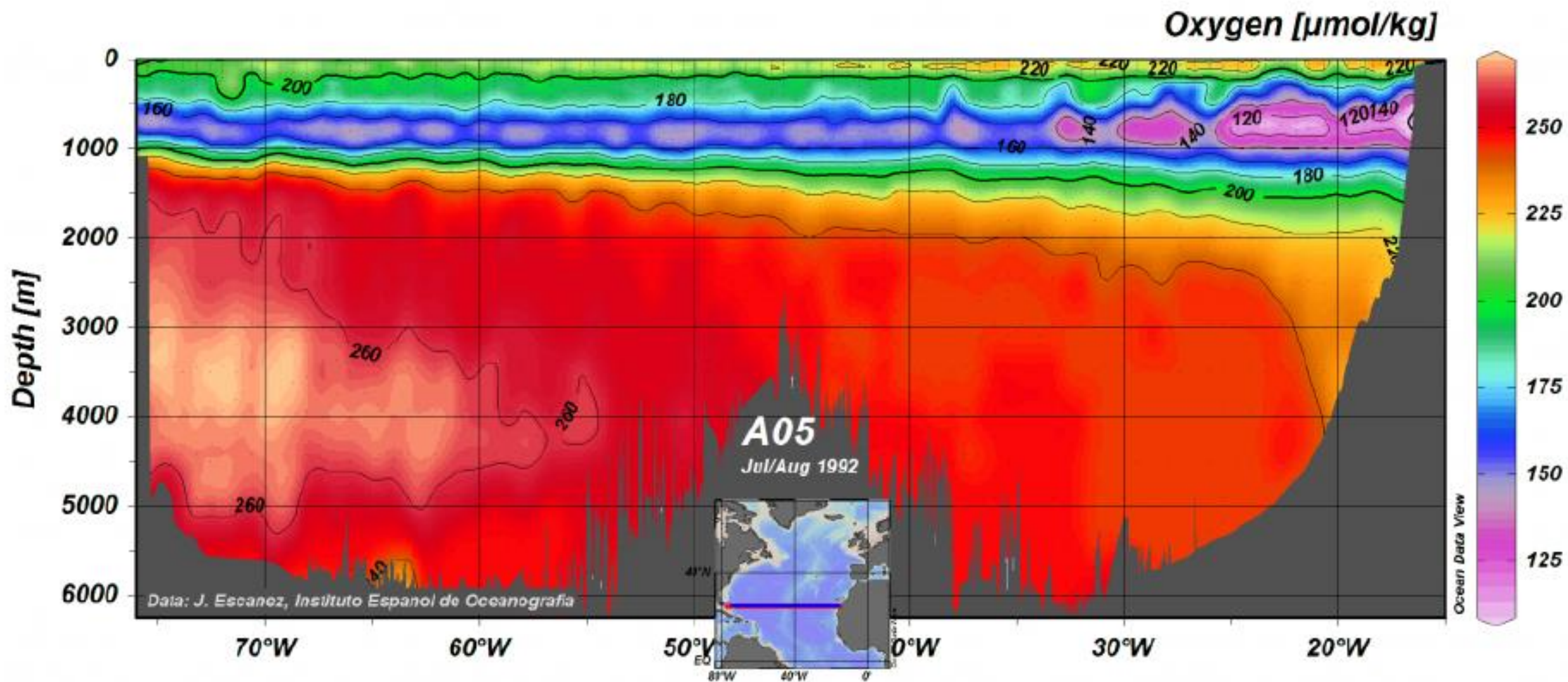
Katlin L. Bowman<sup>a</sup>  , Chad R. Hammerschmidt<sup>a</sup> , Carl H. Lamborg<sup>b 1</sup> ,  
Gretchen J. Swarr<sup>b</sup> , Alison M. Agather<sup>a</sup> 

