

Mercury in the North

Kendra Zamzow, PhD

Center for Science in Public Participation

ACAT – CHE, June 15 2016

kzamzow@csp2.org www.csp2.org

Connect the dots

2

Source.....Path.....Receptor

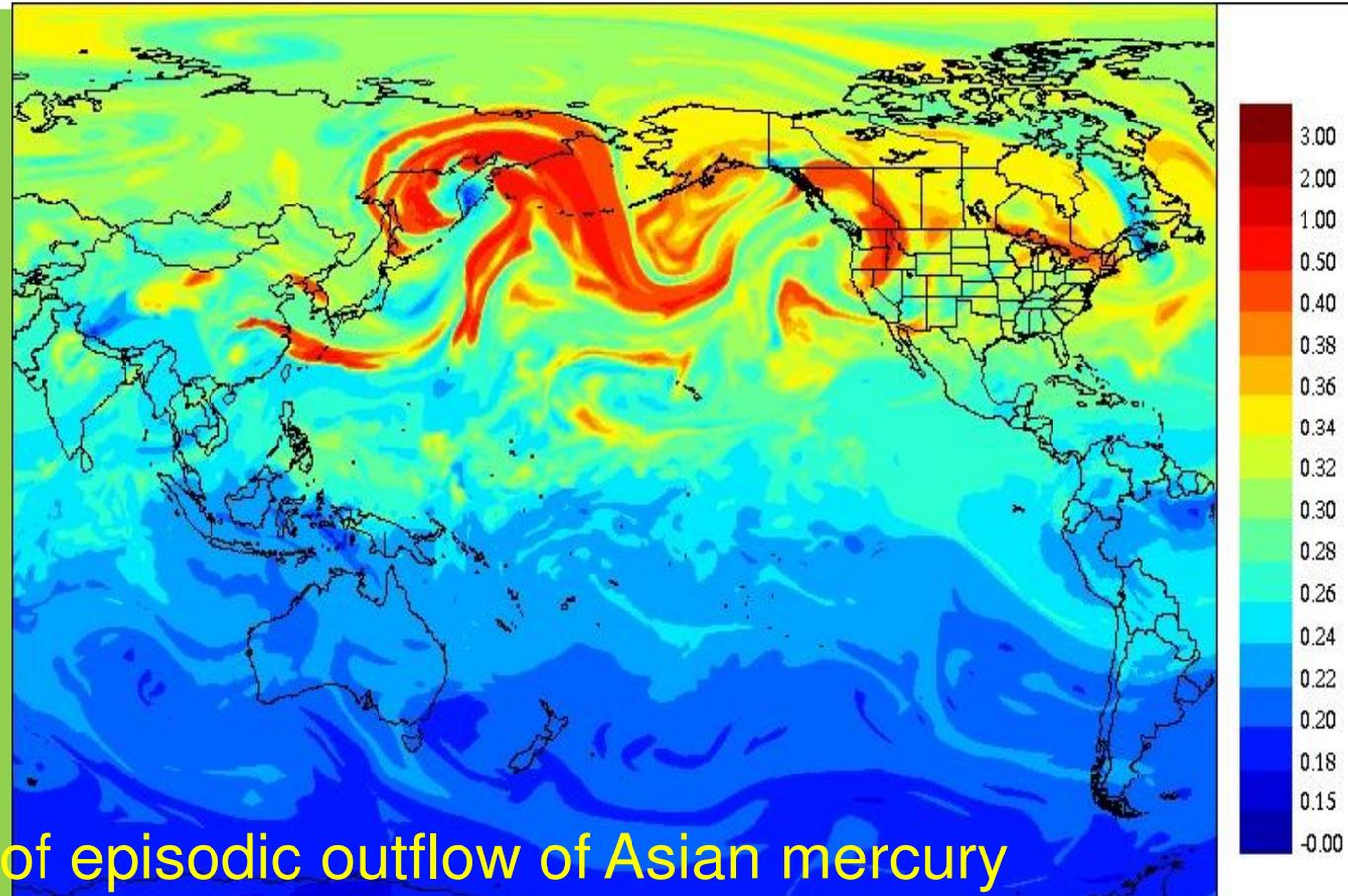


Sources

3

- Wildfires, volcanoes, erosion of soil & natural rock
- Industry
 - Coal plants
 - Incinerators
 - Gold mines – *no gold mines currently in Alaska release mercury*

