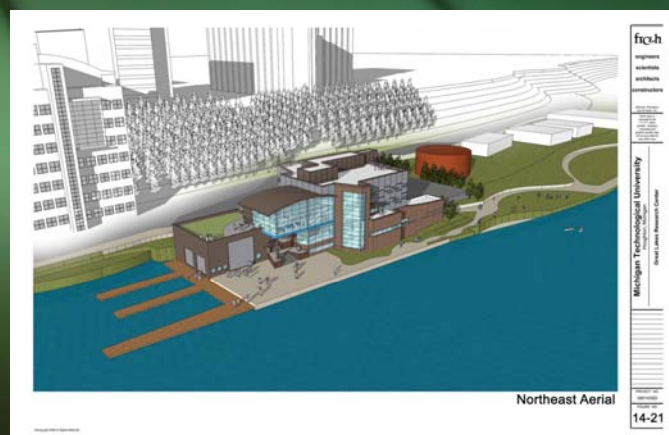


METAL MINING AND MERCURY

W. Charles Kerfoot & Noel Urban
(Michigan Tech University), Ron
Rossmann (EPA-Grosse Isle),
John Robbins (NOAA-GLERL)

Lab Setting-Water View

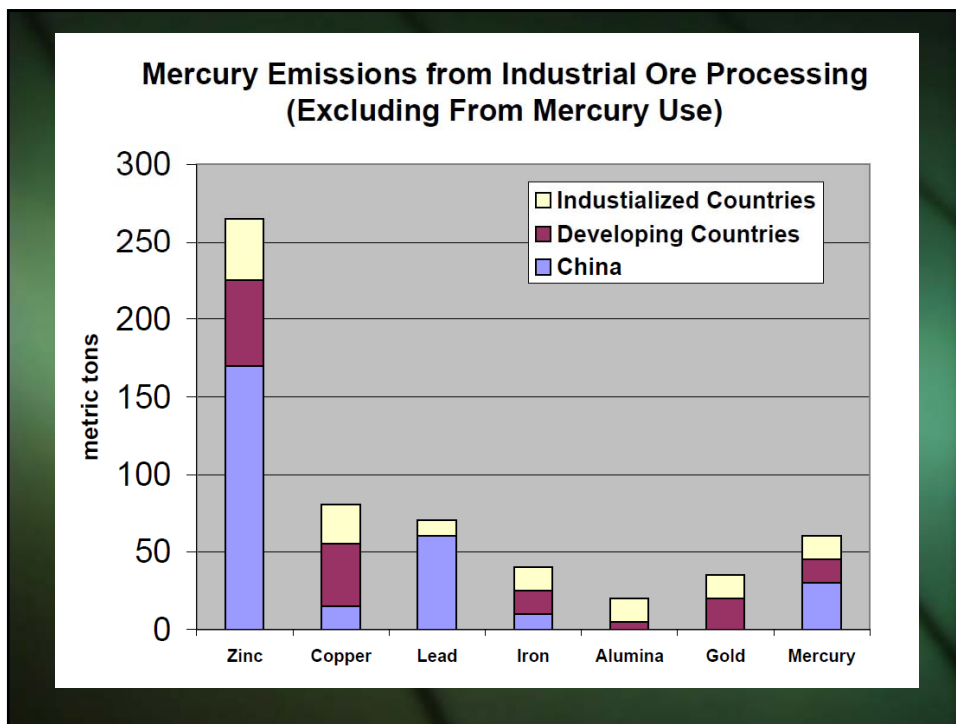


Funding Sources

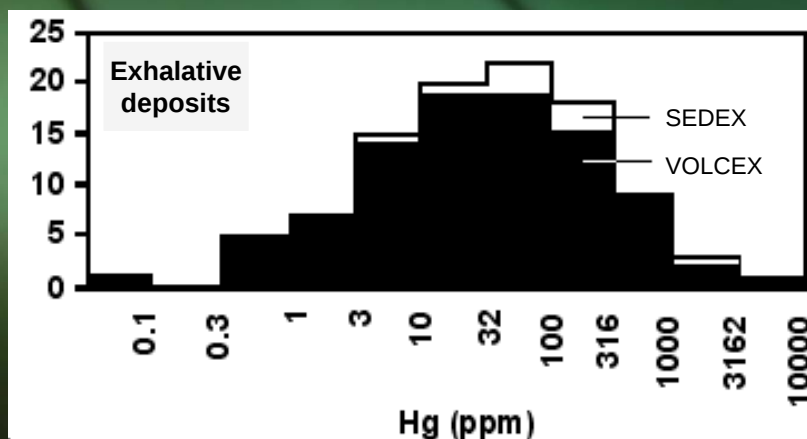
- NOAA/NSF KITES Project (NSF OCE)
- U.S. EPA Region V Grant to Baraga Tribal Council
- Michigan Department of Environmental Quality (MDEQ)
- U.S. ACE Vicksburg ERDC-EL (LiDAR CHARTS)

Changing Beliefs

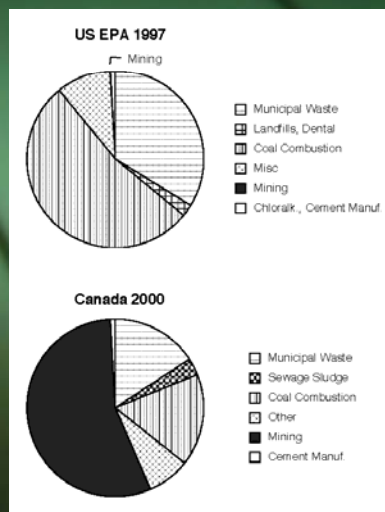
