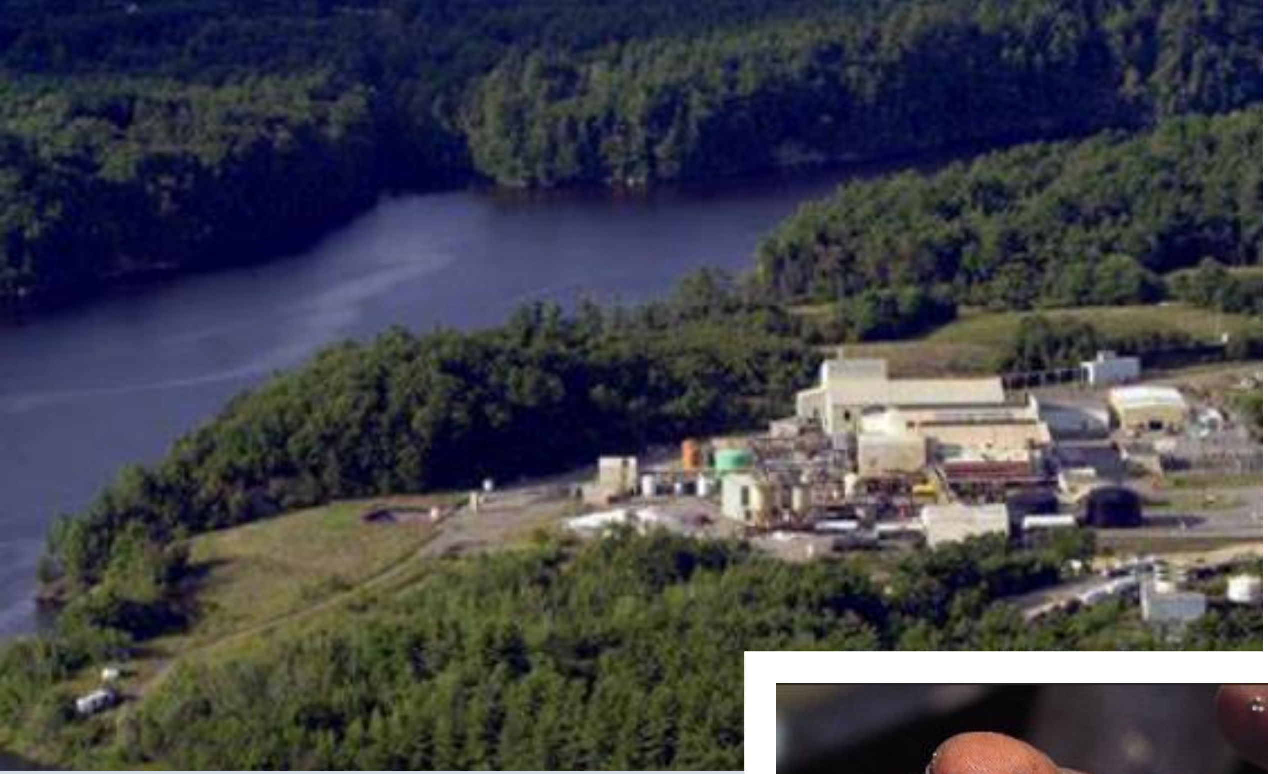
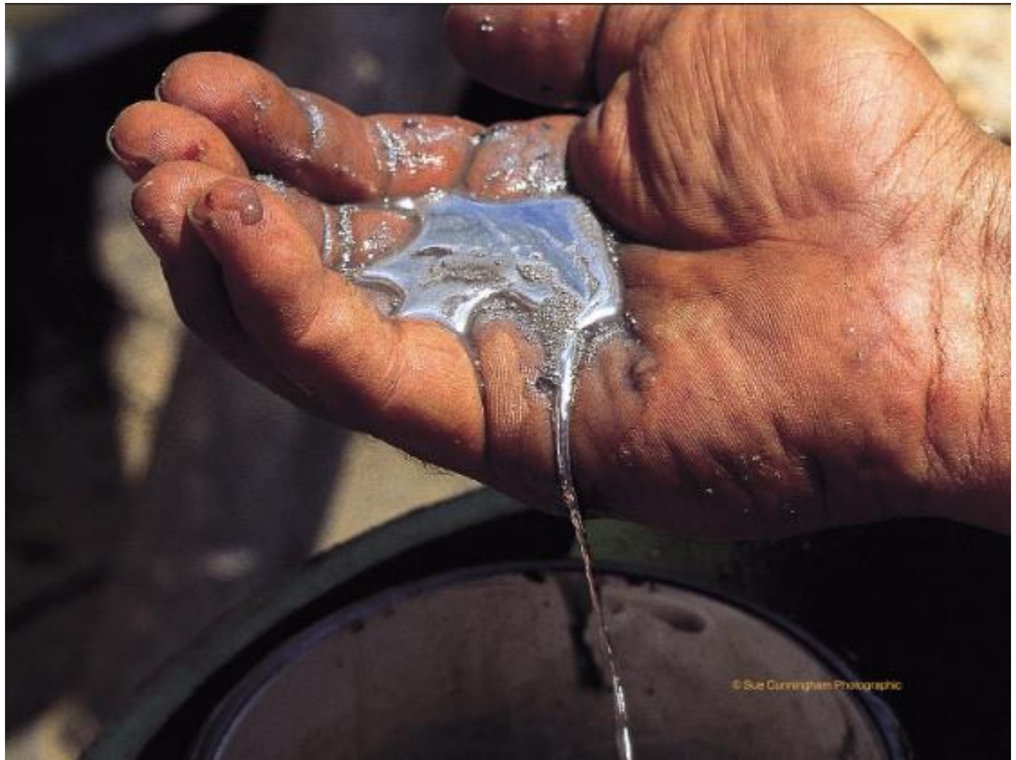


Mercury Pollution in Aquatic Ecosystems

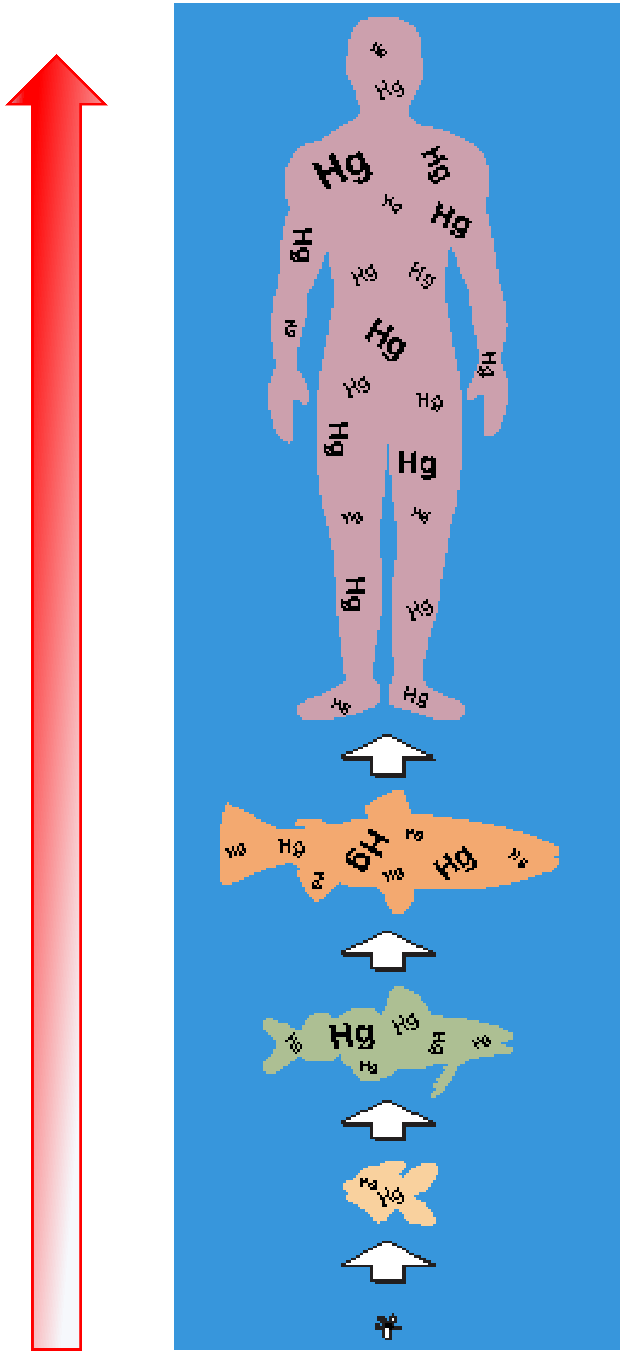


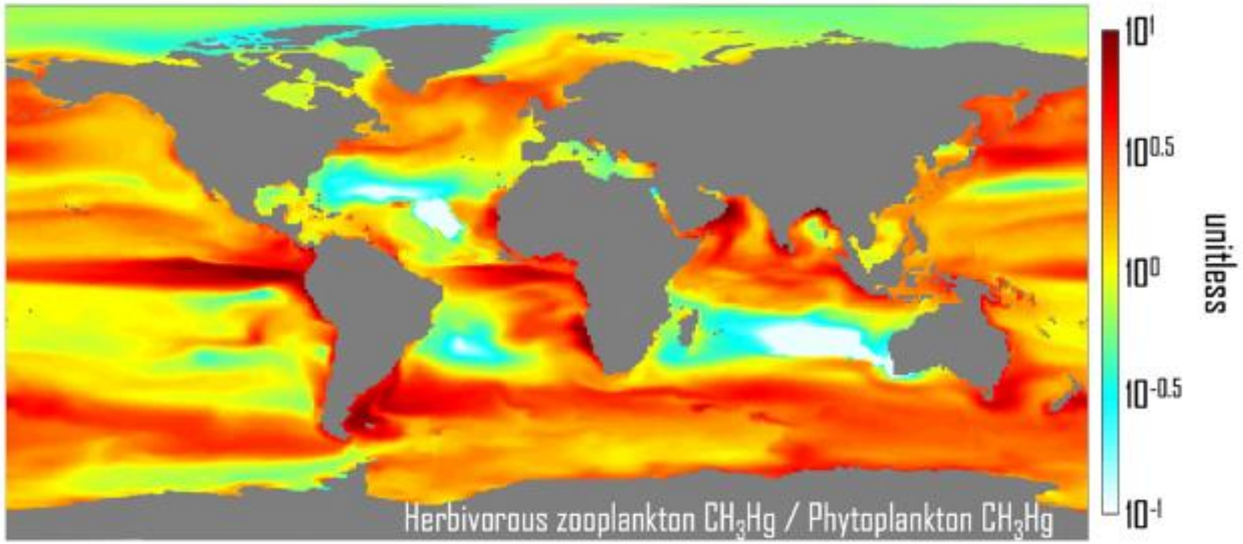
Karen A. Merritt, PhD MPH

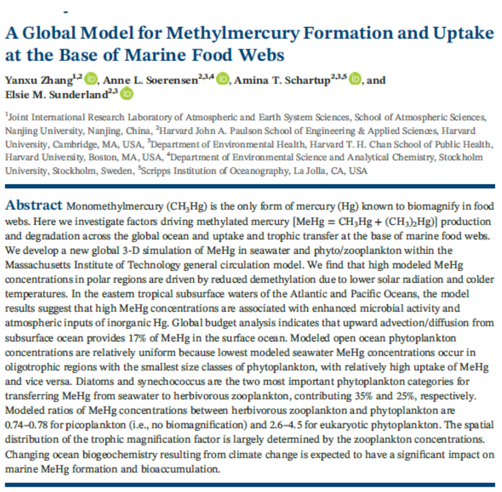
What do we know regarding the biomagnification process?