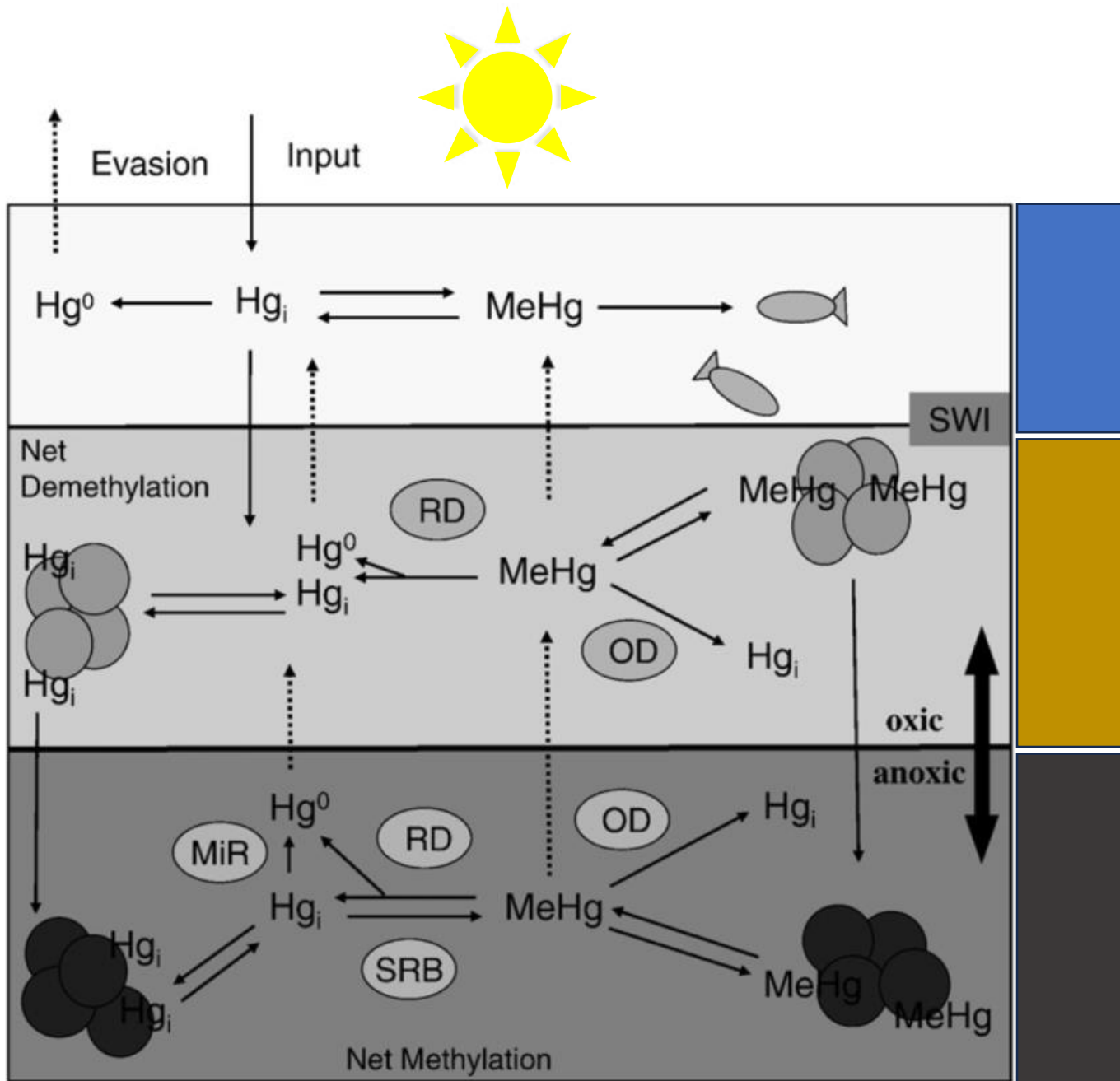
### Highlights

- Total mercury was enriched in the Peru upwelling region and up to 20% of the upwelling flux was as monomethyl-mercury.
- Subsurface maxima of monomethyl-mercury and dimethyl-mercury were found in oxic and suboxic water.
- Methylated mercury concentrations were greatest in the eastern part of the section underlying productive surface waters.
- Mercury was not elevated in a metal-rich hydrothermal vent plume extending 4000km west from the East Pacific Rise.
- Deep water below 2500m was enriched with Hg, especially in warm bottom waters in the eastern part of the section.









- Significant organic matter breakdown consumes dissolved oxygen ( $\text{dO}_2$ );
- Sulfate ( $\text{SO}_4^{2-}$ ) + very low  $\text{dO}_2$  increases activity of sulfate-reducing **bacteria** (SRB);
- SRB in the presence of inorganic mercury ( $\text{Hg}^{2+}$ ) generate methyl mercury ( $\text{CH}_3\text{Hg}^+$ ) as a **by-product of respiration**;
- $\text{CH}_3\text{Hg}^+$  is 100× more toxic than  $\text{Hg}^{2+}$  and is retained in biological tissue to a greater extent than  $\text{Hg}^{2+}$



# PHYSICAL

Thermohaline Circulation  
(+ time since the Industrial  
Revolution and significant  
global increase in coal  
combustion)