- Mining is a serious source of atmospheric mercury discharge in the world & U.S. (historic legacy, current practice)
- The mineral cinnabar (HgS) is present in the Lake Superior watershed
- Mercury is associated with metal mining (Copper, Iron) in the Upper Peninsula



*Solid Solution Substitution Of Hg For
Zn In Sphalerite (Schwartz 1997)*

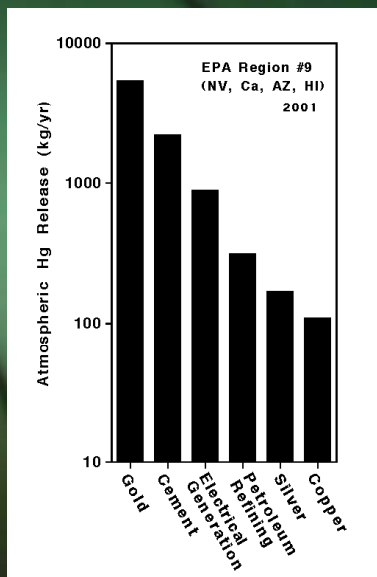


Sources For Atmospheric Hg Discharges (2000 Environment Canada vs 1997 U.S. EPA Report To Congress)

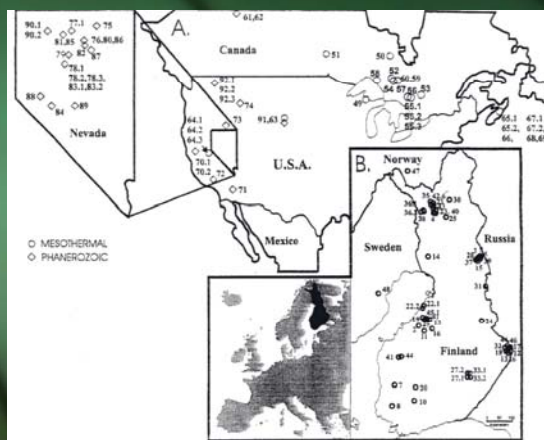
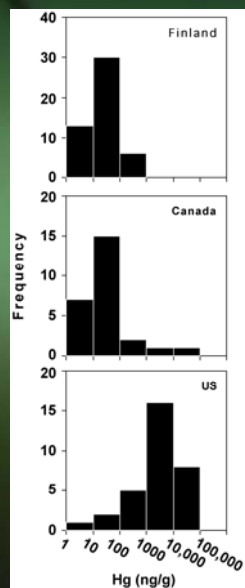