- Sulfate (SO_4^{2-}) + low-to-no dissolved oxygen (O_2) increases activity of sulfate-reducing bacteria (SRB);
- SRB in the presence of inorganic mercury (Hg^{2+}) generate methyl mercury (CH_3Hg^+) as an accident/by-product of respiration;
- Methyl mercury is retained in biological tissue more significantly than inorganic mercury because of the additional $-CH_3$ (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)

Zhang et al., 2020, https://doi.org/10.1029/2019GB006348





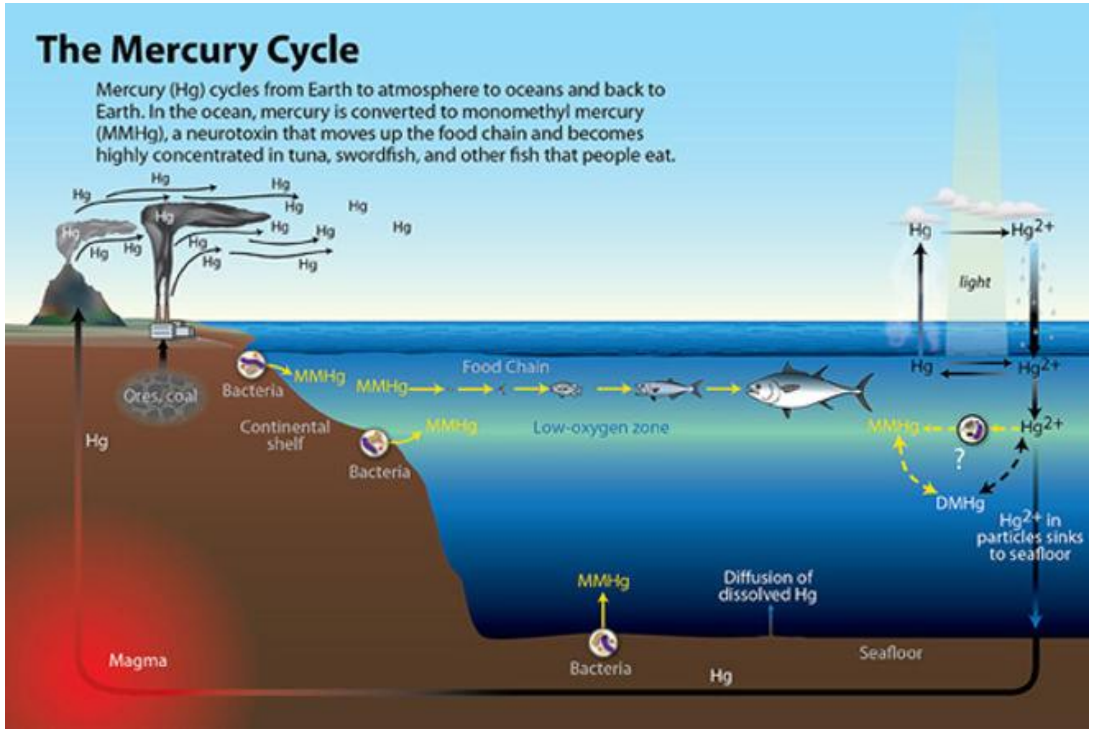


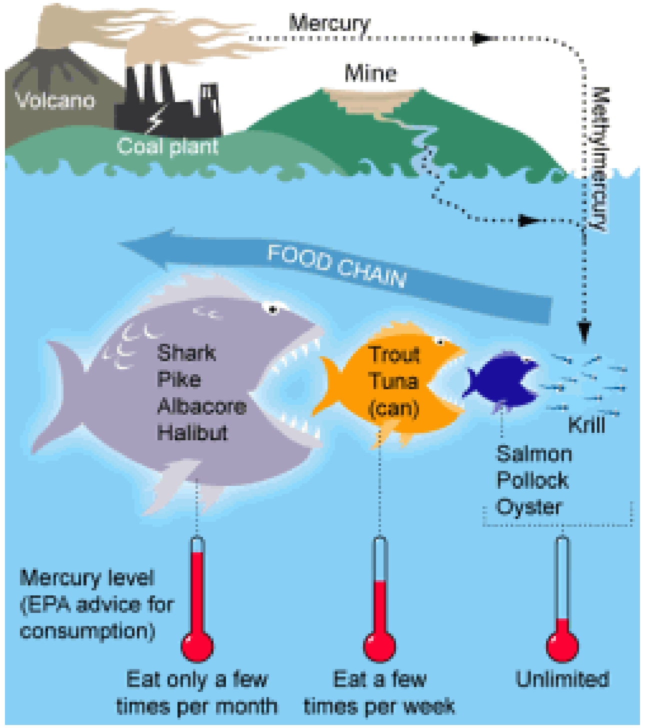
A Global Model for Methylmercury Formation and Uptake at the Base of Marine Food Webs

Yanxu Zhang[1,2], Anne L. Soerensen[2,3,4], Amina T. Schartup[2,3,5], and Elsie M. Sunderland[2,3]

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

Abstract Monomethylmercury (CH_3Hg) is the only form of mercury (Hg) known to biomagnify in food webs. Here we investigate factors driving methylated mercury [$MeHg = CH_3Hg + (CH_3)_2Hg$)] 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.



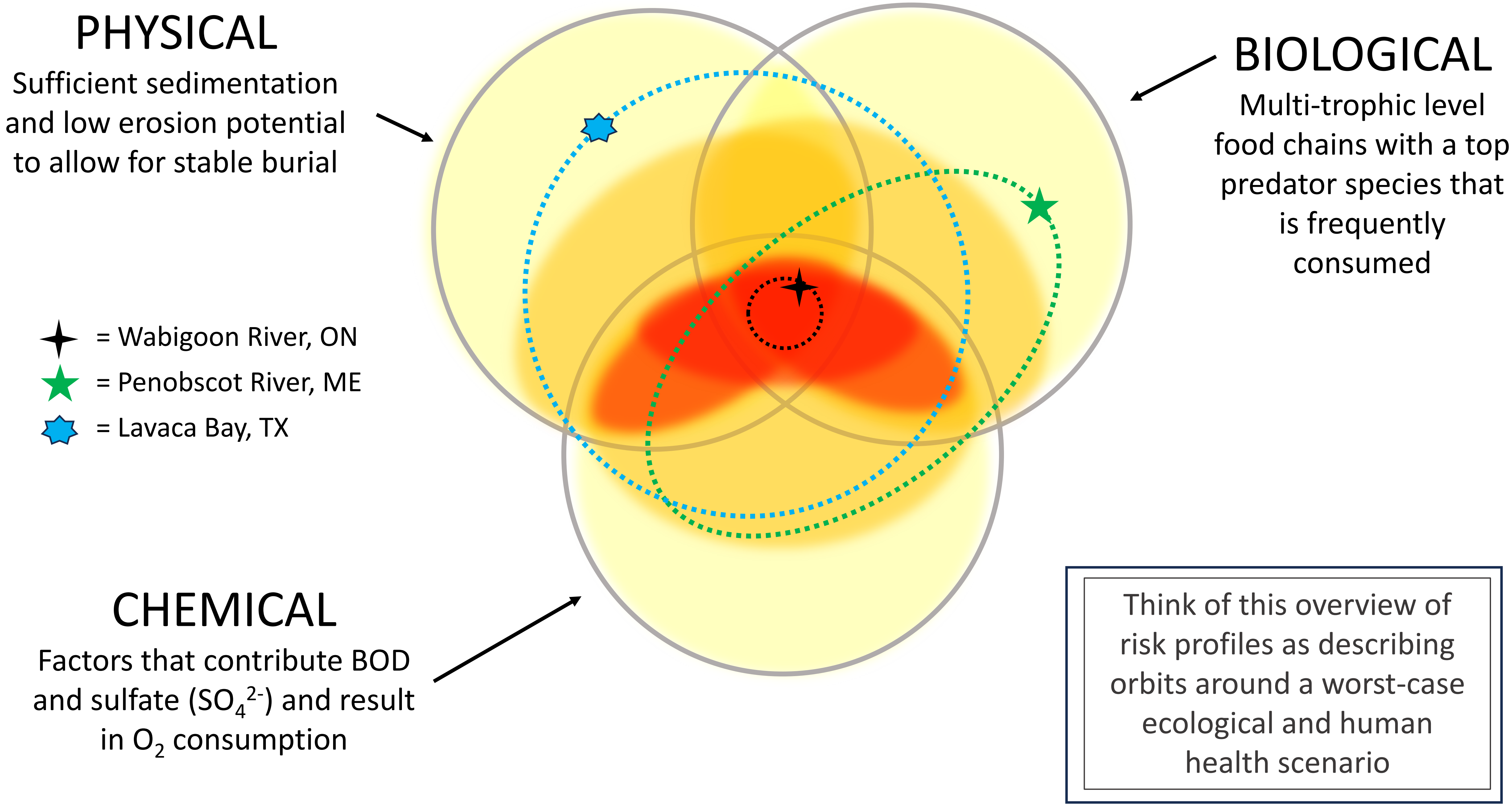


Think about **risk profiles** for different locations in terms of:

- **<u>Physical factors</u>** – 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 to hydrodynamics impact stable burial?

- **<u>Chemical factors</u>** – what factors are present that can create the conditions in which SRB are active? Factors of concern are those that contribute sulfate (SO_4^{2-}) and biochemical oxygen demand (BOD) such that significant O_2 consumption occurs. Factors can be anthropogenic but aren't always.

- **<u>Biological factors</u>** – 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
BIOLOGICAL
Multi-trophic level food chains with a top predator species that is frequently consumed
CHEMICAL
Factors that contribute BOD and sulfate (SO_4^{2-}) and result in O_2 consumption
= Wabigoon River, ON
= Penobscot River, ME
= Lavaca Bay, TX
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 (~ 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 (~ 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 ~ 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.