Winds Water Migration

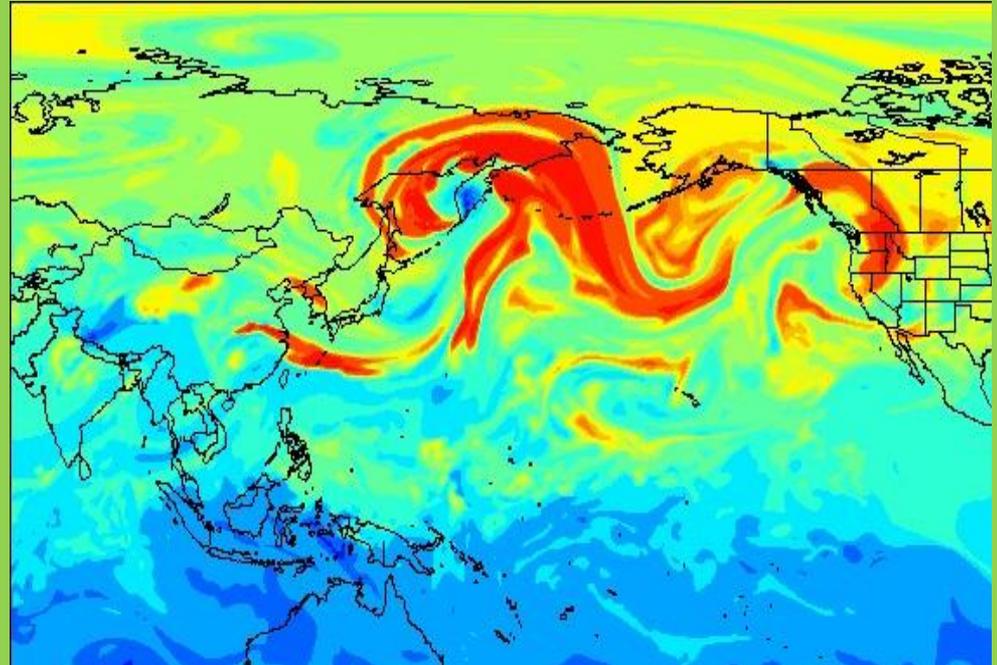


Prediction of episodic outflow of Asian mercury
on April 25, 2004 measured at Mt. Bachelor
observatory, Oregon, USA

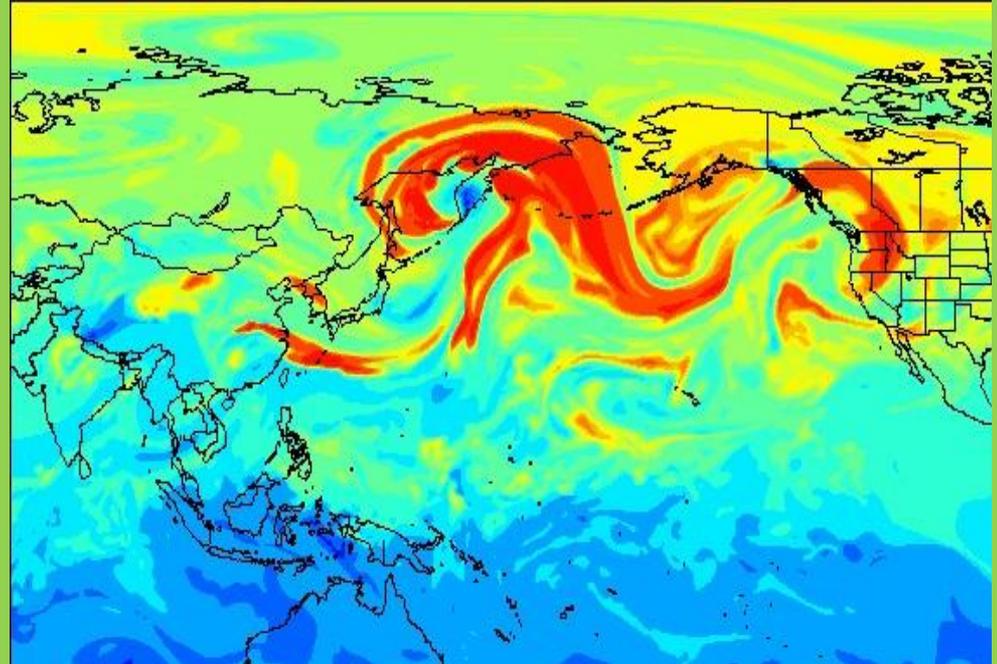
Elemental Hg^0

- ▣ Stable and happy
- ▣ Gas
- ▣ “gaseous elemental mercury” GEM

Stays in this form for years
(half life of a year)



If it stays up there
... how does it get into
fish and into us?



Ionic Hg^{2+}

- ▣ Wants a hand to hold
- ▣ Gas
- ▣ “reactive gas mercury”



Before it becomes stable

Water	Dissolved HgX
Rock	Solid HgX



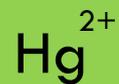
Hg “species”

Ligands – just a hand to hold

8



□ Toddler Hg

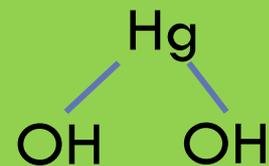


Ligands – just a hand to hold

9



- Toddler Hg
- Aunties



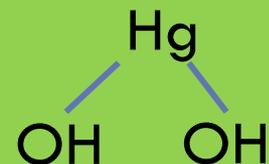
Ligands – just a hand to hold

10



□ Toddler Hg

□ Aunties



□ Momma S



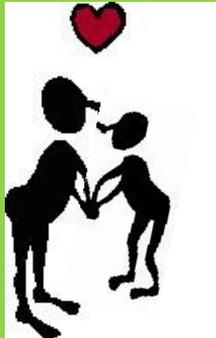
Ligands – just a hand to hold

11



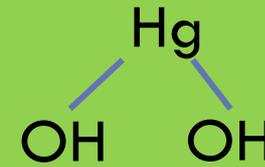
□ Toddler Hg

□ Aunties



□ Momma S

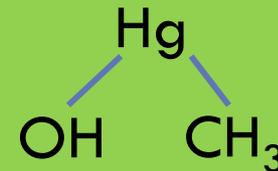
□ Methyl Hg
(MeHg)



Not toxic



Not toxic



SRB

Only bacteria can put a methyl group on!