On Site Mercury Releases (atmospheric):

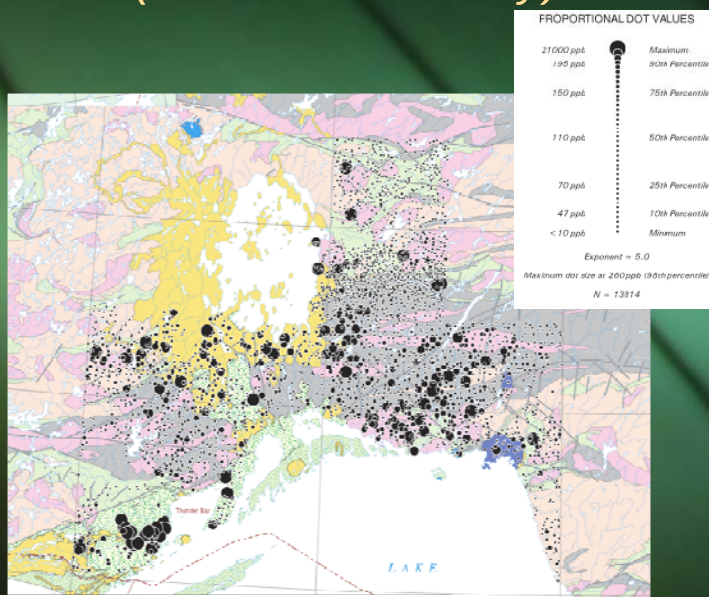
2001 EPA Region #9



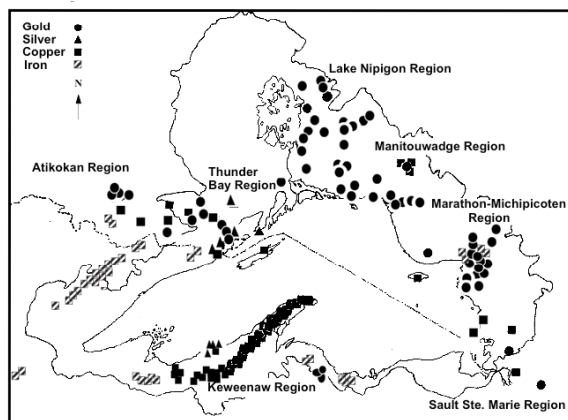
Mercury In Gold Ore Samples: Geographic Comparisons



Mercury In Lake Sediment (Can. Geol. Survey)



Lake Superior Watershed: Precious And Base Metal Mining



Lake Superior Watershed: Cinnabar And Mercurian Sphalerite

- Hemlo Gold Deposit near Marathon: Williams, Golden Giant, David Bell Mines (Michibayashi 1995; Powell and Pattison 1997; Tomkins et al. 2004): Hg 6% in ore samples, 6.7% in concentrates
- Massive Sulfide Deposits (12 locations), includes Flambeau Mine, Ladysmith, Ws (Motti et al. 1999): 0.11% Hg in Cu, 1.13% in Ag

Lake Superior Basin-Estimated Atmospheric Mercury Releases (kg/yr)