Walleye (1970 – 2017)

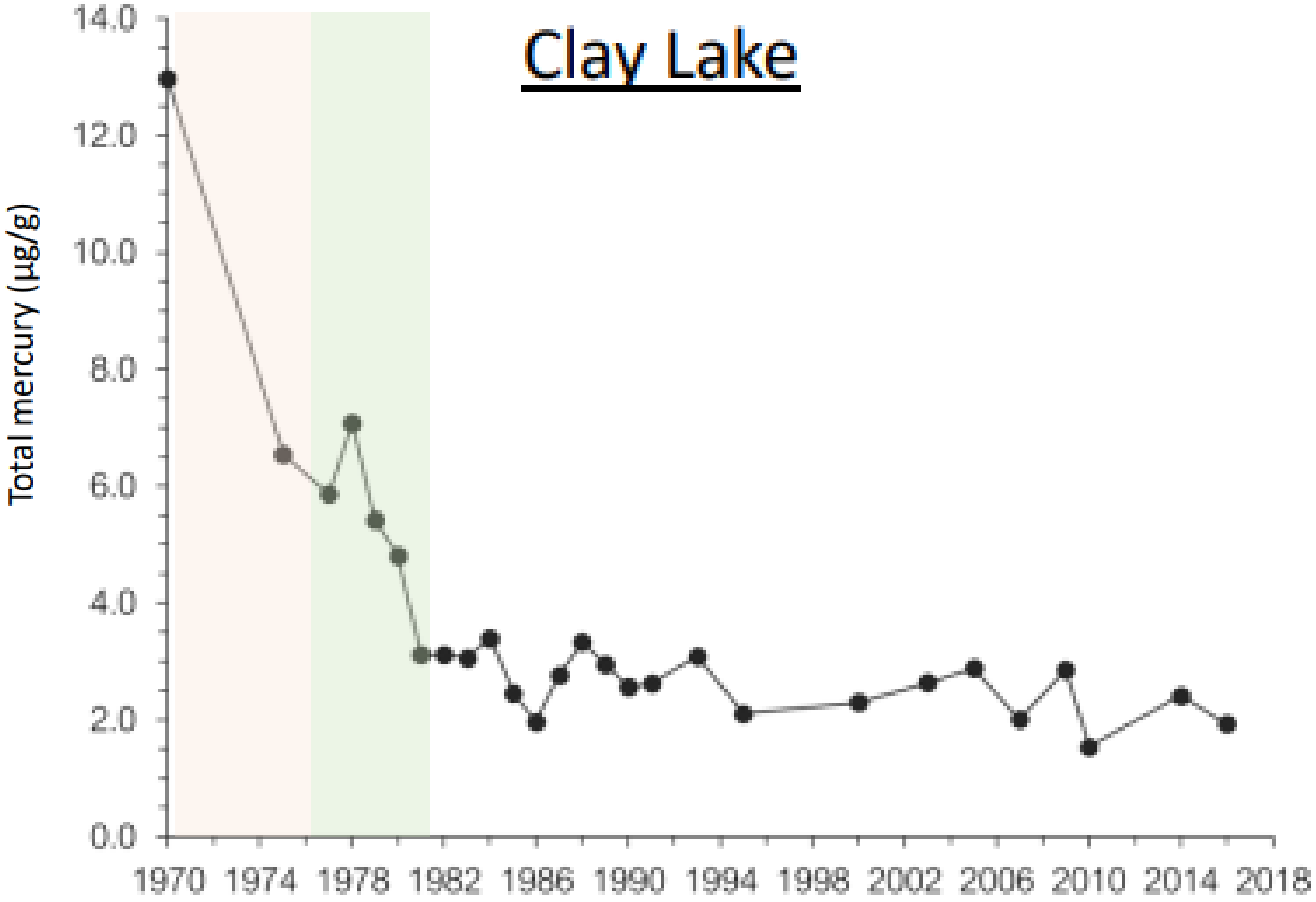


TABLE 7.1. Annual mercury discharges from the chlor-alkali plant, Great Lakes Forest Products Limited, Dryden.

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

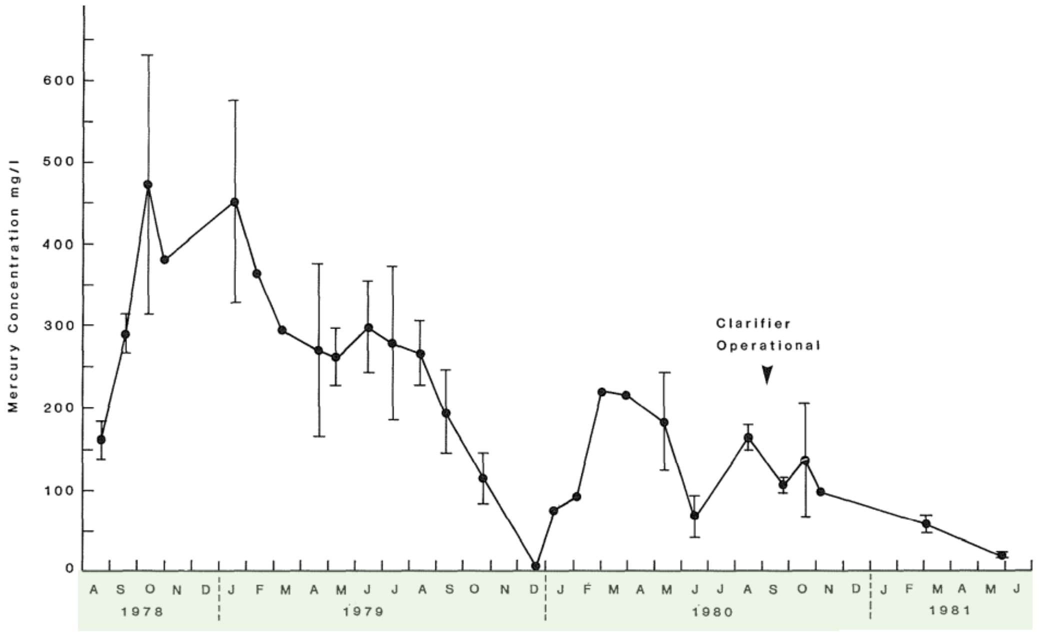


Figure 7.1 Mean monthly mercury concentrations of mill effluent, August, 197

Relationship between total mercury (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 (chlor-alkali, smelters, mine tailings, pipeline fields etc.)

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 Hg_T necessarily results in predictable declines in MeHg).

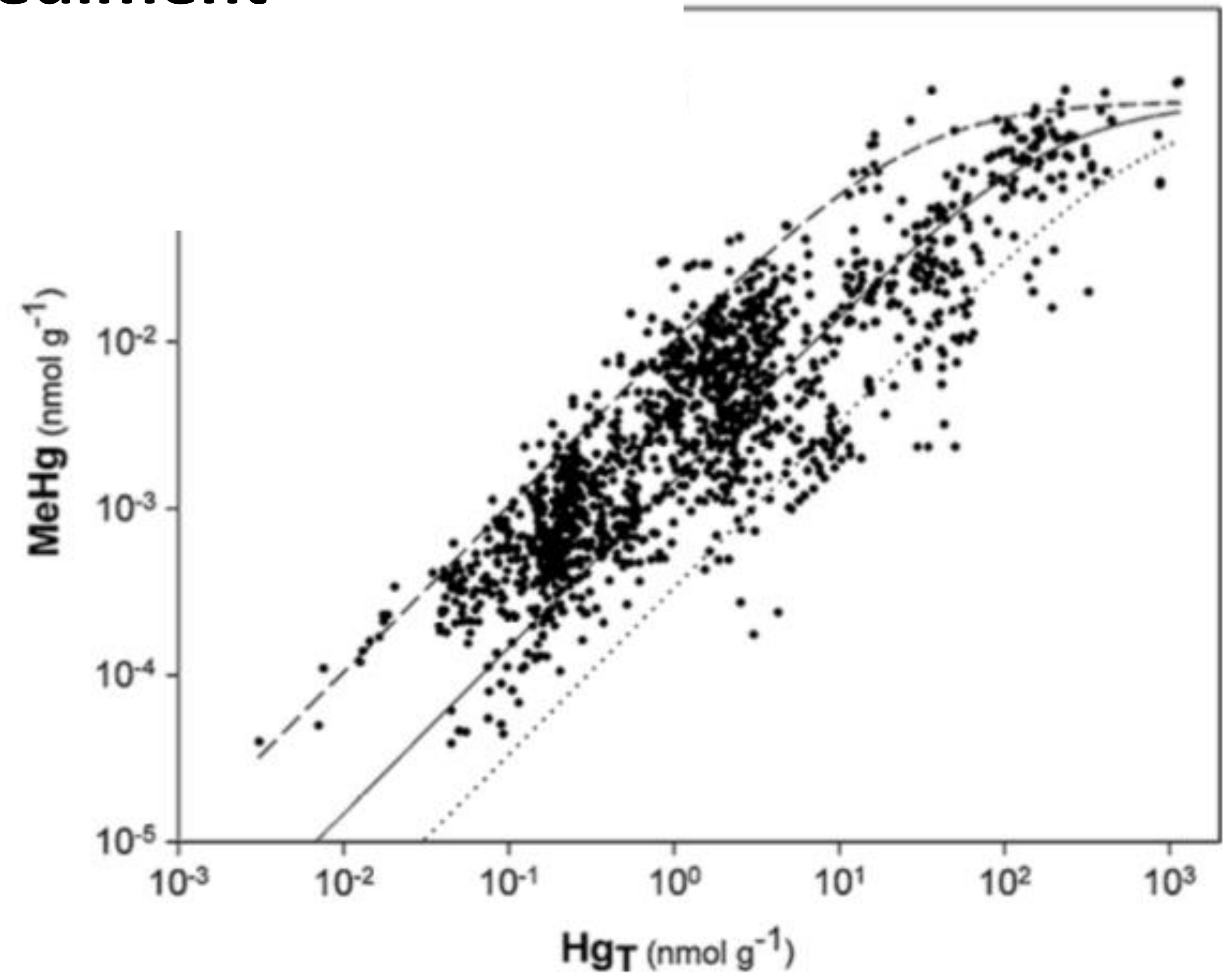
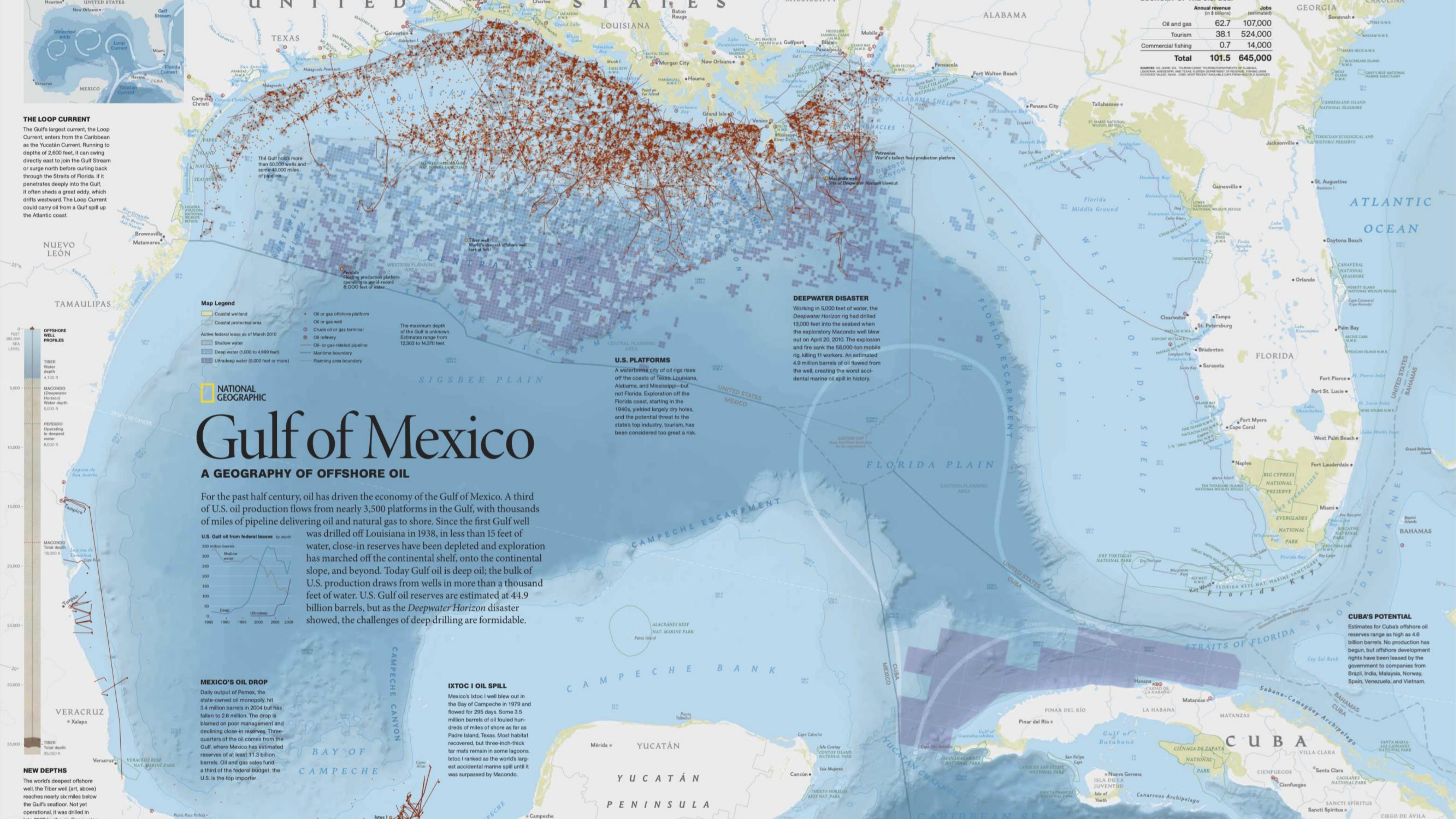