Happy places for methylating bacteria

Path

12

- Gaseous, stable Hg^0 floats around until it becomes gaseous, reactive Hg^{2+} , which wants to partner up (HgX) and precipitate to ground
- If it lands in a wet area without oxygen, this is the home of bacteria that can make methyl mercury (MeHg)

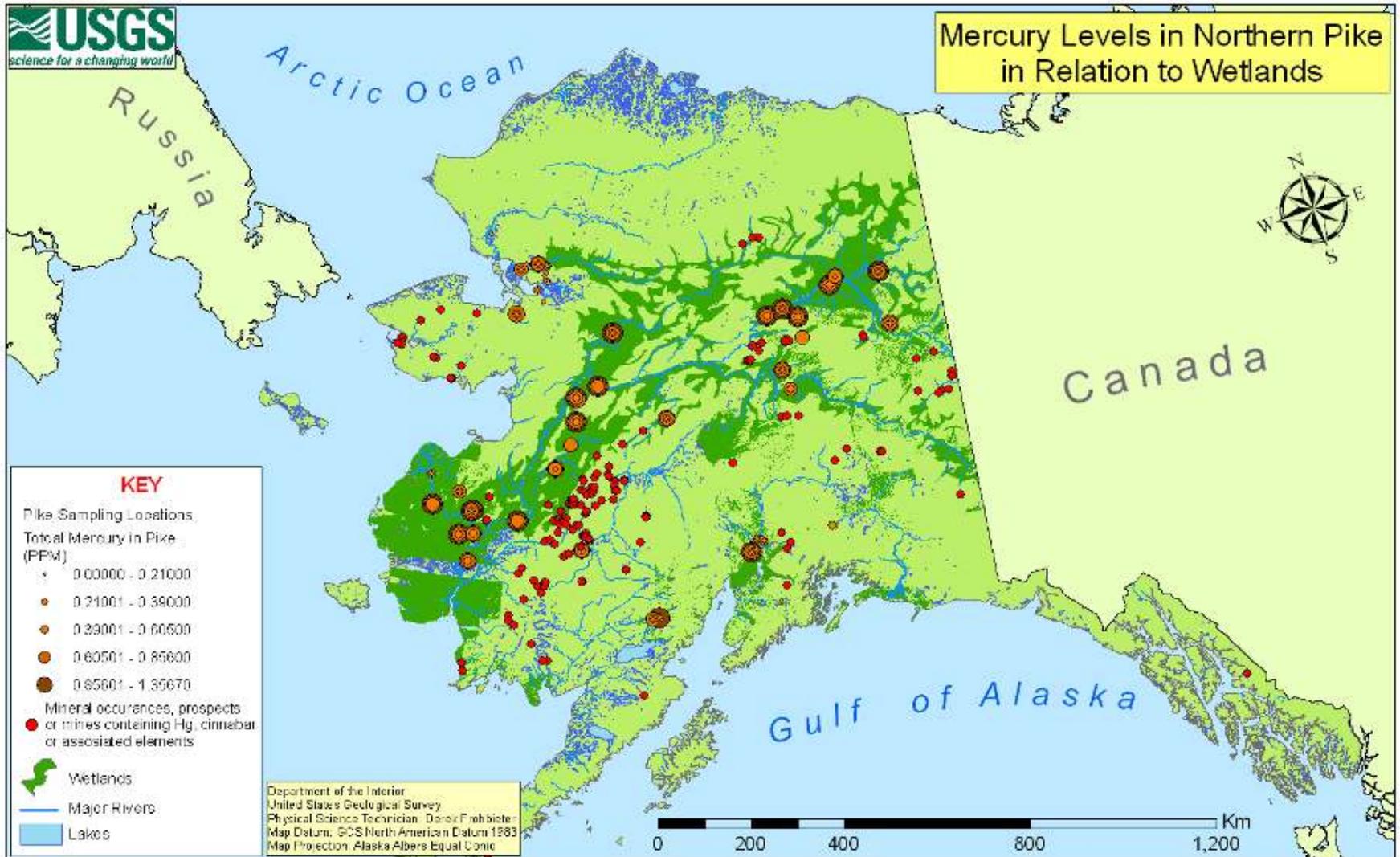
- Estuaries
- Wetlands

NOT

- Running streams
- Mountaintops
- Dry tundra

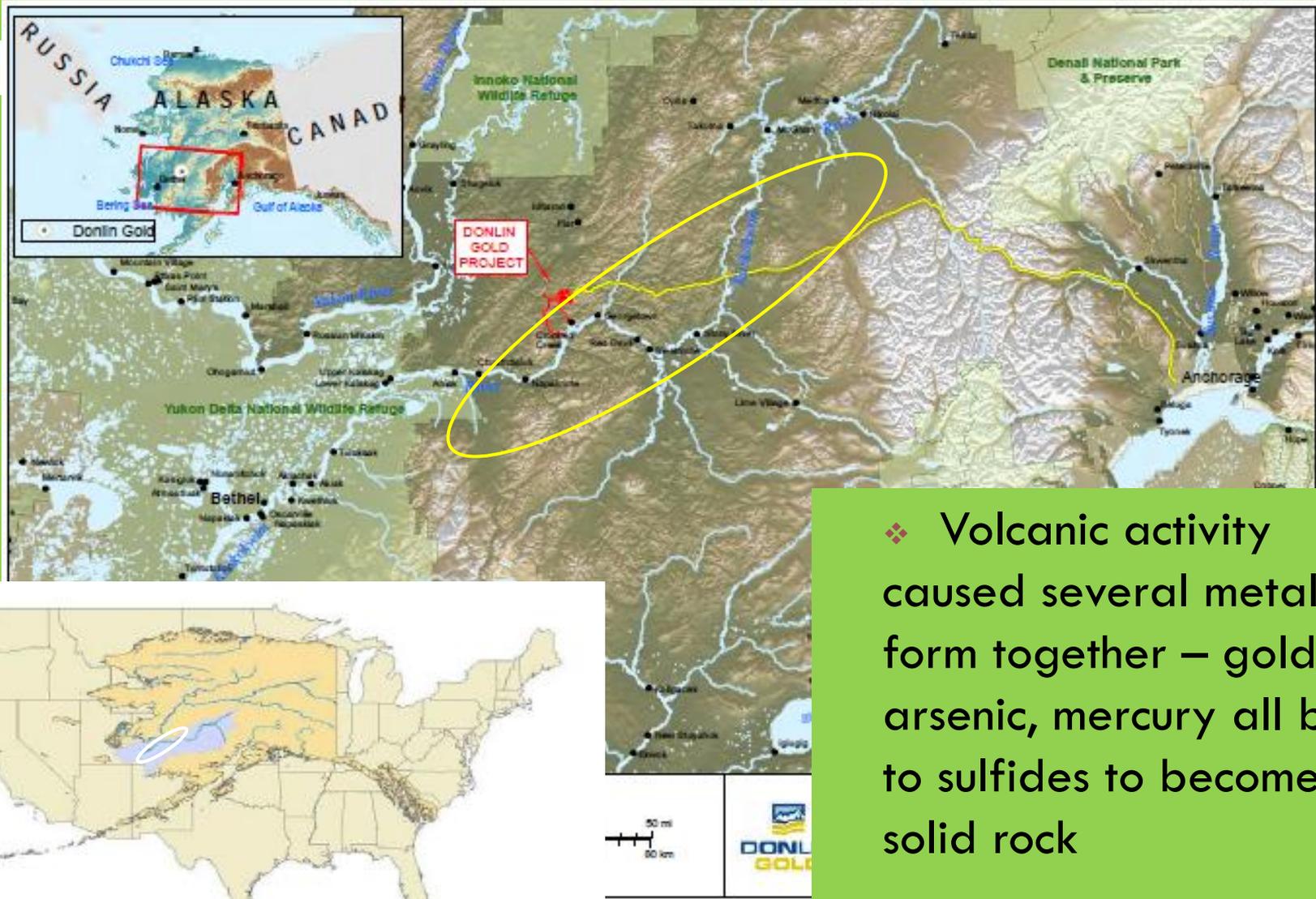


- *Pathways are not complete unless bacteria methylate the mercury*
- *Once methylated, mercury can cross into cells*
- *What can be methylated can also be DE-methylated*