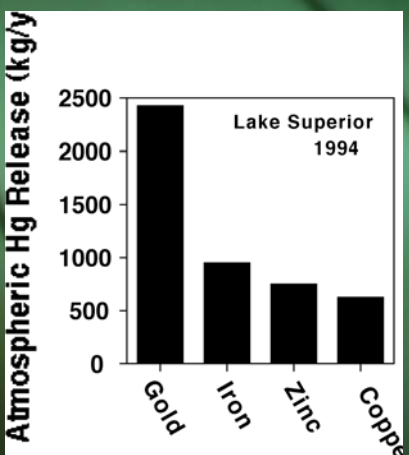


Table 4. Mercury release estimates (preliminary) from mining for the year 1994, Lake Superior watershed. Site estimates of Canadian Ore milled and metal produced are taken from Jen and McCutcheon (1995). The mercury emission factor for Hemlo operations is calculated from the mercury:g in Golden Giant concentrates (Hendriks and Chevalier 2001), whereas the iron pellet value comes from Jiang et al. (2002). The White Pine mercury estimate is from MDNR, cited in LSBP (2002). For copper and zinc mines, emissions are based on 4.0 ug Hg/g for copper ore, 110 ug Hg/g for silver 10.0 ug Hg/g for Geco zinc (Schwartz 1997).

Mine	Ore Milled (10 ³ tonnes)	Metal Produced				Emission Factor	Release(kg)
		Copper (tonnes)	Zinc (tonnes)	Silver (kg)	Gold (kg)		
Golden Giant	1,107	---	---	737	13,900	.080 g Hg/g Au	998
David Bell	465	---	---	150	6,012	"	432
Williams	2,303	---	---	815	13,851	"	995
Winston Lake	358	3,419	50,244	6,887	307	---	557
Geco	799	16,056	19,476	29,752	69	---	202
White Pine	---	43,200	---	---	---	(MDNR)	635
Taconite Pellet	47.35 x 10 ⁸ kg (Pellets)	---	---	---	---	7.48 ng Hg/g (Pellets)	354

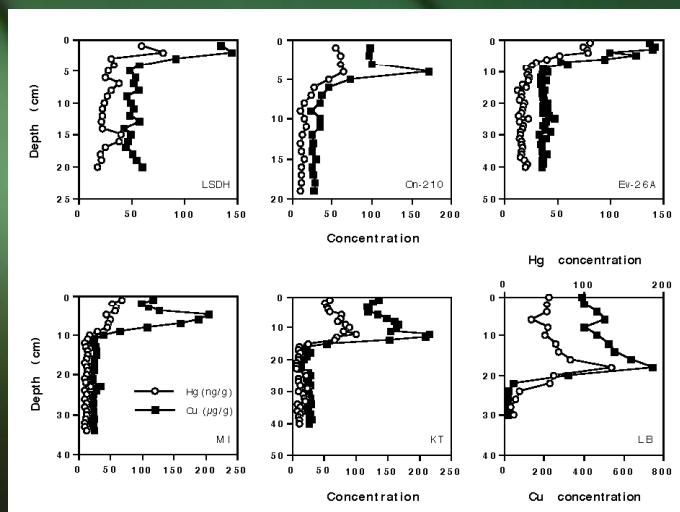
Quincy Shafthouse

- Keweenaw National Park (Native Copper Mining)
- 140 Mines, 40 Stamp Mills
- 5 Smelters
- Torch Lake Superfund Site





Copper/mercury profiles (NSF/NOAA KITES Project) From Deep Water (LSDH) to L'Anse Bay