Figure from: Cossa et al. 2013. A Michaelis–Menten type equation for describing methylmercury dependence on inorganic mercury in aquatic sediments. Biogeochemistry. 119, 35–43.



THE LOOP CURRENT

The Gulf's largest current, the Loop Current, enters from the Caribbean as the Yucatán Current. Running to depths of 2,600 feet, it can swing directly east to join the Gulf Stream or surge north before curling back through the Straits of Florida. If it penetrates deeply into the Gulf, it often sheds a great eddy, which drifts westward. The Loop Current could carry oil from a Gulf spill up the Atlantic coast.

	Annual revenue (in $ billions)	Jobs (estimated)
Oil and gas	62.7	107,000
Tourism	38.1	524,000
Commercial fishing	0.7	14,000
Total	**101.5**	**645,000**

SOURCES: OIL (2008): EIA. TOURISM (2008): TOURISM DEPARTMENTS OF ALABAMA, LOUISIANA, MISSISSIPPI, AND TEXAS; FLORIDA DEPARTMENT OF REVENUE. FISHING (2008 DOCKSIDE VALUE): NOAA. JOBS: MOST RECENT AVAILABLE DATA FROM MULTIPLE SOURCES

Map Legend

- Coastal wetland
- Coastal protected area
- Active federal lease as of March 2010
  - Shallow water
  - Deep water (1,000 to 4,999 feet)
  - Ultradeep water (5,000 feet or more)
- Oil or gas offshore platform
- Oil or gas well
- Crude oil or gas terminal
- Oil refinery
- Oil- or gas-related pipeline
- Maritime boundary
- Planning area boundary

The maximum depth of the Gulf is unknown. Estimates range from 12,303 to 14,370 feet.

NATIONAL GEOGRAPHIC

Gulf of Mexico

A GEOGRAPHY OF OFFSHORE OIL

For the past half century, oil has driven the economy of the Gulf of Mexico. A third of U.S. oil production flows from nearly 3,500 platforms in the Gulf, with thousands of miles of pipeline delivering oil and natural gas to shore. Since the first Gulf well was drilled off Louisiana in 1938, in less than 15 feet of water, close-in reserves have been depleted and exploration has marched off the continental shelf, onto the continental slope, and beyond. Today Gulf oil is deep oil; the bulk of U.S. production draws from wells in more than a thousand feet of water. U.S. Gulf oil reserves are estimated at 44.9 billion barrels, but as the *Deepwater Horizon* disaster showed, the challenges of deep drilling are formidable.

DEEPWATER DISASTER

Working in 5,000 feet of water, the *Deepwater Horizon* rig had drilled 13,000 feet into the seabed when the exploratory Macondo well blew out on April 20, 2010. The explosion and fire sank the 58,000-ton mobile rig, killing 11 workers. An estimated 4.9 million barrels of oil flowed from the well, creating the worst accidental marine oil spill in history.

U.S. PLATFORMS

A waterborne city of oil rigs rises off the coasts of Texas, Louisiana, Alabama, and Mississippi—but not Florida. Exploration off the Florida coast, starting in the 1940s, yielded largely dry holes, and the potential threat to the state's top industry, tourism, has been considered too great a risk.

CUBA'S POTENTIAL

Estimates for Cuba's offshore oil reserves range as high as 4.6 billion barrels. No production has begun, but offshore development rights have been leased by the government to companies from Brazil, India, Malaysia, Norway, Spain, Venezuela, and Vietnam.

MEXICO'S OIL DROP

Daily output of Pemex, the state-owned oil monopoly, hit 3.4 million barrels in 2004 but has fallen to 2.6 million. The drop is blamed on poor management and declining close-in reserves. Three-quarters of the oil comes from the Gulf, where Mexico has estimated reserves of at least 11.3 billion barrels. Oil and gas sales fund a third of the federal budget; the U.S. is the top importer.

IXTOC I OIL SPILL

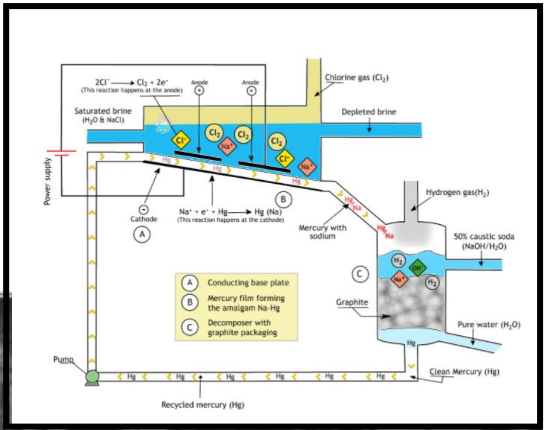
Mexico's Ixtoc I well blew out in the Bay of Campeche in 1979 and flowed for 295 days. Some 3.5 million barrels of oil fouled hundreds of miles of shore as far as Padre Island, Texas. Most habitat recovered, but three-inch-thick tar mats remain in some lagoons. Ixtoc I ranked as the world's largest accidental marine spill until it was surpassed by Macondo.

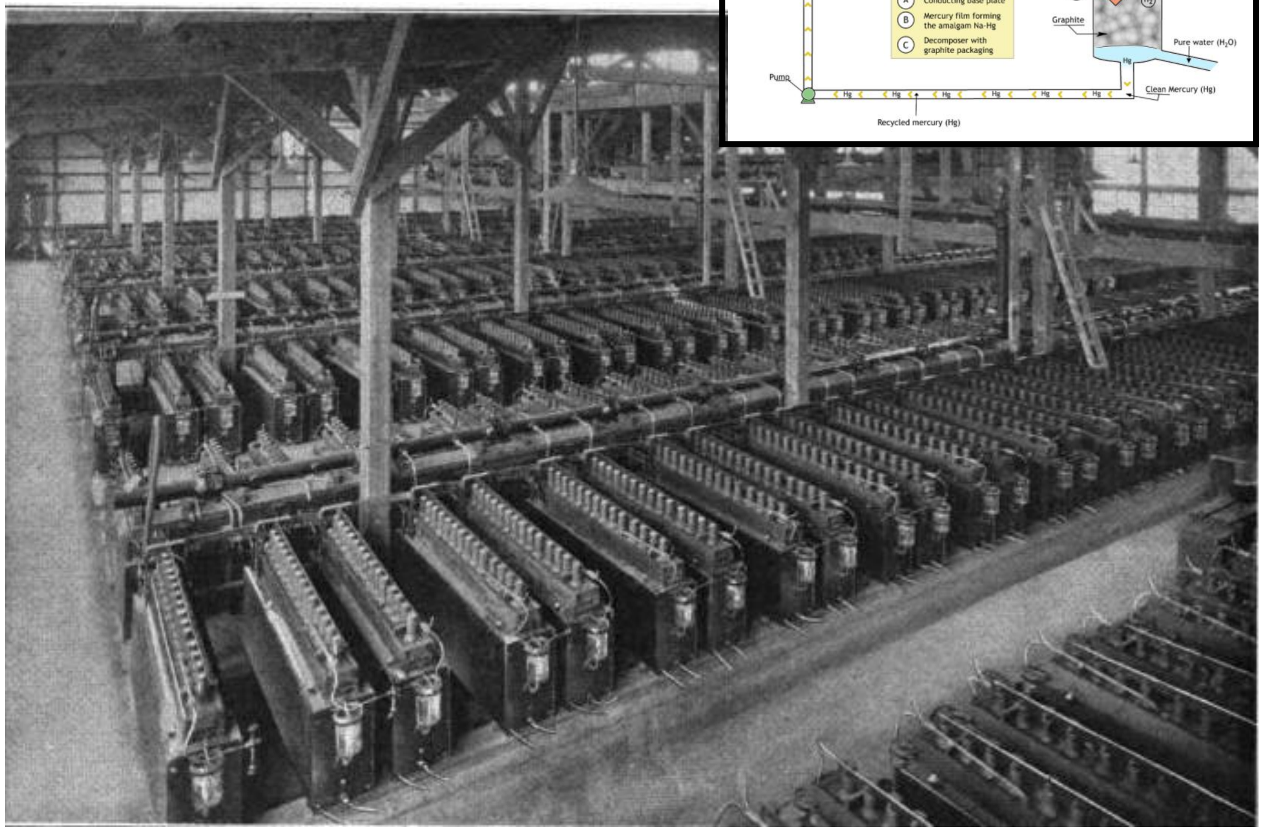
NEW DEPTHS

The world's deepest offshore well, the Tiber well (art, above) reaches nearly six miles below the Gulf's seafloor. Not yet operational, it was drilled in