Source Kuskokwim Mercury Belt

15



❖ Volcanic activity caused several metals to form together – gold, arsenic, mercury all bind to sulfides to become solid rock

Hg = S

Source Donlin's ore processing

16

Ore is heated to extract the gold, heating causes mercury to vaporize (Hg=S become gaseous mercury and sulfuric acid)



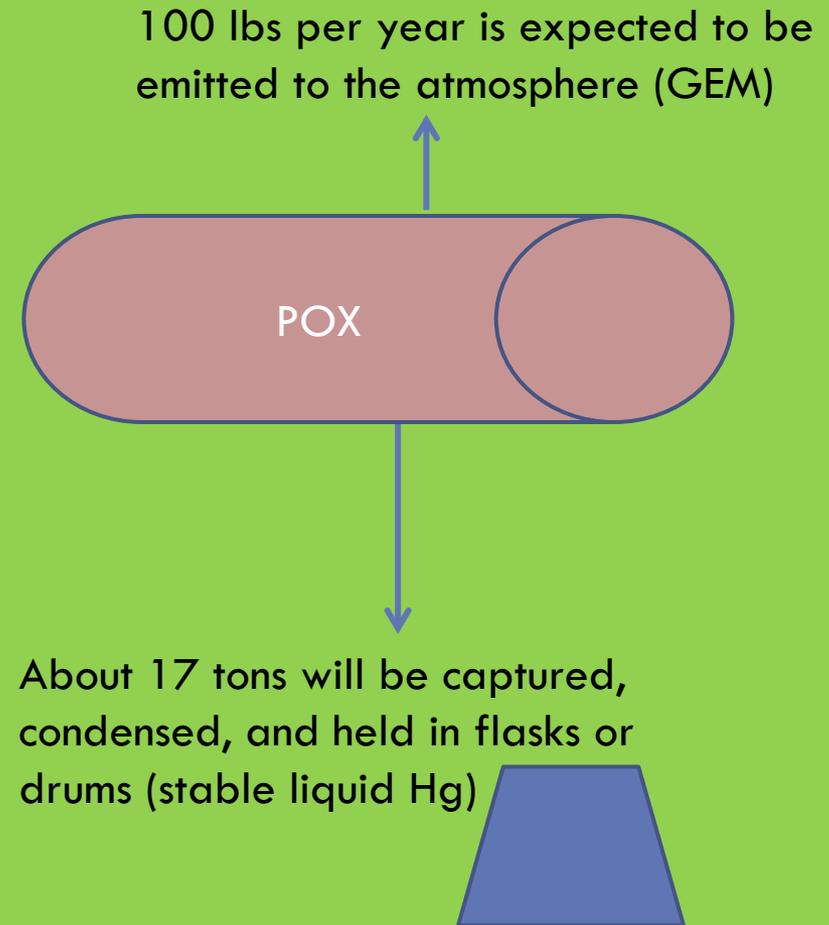
Source Donlin's ore processing

17

Ore is heated to extract the gold, heating causes mercury to vaporize (Hg=S become gaseous mercury and sulfuric acid)

Some will remain as solids in tailings (Hg=S)
Tailings water will have high concentrations of dissolved mercury –

Leakage?