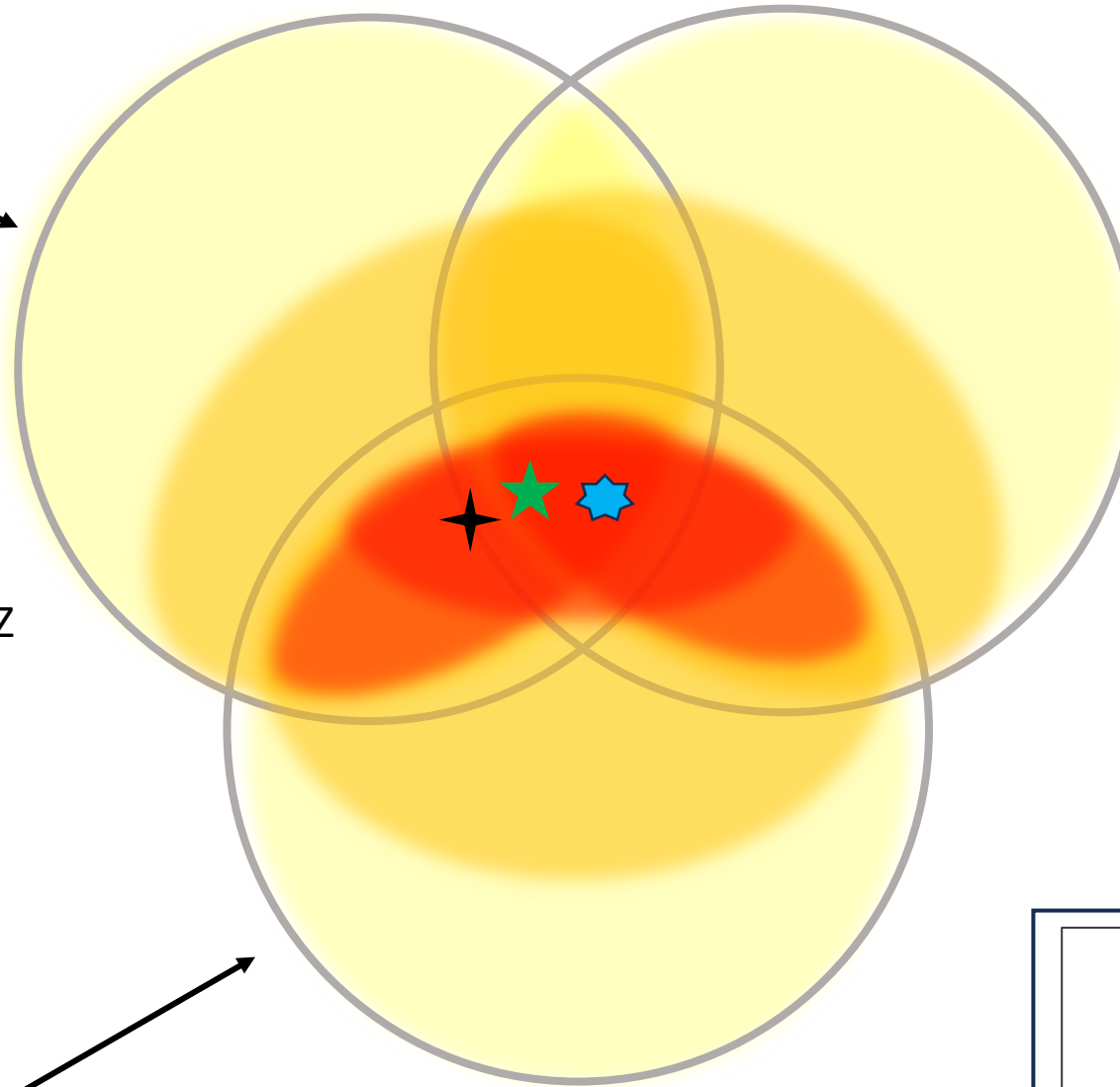
- ✦ = North Atlantic (+ Polar)
- ★ = Upwelling Zones and OMZ
- ✧ = Photic Zone (CMZ)

# CHEMICAL

Factors that contribute BOD  
and result in  $O_2$  consumption  
(there's no shortage of  $SO_4^{2-}$ );  
consider this spatially

# BIOLOGICAL

Single most significant  
bioaccumulation step  
is between water  
column and uptake by  
phytoplankton



Think of this overview of  
risk profiles as describing  
regions of the global ocean  
and considering residence  
time ( $\tau$ ) in the oceans