Mercury cell chlor-alkali process

$$2NaCl + 2H_2O + ✵ \rightarrow 2NaOH + Cl_2 + H_2$$





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
Ashtabula, OH
Augusta, GA
Bellingham Bay, WA
Berlin, NH
Brunswick, GA
Calvert City, KY
Charleston, TN
Deer Park, TX
Delaware City, DE
East St. Louis, IL
Lake Charles, LA
Lavaca Bay, TX
Lemoyne, AL
Linden, NJ
McIntosh, AL
Midland, MI
Mobile, AL
Moundsville, WV
Muscle Shoals, AL
New Castle, DE
New Martinsville, WV
Niagara Falls, NY (×2)
Orrington, ME
Port Edwards, WI
St. Gabriel, LA
Syracuse, NY

Dalhousie, NB
Saguenay, Quebec
Beauharnois, Quebec
Marathon, ON
Cornwall, ON
Sarnia, ON
Dryden, ON
Ontario - 5
Port Abercrombie, NS
Squamish, BC

Coatzacoalcos-Minatitlán, Mexico
Garcia Nuevo León, Mexico
Santa Clara, Mexico
Sagua la Grande, Cuba
Cartagena, Colombia
Colombia -2
Botafogo River estuary, Brazil
Ribeira Bay, Brazil
Santos- Cubatão, Brazil
Acari-São João de Meriti River, Brazil
Cinco Saltos / Upper Negro River, Argentina
Bahia Blanca, Argentina
Argentina -3
Montevideo, Uruguay
Peru-1
Peru-2

Algeria-1
Algeria-2
Angola-1
Libya-1
Morocco-1

Bohus, Sweden
Stenungsund, Sweden
Skoghall, Sweden
Domsjø, Sweden
Koepmanholmen, Sweden
Sweden-6
Sarpsborg, Norway
Kokemäenjoki, Finland
Oulu, Finland
Aetna, Finland
Kuusankoski, Finland
Pallanza Bay, Italy
Priolo, Italy
Augusta Bay, Italy
Montova, Italy
Tavazzano, Italy
Gela, Italy
Saline di Volterra Italy
Rosignano Solvay, Italy
Brescia, Italy
Bussi, Italy
Pieve Vergonte, Italy
Volterra, Italy
Toreviscosa, Italy
Porto Marghera/Venice, Italy
Ravenna, Italy
Hallein, Austria
Brückl, Austria
Vieux-Thann, France
Tavaux, France
St. Auban, France
Jarrie, France
Loos, France
Lavéra, France
Jemeppe, Belgium
Antwerp, Belgium
Tessenderlo, Belgium
Linne Herten, Netherlands
Hengelo, Netherlands
Slovenia -1
Slovenia -2
Bosnia - 1
Serbia -1
Montenegro -1
Switzerland-1
Fermoy, Ireland
Runcorn, UK
Sandbach, UK
Staveley, UK
Fleetwood, UK

Locations of Former or Current Mercury Cell Chlor-Alkali Facilities

Ellesmere Port, UK
Torrelavega, Spain
Vilaseca, Spain
Huelva, Spain
Flix, Spain
Jodar, Spain
Monzon, Spain
Hernani, Spain
Sabinanigo/Huesca, Spain
Povoa de Santa Ir. , Portugal
Ria de Aveiro, Portugal
Thessaloniki, Greece
Bitterfeld, GR
Burghausen, GR
Dormagen, GR
Frankfurt, GR
Gendorf, GR
Gersthofen, GR
Ibbenbüren, GR
Knapsack, GR
Krefeld-Uerdingen, GR
Lampertheim, GR
Leverkusen, GR
Ludwigshafen, GR
Lülsdorf, GR (×2)
Marl, GR (×2)
Marktredwitz, GR
Rheinfelden, GR
Schkopau, GR
Schkopau, GR
Uerdingen, GR
Wilhelmshafen, GR
Neratovice, Czech Republic
Ústi nad Labem, Czech Republic
Pardubice, Czech Republic
Nováky, Slovakia
Tarnów, Poland
Bydgoszcz, Poland
Włocławek, Poland
Brzeg Dony, Poland (?)
Varna, Bulgaria
Kazincbarcika, Hungary
Ramnicu Valcea, Romania
Vlora, Albania
Kyiv, Ukraine
Kalush, Ukraine (?)

Kirovo-Chepetsk, Russia
Sterlitamak, Russia (possibly ×2)
Volgograd, Russia (possibly ×2)
Sayansk, Russia
Ufa, Russia
Dzerzhinsk, Russia
Novodvinsk, Russia
Chapaevsk, Russia
Irkutsk, Russia

Komsomolsk-on-Amur, Russia
Usolye-Sibirskoye, Russia
Koryazhma, Russia

Yavan, Tajikistan
Turkmenistan -1
Sumgait, Azerbajain
Pavlodar, Kazakhstan
Temirtau, Kazakhstan

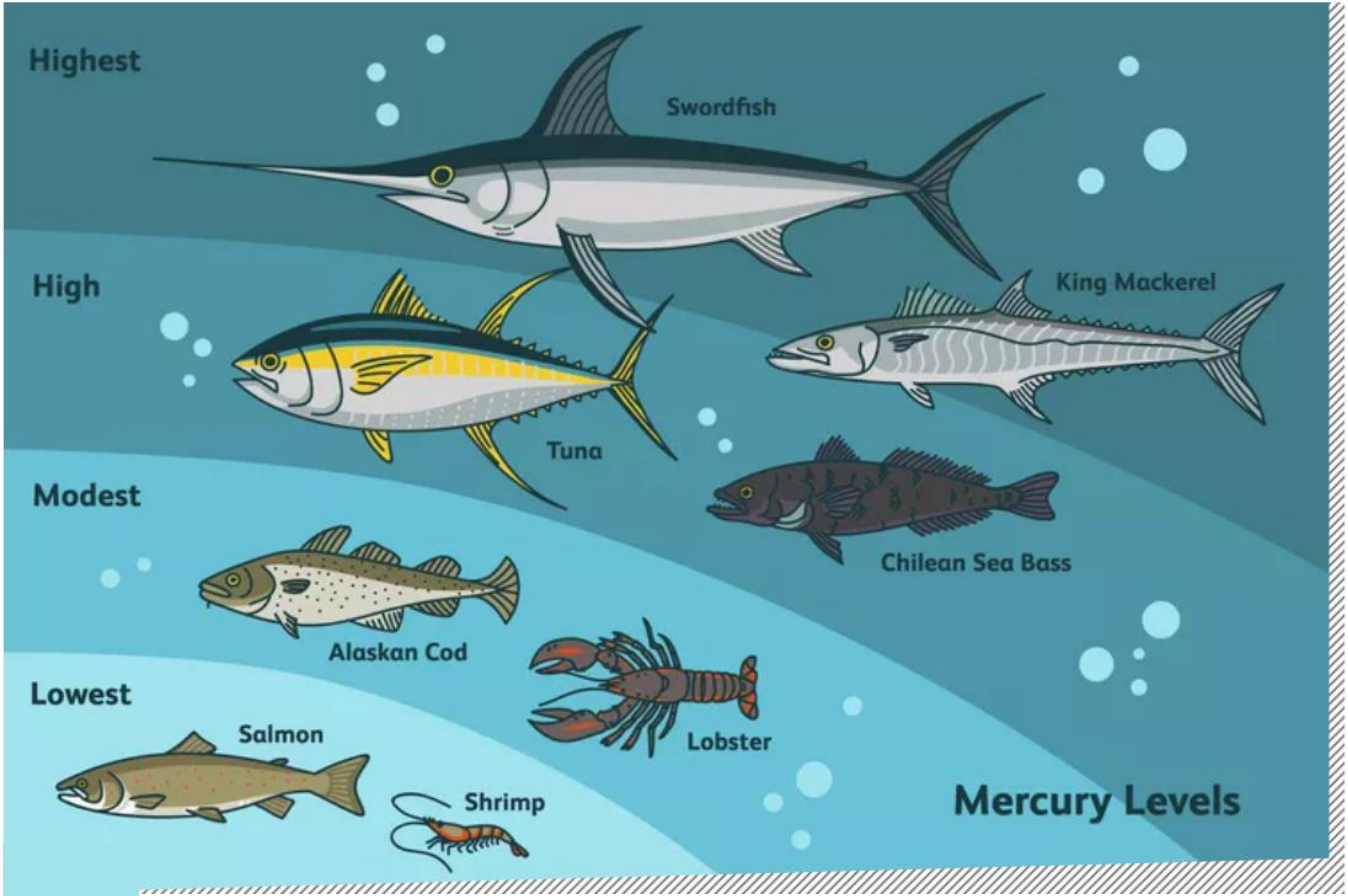
Bandar Imam, Iran
Kor River site, Iran (?)
Iran -3
Iran -4
Iraq -1
Iraq -2
Iraq -3
Israel-1
Syria-1
United Arab Emirates-1