Receptors Toxicity

18

- Wildlife (animals eating contaminated food)
 - Physical deformities
 - Slow growth
 - Lower reproductive success
 - Lower survival

- Humans (eating contaminated food)
 - unborn children, infants at most risk
 - Nerve damage – speech, vision, walking
 - Immune system damage

- Humans (inhalation)
 - Industrial plant workers most at risk
 - Nerve damage – walking, fatigue, dizziness
 - Can be fatal

at the cellular level

- Toxicity occurs when MeHg becomes reactive Hg^{2+} and then attaches to $-\text{S}$ ligands (“Momma S”) on proteins or other cellular molecules, particularly fast-dividing ones like nerve cells

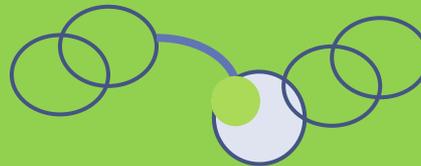


Toxicity at the cellular level

- Toxicity occurs when MeHg becomes reactive Hg^{2+} and then attaches to $-\text{S}$ ligands (“Momma S”) on proteins or other cellular molecules, particularly fast-dividing ones like nerve cells



1 – Momma S
Ligand available



2 – Momma S in action,
binding molecules



3 – Momma S
Blocked

Path-Receptor

Natural Hg in vegetation

21

Vegetation (lichens, berries, spruce, willow, alder) in the Donlin “mercury belt” area had about the same mercury as has been found in other areas of Alaska

○ Donlin area

- highest in lichen (9-36 ng/g)
- lowest in cranberry, blueberry (<8 ng/g)



○ Lichen throughout Alaska (EPA, UAF stud

- Alaska parks 20-30 ng/g mercury
- Reindeer ranges 37-47 ng/g mercury

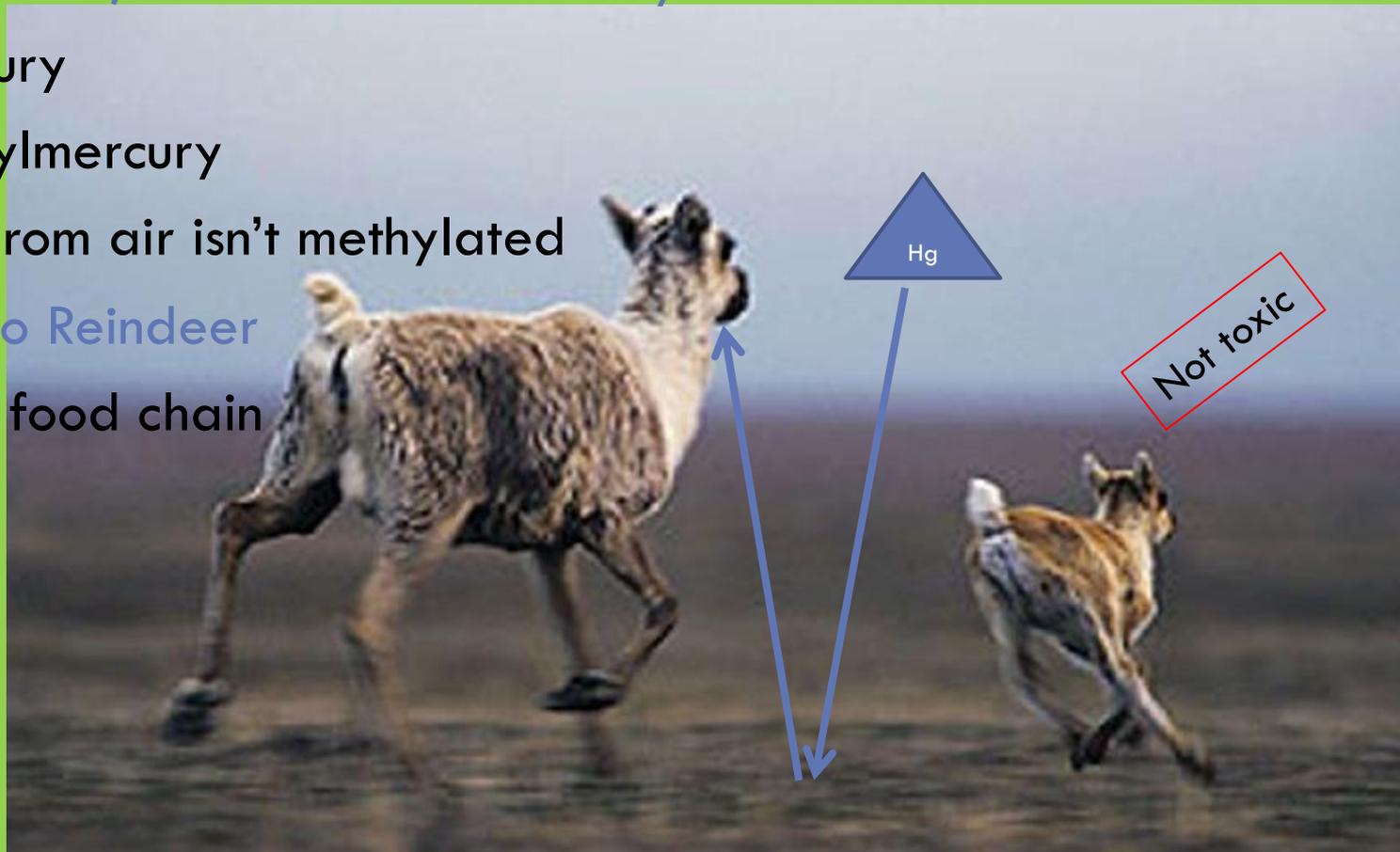
• Lichen don't get mercury from the soil and don't pass mercury on to reindeer

- Lichen < 40 ng/g
 - Hair 15-83 ng/g
- (Fish is safe at 300-1,000 ng/g)

Why are reindeer low in Hg?