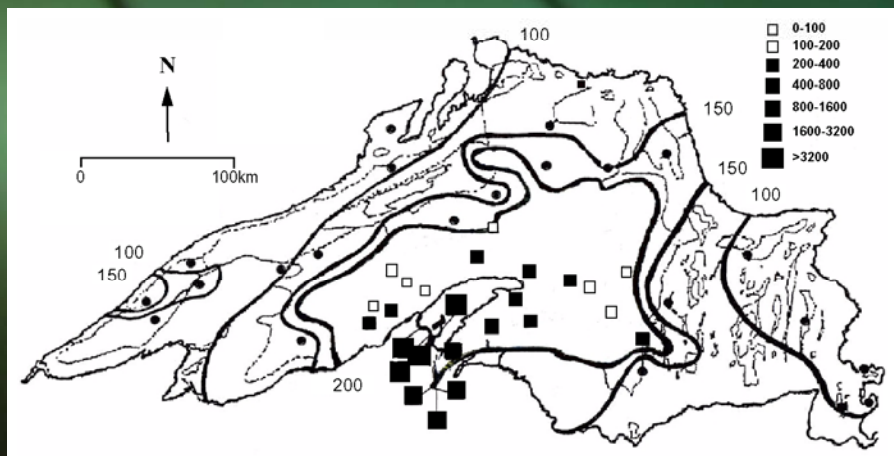
Surface Fluxes

Copper ($\mu\text{g}/\text{cm}^2/\text{yr}$)	N	Range	Mean $\pm$ 95 C. L.
Small Lake	16	0.2-1.9	0.4 $\pm$ 0.2
Lake Superior	16	1. -7.7	3.0 $\pm$ 1.0 (corrected)
Lake Superior	16	1.1-19.9	5.0 $\pm$ 2.5 (uncorrected)
Keweenaw Waterway	18	3.0-57.0	25.5 $\pm$ 8.2
Mercury ($\text{ng}/\text{cm}^2/\text{yr}$)			
Small Lake	16	0.5-2.4	1.1 $\pm$ 0.4
Lake Superior	19	0.8-10.0	3.9 $\pm$ 1.4 (corrected)
Lake Superior	19	1.0-36.0	7.3 $\pm$ 4.8 (uncorrected)
Keweenaw Waterway	14	2.1-41.1	10.9 $\pm$ 6.9

Anthropogenic Inventories

Copper ($\mu\text{g}/\text{cm}^2$)			
Small Lake	16	1-180	50 $\pm$ 31
Lake Superior	30	45-472	161 $\pm$ 33 (corrected)
Lake Superior	30	47-1,130	229 $\pm$ 89 (uncorrected)
KITES	22	10-2,968	497 $\pm$ 407
Keweenaw Waterway	21	1,081-20,163	8,571 $\pm$ 2,264
Mercury (ng/cm^2)			
Small Lake	16	67-298	64 $\pm$ 34
Lake Superior	25	6 -1,858	293 $\pm$ 165 (corrected)
Lake Superior	25	41-4,460	470 $\pm$ 307 (uncorrected)
KITES	22	19-487	206 $\pm$ 63
Keweenaw Waterway	23	187-7,758	2,696 $\pm$ 854

Anthropogenic Copper Inventories: Spatial Pattern



Anthropogenic Mercury Inventories: Spatial Pattern

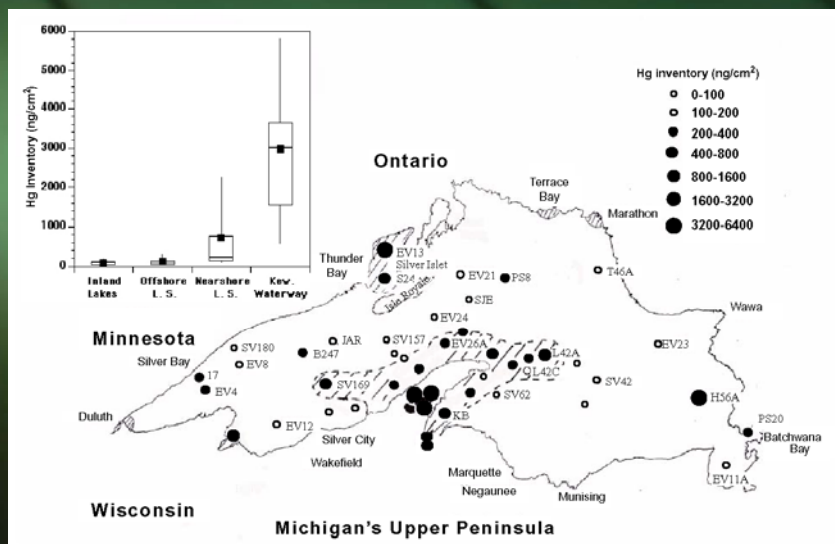
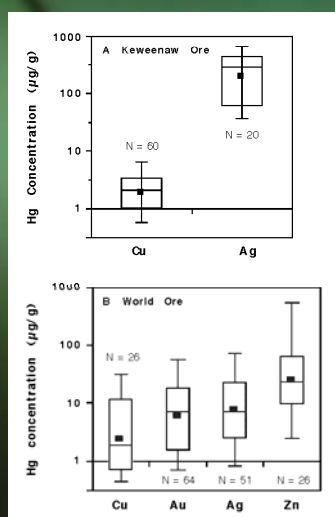