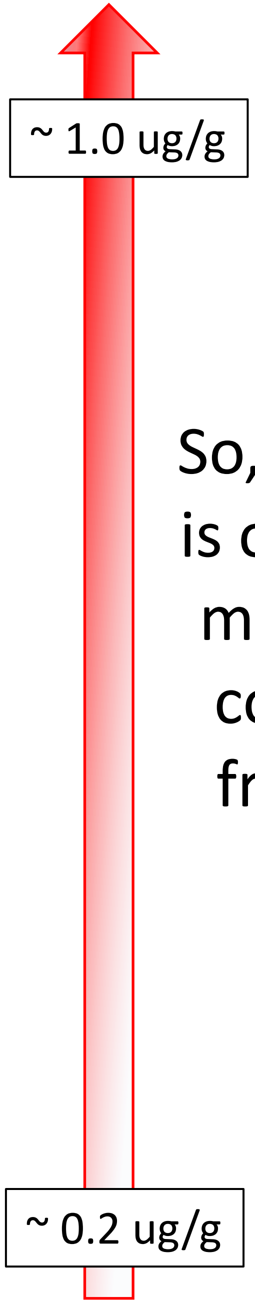
Alroli, India
Mumbai, India
Ganjam, India
Singrauli, India
India -5
India -6
India -7
Kala Shah Kaku, Pakistan
Myanmar -1
Minamata Bay, Japan
Niigata, Japan
Omi, Japan
Arai/Kosai, Japan
Uto, Japan
An Ning, China
Huludao, China
Tianjin, China
Yongjing, China
Qingzhen, China
Jilin City, China
China-7
China-8
Indonesia-1
Indonesia-2
Indonesia-3
Indonesia-4
Indonesia-5
Phillipines-1
Hamhung, North Korea
North Korea-2

Chlor-Alkali Facility – identified
Chlor-Alkali Facility– not confirmed
Acetaldehyde Facility – identified

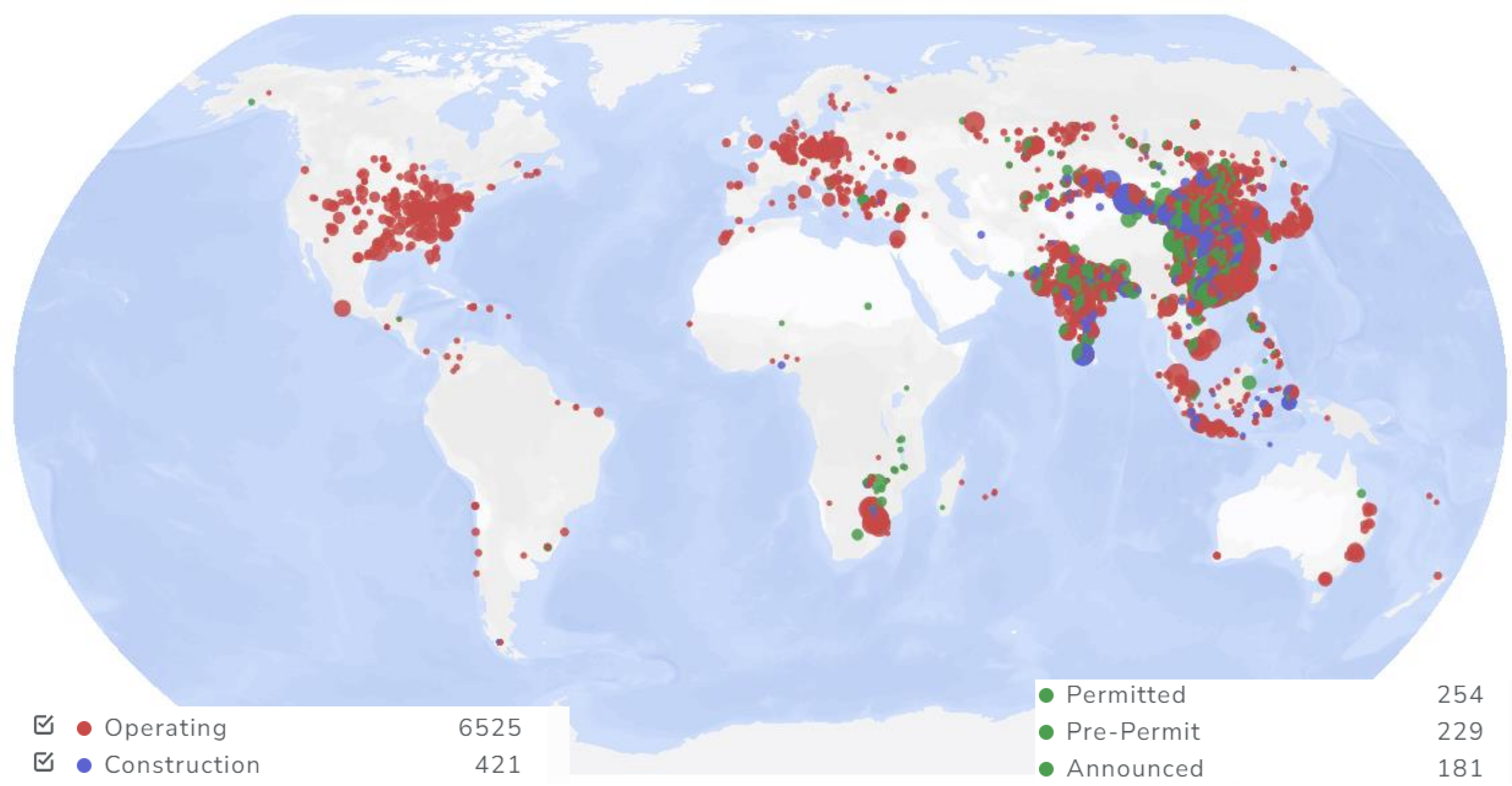
- The **Penobscot River** is the second largest river system in New England
- The estuary is:
  - ~20 miles long
  - 12 ft tidal range
- Seasonally variable discharge:
  - 5000 – 60,000 cfs
- Glaciated terrain and a long narrow river channel upgradient of Frankfort
- A mercury cell chlor-alkali facility 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


NORTH AMERICA
ATLANTIC OCEAN
PACIFIC OCEAN
SOUTH AMERICA
ASIA
SOUTHERN OCEAN

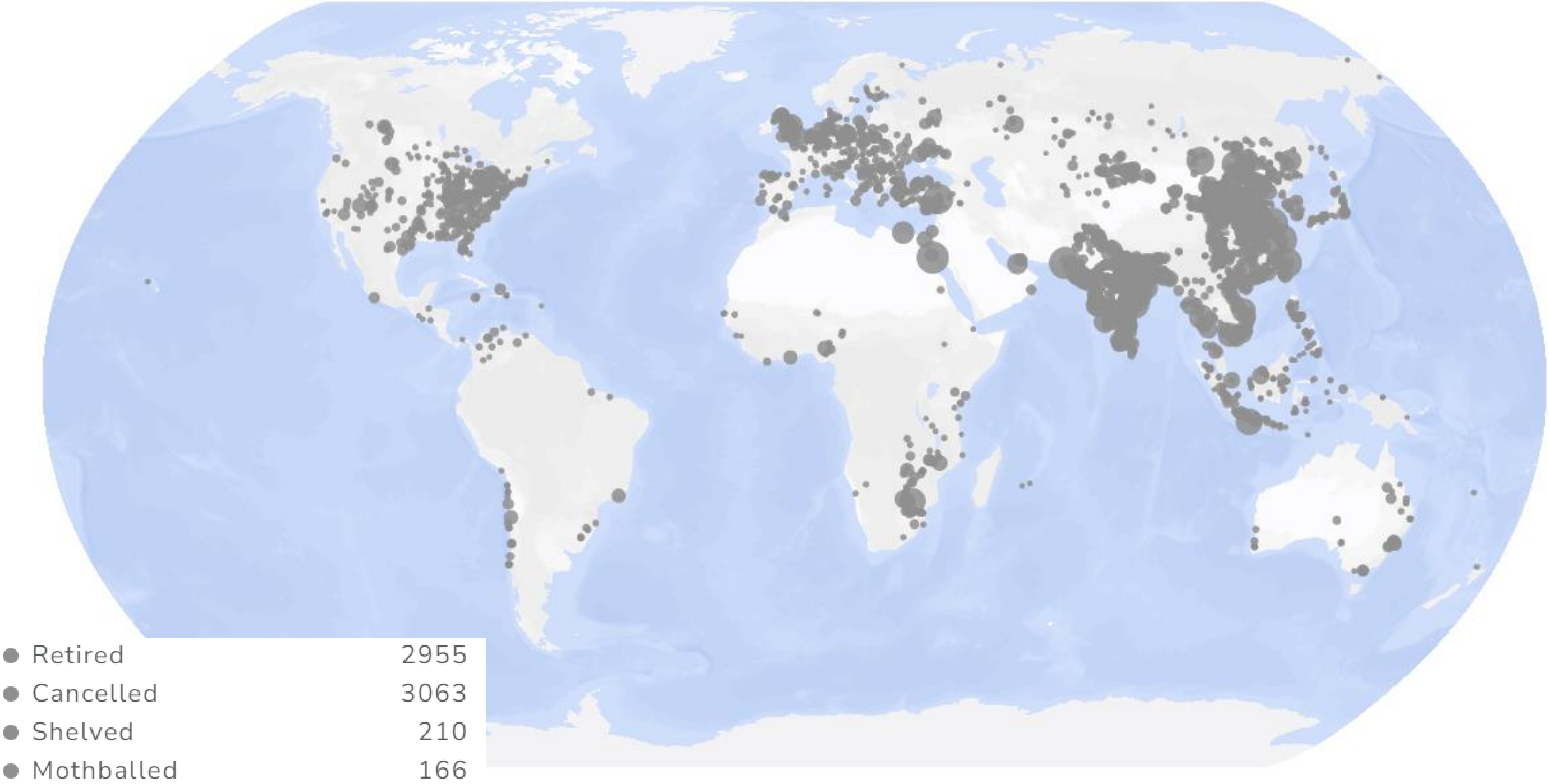




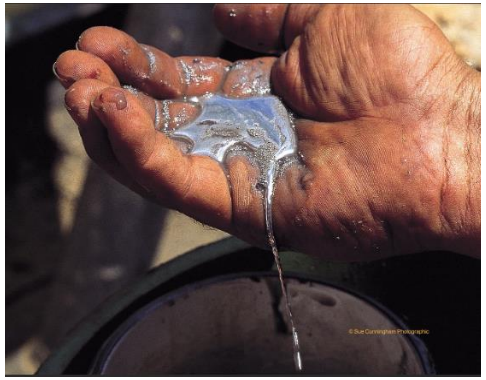
So, where is oceanic mercury coming from??