22

- Lichen and water, even near old mercury mines
 - ▣ Low mercury
 - ▣ Low methylmercury
 - ▣ Mercury from air isn't methylated
- Vegetation to Reindeer
 - ▣ One-step food chain



Path - Receptors

Water - Kuskokwim Fish

23

- Water near old mercury mines
 - Less than 50 ng/L (safe)
 - 500-2500 ng/L with sediment
 - Very **little** methylmercury

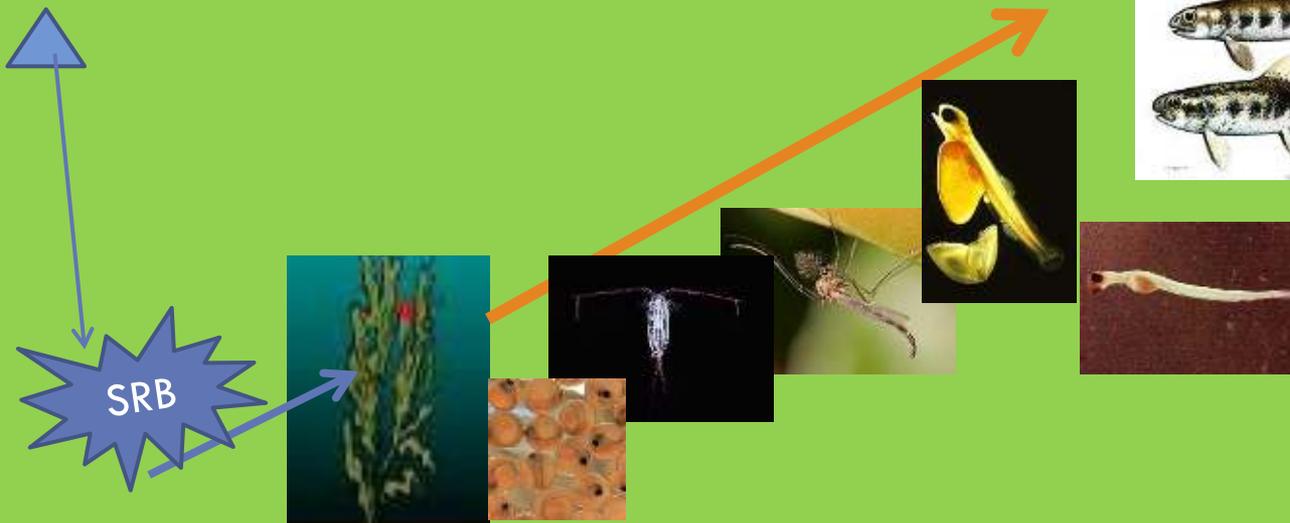
- Fish near old mercury mines
 - 620 ng/g mercury (potentially unsafe)
 - nearly **all** is methylmercury
 - 300-1000 ng/g considered safe

(Gray, JE, PM Theodorakos, EA Bailey, and RR Turner. 2000. Distribution, speciation, and transport of mercury in stream-sediment, stream-water, and fish collected near abandoned mercury mines in southwestern Alaska, USA. *Sci. Tot. Env.* 260: 21-33.)

Why are some fish higher in mercury?

24

- Pike can have high mercury
 - ▣ Hg in water more likely to methylate
 - ▣ Hg concentrates up the food chain
 - ▣ Aquatic food chains are longer than on land



Are we doomed?

25

No

- Not all fishy areas are places where mercury will methylate

Methylmercury is not related to the amount of Hg that enters the environment, but whether the environment supports bacteria that can add methyl groups

- What can be methylated can be DE-methylated

Even where bacteria are tacking methyl groups on, UV light is busy taking them off. It's a balance.

- Fish, mink, us, and other animals get rid of mercury

For MeHg to pose a risk, it must come in faster than it goes out. MeHg has a half life of about 90 days in humans and fish (Young, 2001; ICPS 1990; Kramer and Neidhart 1975)

So everything's fine, no worries?

26



Monitor!

- Industrial facilities should measure mercury releases

Monitor levels in stacks, air, dust/soil, water

Monitor processing areas – inhaling gaseous Hg is extremely toxic to adults as well as children

- Fish tissue, human hair should be tested

Can request fish tissue monitoring as part of mine activity environmental monitoring

Human hair testing is free through the state of Alaska

So everything's fine, no worries?

27



- Packaging for storage and transport
- Spills of Hg into rivers and estuaries are a risk
About 17 tons of mercury will be transported out of Donlin



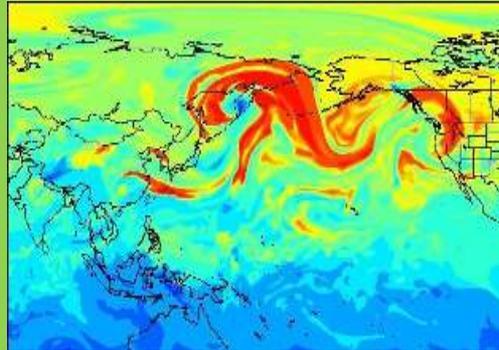
Drum packing,
Sealed warehouse
floors, monitored with
mercury vapor monitor
GPS tracking

Several layers of protection have been added inside the drums: (1) The drums are lined with an epoxy-phenolic coating; (2) a cushioning material is located in the bottom of each drum; (3) the flasks are separated by a cardboard divider for additional cushioning; (4) the contents are sealed in a thick plastic bag; and (5) each drum lid is equipped with a half-inch rubber gasket and a steel-locking ring that is bolted to seal the drum. The drums are very secure and both airtight and liquid-tight.

Summary

28

Source....