Table 3. Concentrations of metals in Keweenaw poor rock, stamp sands and various ores (N = sample size, CV = standard deviation/mean).

Ore Type	Element	N	Range	Mean $\pm$ 95 C. L.	CV (%)
Poor Rock	Cu ($\mu\text{g/g}$)	32	151-6,457	2,295 $\pm$ 599	74
	Ag ($\mu\text{g/g}$)	32	0.3-7.0	2.4 $\pm$ 0.6	73
	Hg (ng/g)	32	9-281	85 $\pm$ 25	82
Stamp Sands	Cu ($\mu\text{g/g}$)	68	366-16,163	1,364 $\pm$ 900	85
	Ag ($\mu\text{g/g}$)	68	0.6-8.7	3.2 $\pm$ 0.5	69
	Hg (ng/g)	68	2.8-265	48 $\pm$ 12	101
Copper Minera	Hg ($\mu\text{g/g}$)	24	0.5-6.5	2.4 $\pm$ 0.6	65
Native Copper	Hg ($\mu\text{g/g}$)	60	0.1-47.1	3.9 $\pm$ 2.1	203
Half-breed	Hg ($\mu\text{g/g}$)	10	0.7-981.3	154 $\pm$ 198	204
Native Silver	Hg ($\mu\text{g/g}$)	30	34-2,548	394 $\pm$ 187	130

Mercury Concentrations In Ore Samples



➤ A) Keweenaw native copper and silver ores

➤ B) World (Cu, Au, Ag) ores and Sphalerite (ZnS)

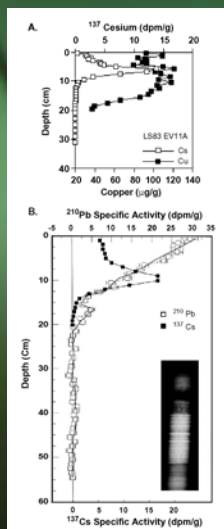
➤ C) Solid solution substitution (native metal-natural amalgamation) or for Zn in Sphalerite



Torch Lake Superfund Project



Radioisotope Profiles: Keweenaw Waterway (Portage Lake)