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)

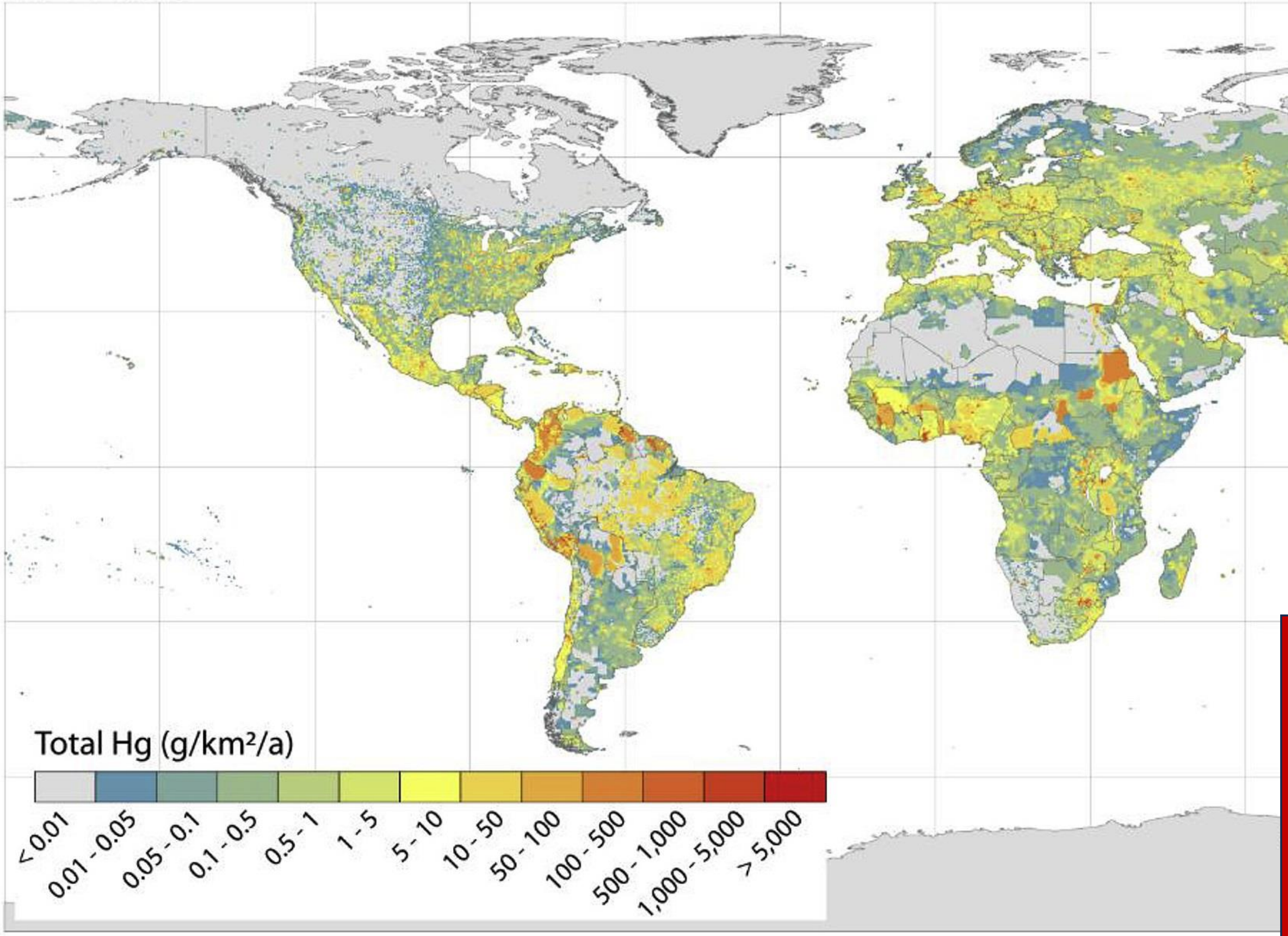
(gold mining is extraordinarily dangerous for those who have to feed their families this way….)

Serra Pelada, Brazil

Photographer:
Sebastiao Salgado
(1944 - 2025)

1986 – 1989 | gold mine

All sectors - Atmospheric emissions



Source	Amount (kg)
Artisanal and Small Scale Mining	837,658
Stationary Combustion of Coal	473,777
Nonferrous Metals Production	326,657
Cement Production	233,168
Waste from Products	146,938

LETTER

doi:10.1038/nature13563

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

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

Abstract Monomethylmercury (CH_3Hg) is the only form of mercury (Hg) known to biomagnify in food webs. Here we investigate factors driving methylated mercury [MeHg = $CH_3Hg + (CH_3)_2Hg$] 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.

https://doi.org/10.1029/2019GB006348

ELSEVIER

Marine Chemistry

Volume 186, 20 November 2016, Pages 156-166

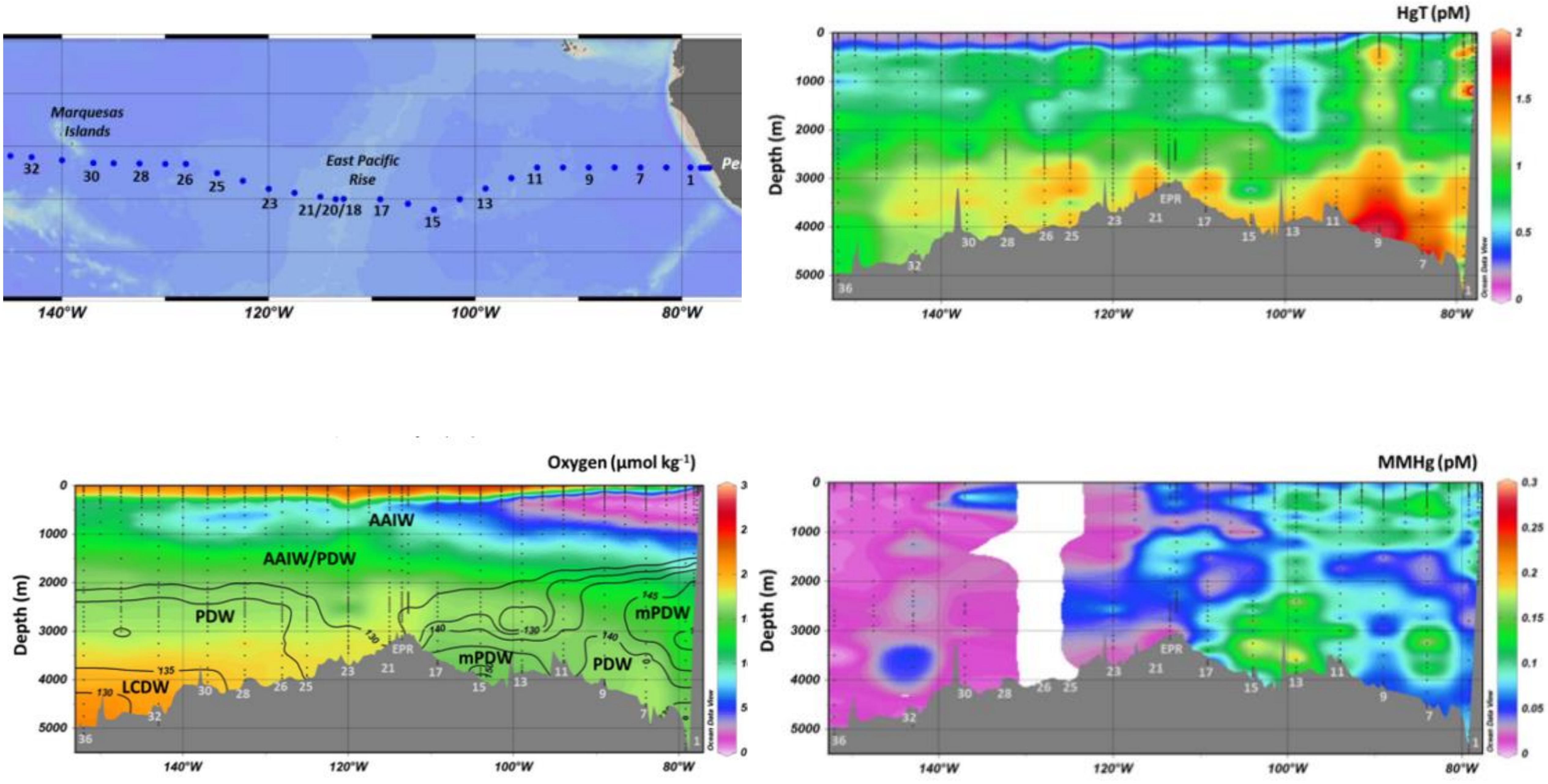
Distribution of mercury species across a zonal section of the eastern tropical South Pacific Ocean (U.S. GEOTRACES GP16)

Katlin L. Bowman [a], Chad R. Hammerschmidt [a], Carl H. Lamborg [b 1], Gretchen J. Swarr [b], Alison M. Agather [a]

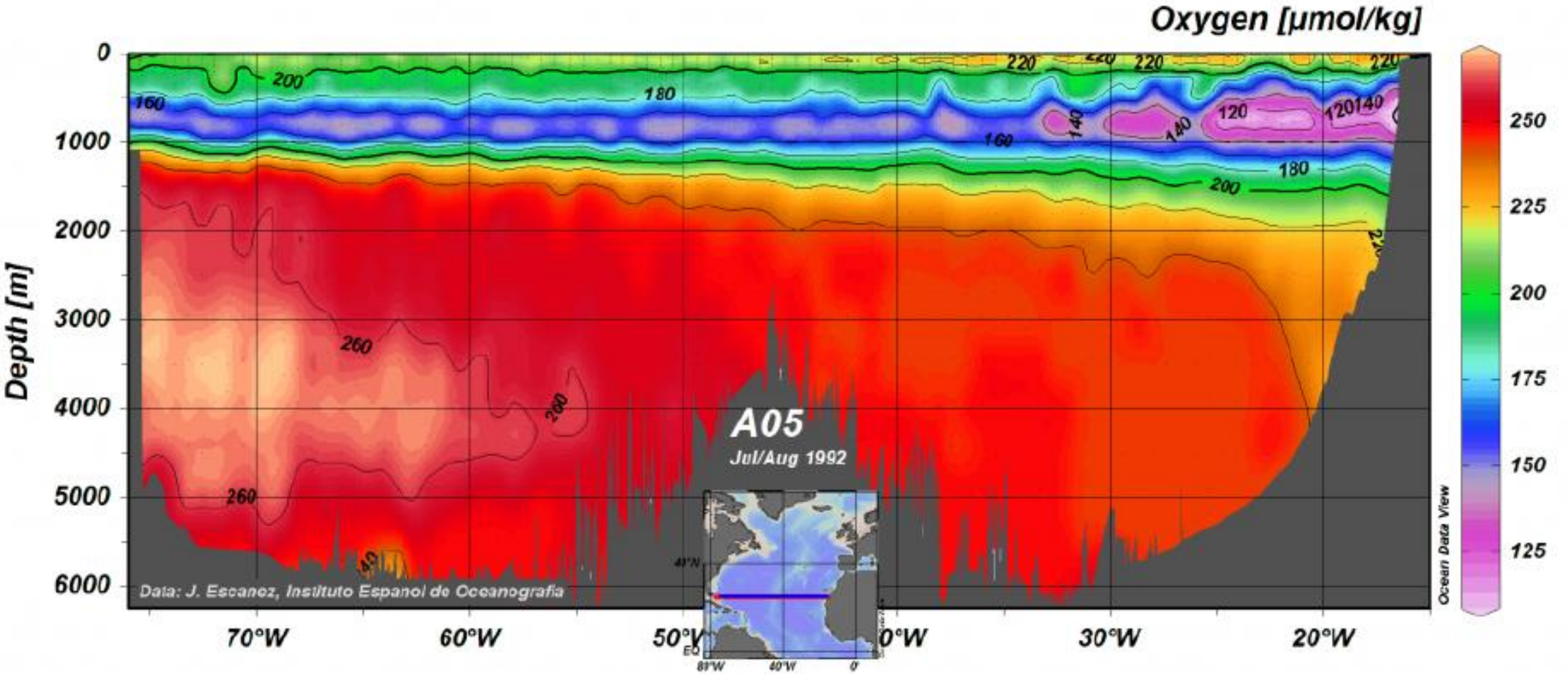
Highlights

- 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 4000 km west from the East Pacific Rise.
- Deep water below 2500 m was enriched with Hg, especially in warm bottom waters in the eastern part of the section.