Path.....



Or direct inhalation

Receptor...



Monitor

Quyana

Tsin'aen

Chin'un

Thank you



Mercury in Northern Pike from the Yukon Delta National Wildlife Refuge

U.S. Fish and Wildlife Service and Alaska Dept. of Health and Social Services – Division



How much pike from the Yukon Delta area should women and children eat?

Should I worry about eating fish?

Overall, mercury levels in Alaska fish are low, so the **only** people who need to think about limiting the amount of fish they eat are **women who are or can become pregnant, nursing mothers, and children age 12 years and under**. Women and children can still get the benefits of eating fish by choosing to eat fish that are low in mercury, like salmon.

Men, elders, and teenage boys may eat unlimited amounts of most Alaska fish, including pike.

The State of Alaska has developed guidelines for women and children on how much of each fish they can safely eat, based on the amount of mercury in a variety of fish species. These guidelines:

- Reflect guidelines developed by other states and national agencies.
- Incorporate studies of dietary mercury effects on children.
- Include a large safety factor, so do not have to be viewed as strict dietary limits.

Why study mercury in pike?

There is more of the toxic form of mercury – methylmercury – in fish that eat other fish and in older fish, like large pike. In this study, we measured mercury in pike muscle, from pike caught at traditional and well-used subsistence fishing sites. We are sharing this information with you because you live in an area where people eat a lot of pike. With the help of subsistence fishermen, we collected 163 pike from 11 sites in the Yukon Delta National Wildlife Refuge in 2005 (on the Kuskokwim River) and 2006 (on the Lower Yukon River).



Sample sites in the Kuskokwim River area (2005) and the Lower Yukon River area (2006).

MeHg in fish (mg/kg)	Meals per month	Fresh pike
0 - 0.15	Unlimited	
>0.15 - 0.32	up to 16	Kuskokwim < 2 ft
>0.32 - 0.40	up to 12	
>0.40 - 0.64	up to 8	Kuskokwim < 2 ft
>0.64 - 1.2	up to 4	Kuskokwim < 2 ft
>1.2 - 1.4	up to 3	
>1.4 - 2.0	up to 2	
>2.0 - 3.4	up to 1	Kuskokwim > 2 ft



Fresh pike

Notes: Small pike (< 2 feet long) often have less mercury than large pike (> 2 feet long). Also, dried pike has a higher mercury concentration than fresh pike (the mercury is "diluted" with the water in the fresh pike), so the guidance allows fewer meals of dried pike than fresh pike.

For more information on mercury in pike contact Angela Matz (angela_matz@fws.gov, 907-456-0442), U.S. Fish and Wildlife Service, 101-12th Ave., Room 110, Fairbanks, AK 99701.

Measuring Mercury

A simple hair test can tell you how much mercury you may have in your body. For more information on hair mercury monitoring, or to arrange for testing, contact the Environmental Public Health Program at the Alaska Division of Public Health, 3601 C Street, Suite 540, Anchorage, AK 99503, 907-269-8000,

<http://www.epi.hss.state.ak.us/eh/default/stm>



Deciding

Fish are nutritious, with vitamins A, E, and C, iron, zinc, protein, and very important omega-3 fatty acids. These nutrients help keep your nervous system, your immune system, and your heart healthy, and are important for a healthy pregnancy.

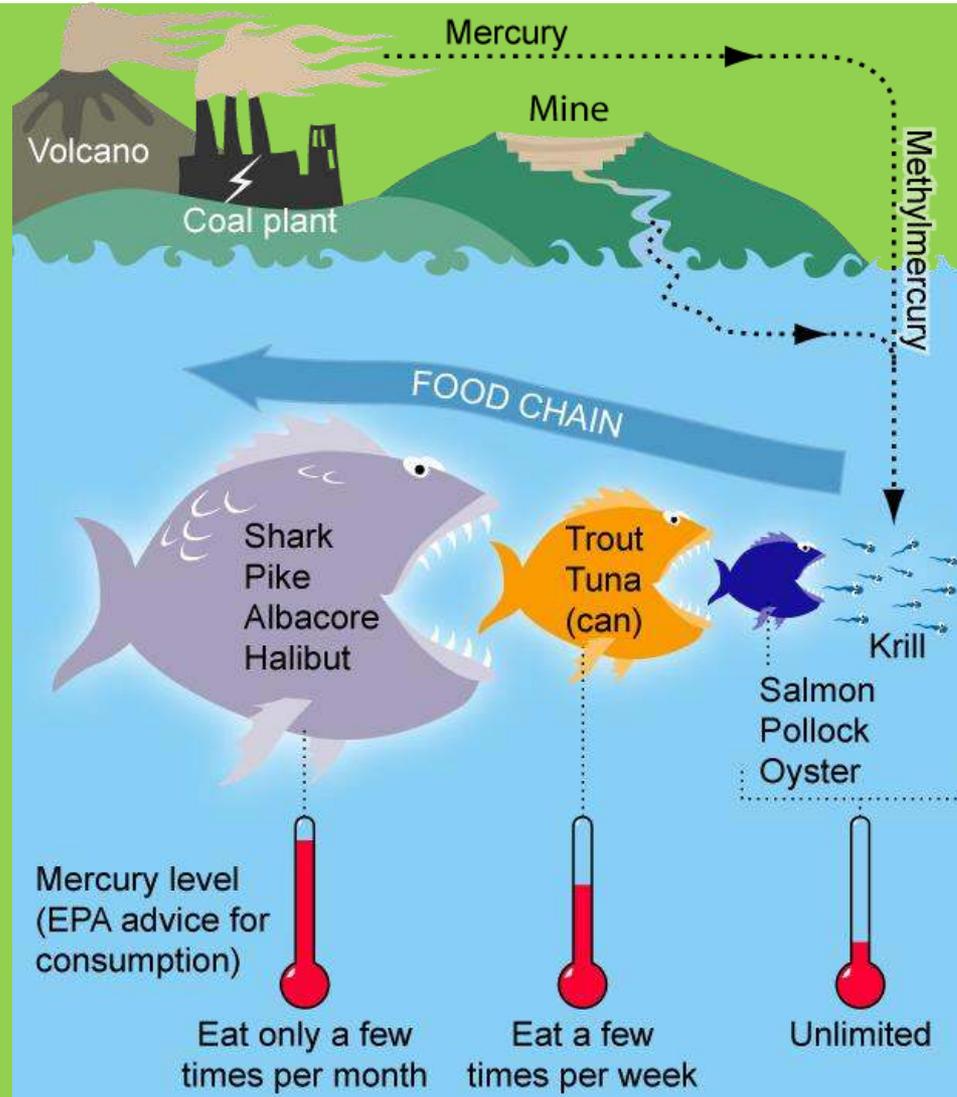
The most recent (2007) guidelines, *Fish Consumption Advice for Alaskans: A Risk Management Strategy to Optimize Public Health*, is available at:

http://www.epi.hss.state.ak.us/bulletins/docs/r2007_04.pdf

What's wrong with this picture?

It doesn't show the methylation pathway

Although most methylation occurs in wetlands and estuaries, new research indicates it may also happen at some depths in the ocean



References

- Gray, JE, PM Theodorakos, EA Bailey, and RR Turner. 2000. Distribution, speciation, and transport of mercury in stream-sediment, stream-water, and fish collected near abandoned mercury mines in southwestern Alaska, USA. *Sci. Tot. Env.* 260: 21-33.
- Young JF. 2001. Analysis of methylmercury disposition in humans utilizing a PBPK model and animal pharmacokinetic data. *J Tox and Env Hlth Part A* 63: 19-52
- IPCS (International Programme on Chemical Safety). 1990. Environmental Health Criteria monograph 101: methylmercury. Geneva, Switzerland. Available online at <http://www.inchem.org/documents/ehc/ehc/ehc101.htm#SectionNumber:2.2>
- Kramer HJ and B Neidhart.1975. The behaviour of mercury in the system water--fish. *Bull. Environ. Contam. Toxicol.* (14):699-704

Photo credits

32

<https://en.wikipedia.org/wiki/Copepod>

https://images.duckduckgo.com/iu/?u=http%3A%2F%2Fwww.alaska-in-pictures.com%2Fdata%2Fmedia%2F1%2Friver-ecosystem_1752.jpg&f=1

<https://images.duckduckgo.com/iu/?u=http%3A%2F%2Fwww.pac.dfo-mpo.gc.ca%2Fscience%2Fspecies-especies%2Fpelagic-pelagique%2Fherring-hareng%2Fhershawn%2Fimages%2Feulachonlarva.jpg&f=1>

https://images.duckduckgo.com/iu/?u=http%3A%2F%2Fmedia.npr.org%2Fassets%2Fimg%2F2014%2F01%2F09%2Fistock_000013943660medium_custom-7f5403743167d226e4e660dc424d454b00ca90d9-s800-c15.jpg&f=1

<http://yourshot.nationalgeographic.com/photos/6151542/?source=gallery>

And various photos from wikipedia sites

More resources

33

Fitzgerald, WF, DR Engstrom, RP Mason, and EA Nater. 1998, The Case for Atmospheric Mercury Contamination in Remote Areas, *Environ Sci and Technol* Vol. 32, No.1

Gray, J, P Theodorakos, J Budahn, and R O'Leary. 1993. Mercury in the Environment and it's Implications, Kuskokwim River Region, *Environment and Climate*, United States Geological Survey Bulletin 2107.

Hammerschmidt and Fitzgerald. 2006. Photodecomposition of MeHg in an Arctic Alaskan lake. *Environ Sci and Technol* 40: 1212-1216

Langer, CS, WF Fitzgerald, PT Visscher and GM Vandal. 2001. Biogeochemical cycling of methylmercury at Barn Island Salt Marsh, Stonington, CT, US. *Wetland Ecology and Management* (9): 295-310

Macdonald, RW, T Harner, and J Fyfe. 2005. Recent Climate Change in the Arctic and its Impact on Contaminant Pathways and Interpretation of Temporal Trend Data, *Science of the Total Environment*, Vol. 342. 5-86.

Martin-Doimeadios RCR, E Tessier , D Amouroux, R Guyoneaud, R Duran, P Caumette, and OFX Donard. 2004. Mercury methylation/demethylation and volatilization pathways in estuarine sediments slurries using species-specific enriched stable isotopes. *Marine Chemistry* 90: 107-123.

Morel, FMM, AML Kraepiel and M Amyot. 1998. The chemical cycle and bioaccumulation of mercury. *Annu. Rev. Ecol. Syst.* 1998.29:543-566

Schuster, PF. 2005. Water and sediment quality in the Yukon River Basin, Alaska, during water year 2002: U.S. Geological Survey Open-File Report 2005-1199, 82 p. <http://pubs.usgs.gov/of/2005/1199/>

Turetsky, MR, JW Harden, HR Friedli, M Flanigan, N Payne, J Crock, and L Radke. Wildfires Threaten Mercury Stocks in Northern Soils, *Geophysical Research Letters* Vol. 33

And

Donlin Gold Draft EIS available at <http://www.donlingoldeis.com/EISDocuments.aspx>