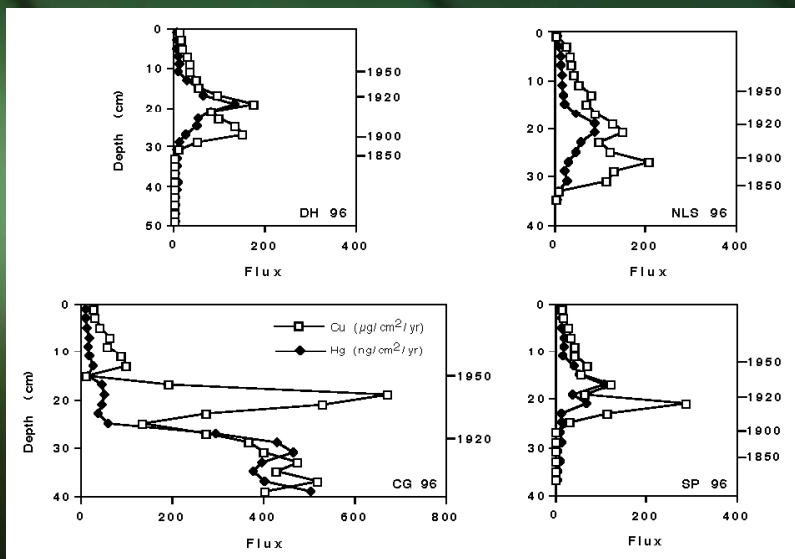


➤ A) ^{137}Cs dating

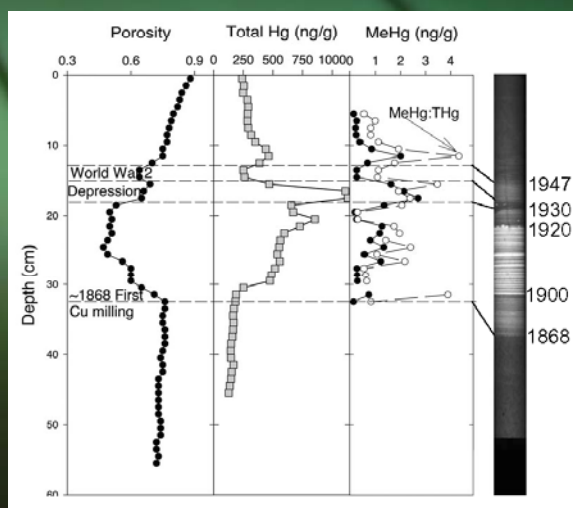
➤ B) ^{210}Pb dating

➤ C) Varves (X-ray bands, Cu-rich)-Insert

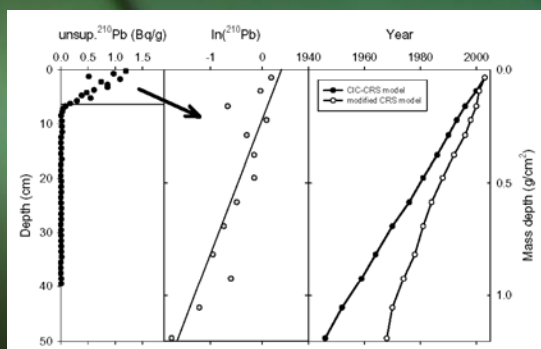
Copper And Mercury Flux Profiles: Keweenaw Waterway (CG: Near Dollar Bay Smelter)