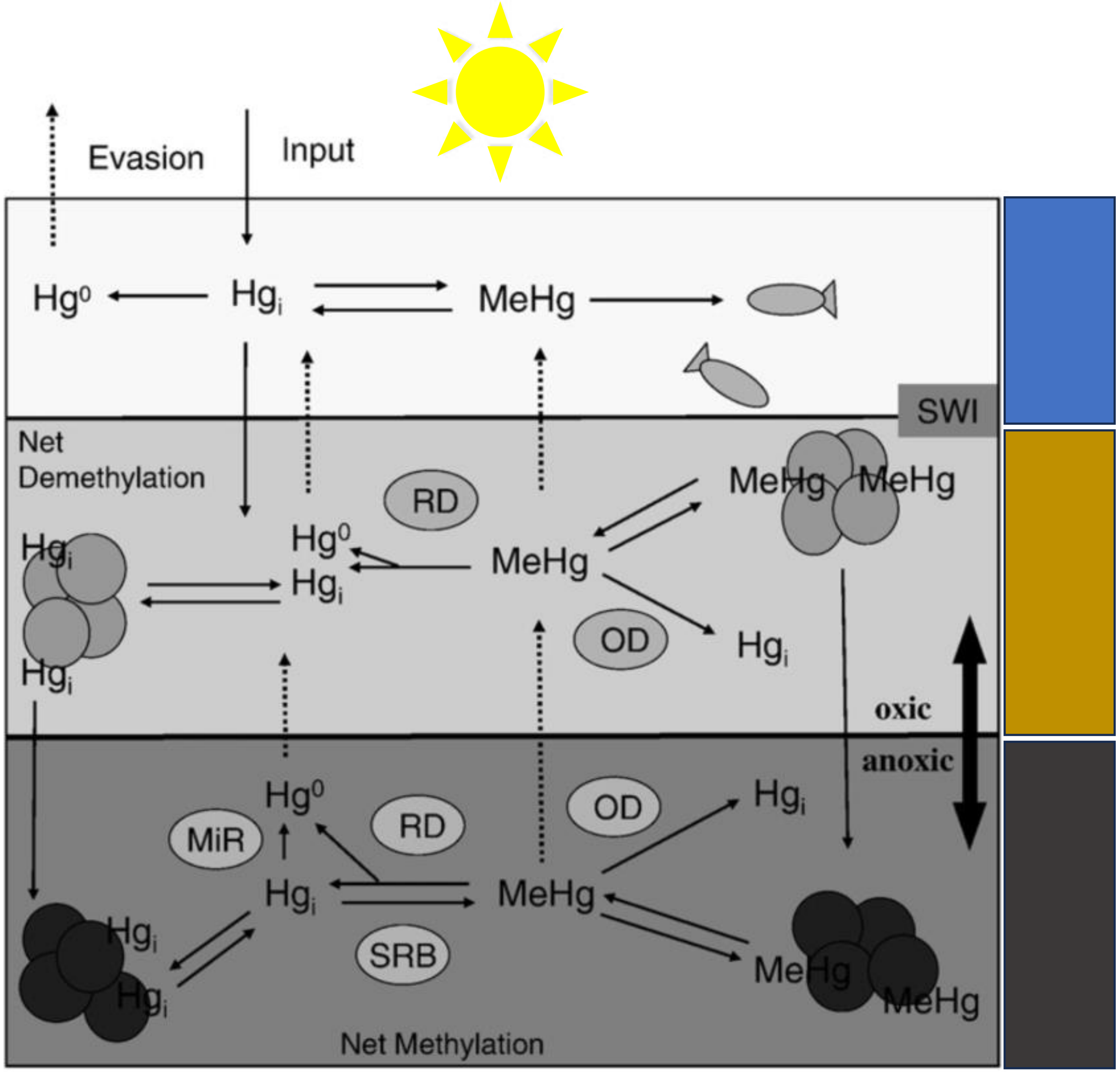
https://doi.org/10.1016/j.marchem.2016.09.005



Marquesas Islands
East Pacific Rise
32
30
28
26
25
23
21/20/18
17
15
13
11
9
7
1
140°W
120°W
100°W
80°W
HgT (pM)
Depth (m)
0
1000
2000
3000
4000
5000
2
1.5
1
0.5
0
EPR
36
Ocean Data View
Oxygen (µmol kg-1)
AAIW
AAIW/PDW
PDW
mPDW
LCDW
145
140
135
130
MMHg (pM)
0.3
0.25
0.2
0.15
0.1
0.05



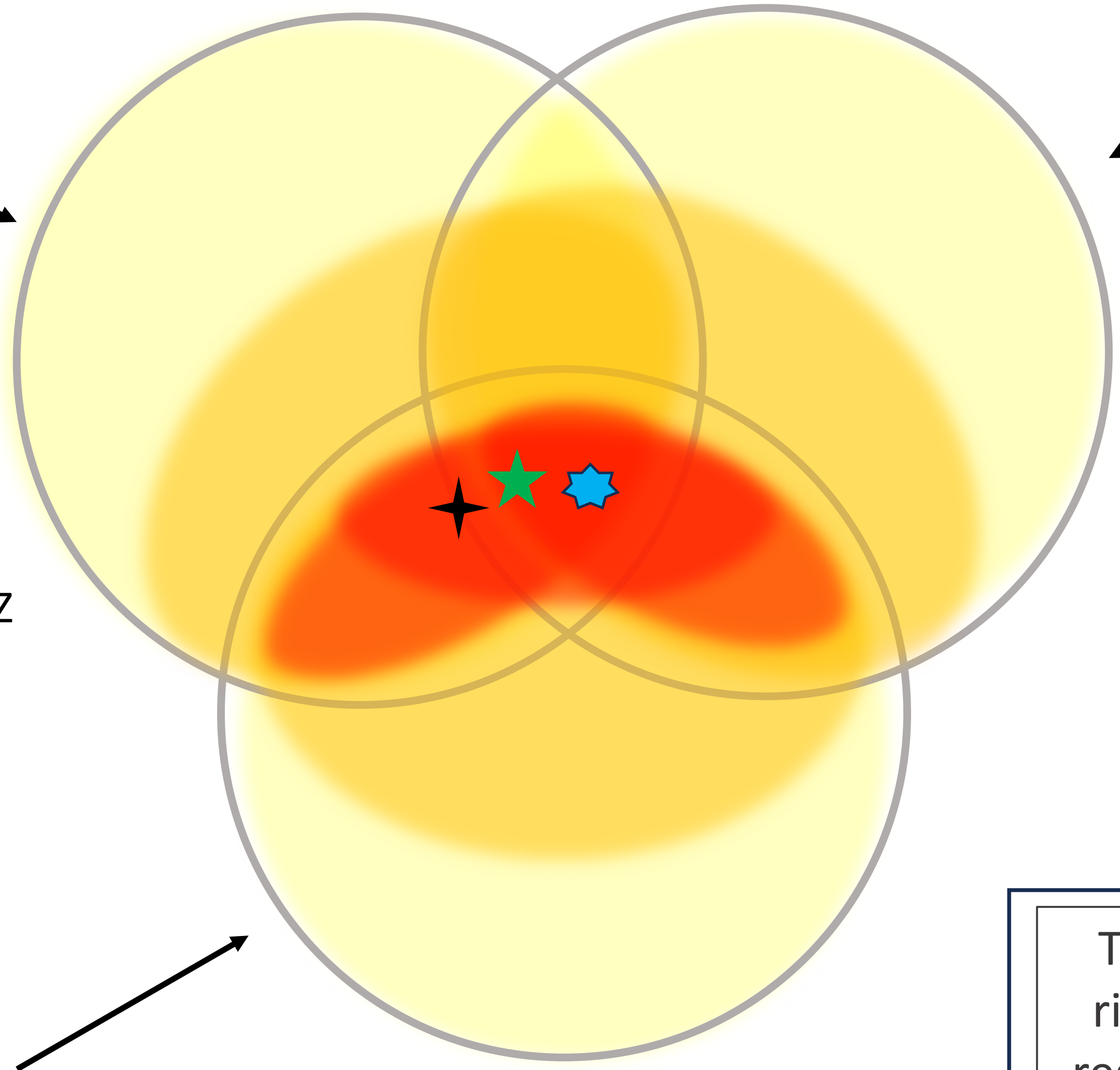
Oxygen [µmol/kg]
Depth [m]
A05
Jul/Aug 1992
Data: J. Escanez, Instituto Espanol de Oceanografia
Ocean Data View
70°W
60°W
50°W
30°W
20°W
0
1000
2000
3000
4000
5000
6000
250
225
200
175
150
125



- Significant organic matter breakdown consumes dissolved oxygen (dO_2);
- Sulfate (SO_4^{2-}) + very low dO_2 increases activity of sulfate-reducing bacteria (SRB);
- SRB in the presence of inorganic mercury (Hg^{2+}) generate methyl mercury (CH_3Hg^+) as a by-product of respiration;
- CH_3Hg^+ is 100× more toxic than Hg^{2+} and is retained in biological tissue to a greater extent than Hg^{2+}

PHYSICAL

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



BIOLOGICAL

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

= 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

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