Portage Lake Sediment Profile

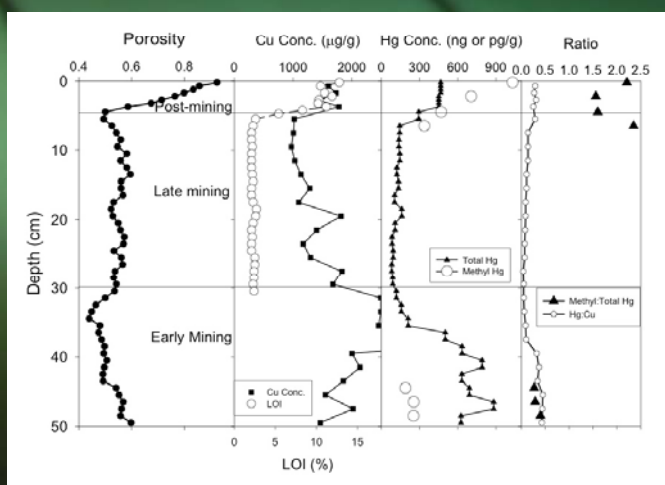


Torch Lake ^{210}Pb Model

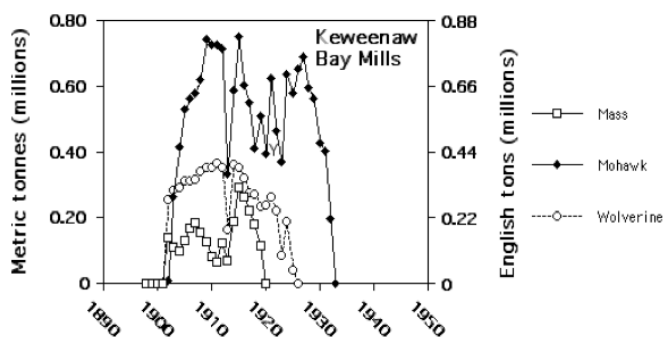


- Unsupported ^{210}Pb profile (20m site)
- CIC-CRS model
- Modified CRS model

Torch Lake Sediment Profile

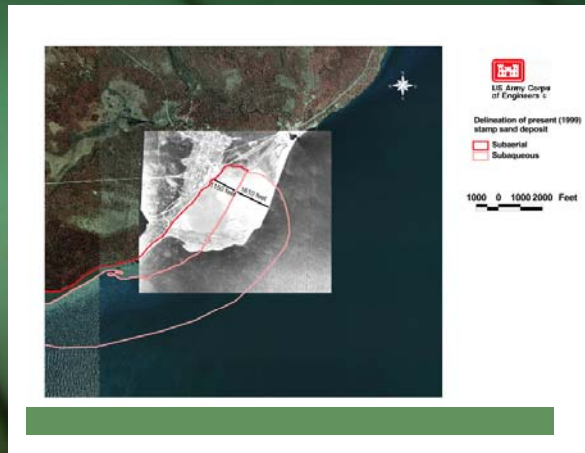


Stamp Sands Discharged By Stamp Mills Along Keweenaw Coastline



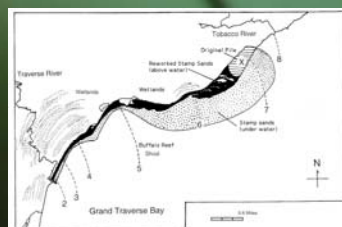
Historical Erosion Of Tailings Cone

- 1938 air photo of the original stamp sand discharge pile (white) superimposed upon a 1999 air photo (red line, natural shoreline; inner pink line, 1999 shoreline of pile and reworked sands ; outer pink, estimated underwater 1999 dispersal of eroded stamp sands)

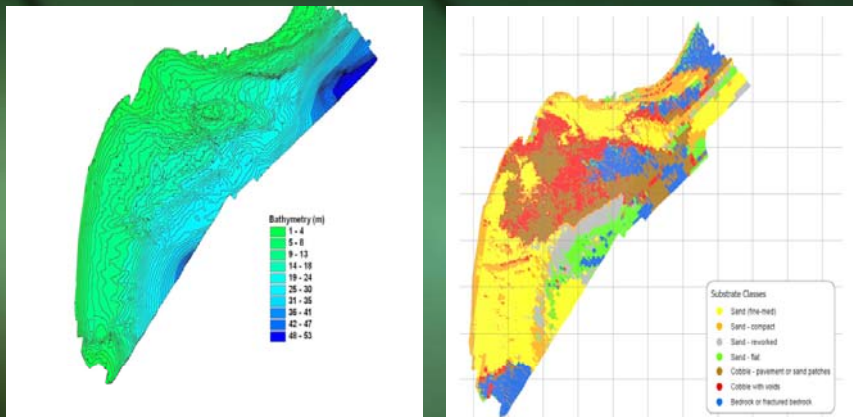


Gay Stamp Sand Site

- The above-water and underwater extent of the Gay Stamp Sand tailings in Grand Traverse Bay, MI. Note the natural white sand beach to the south of the Traverse River (diagram after Army Corps 2001)



Stamp Sands Threaten Buffalo Reef



- Bathymetry and substrate characterization around Buffalo Reef off Gay coastline, Keweenaw Bay. Studies conducted jointly by NWRI (National Research Institute Environment Canada) and GLIFWC (Great Lakes Indian Fish & Wildlife Commission).

US Army Corps of Engineers (Detroit) Remediation



- Positions of proposed revetment, groin
- And dredging zone

MSS Traverse River Jetty



Tailings Are Washing Across Traverse & Tobacco Rivers



Summary

- Historic mining is the dominant source of mercury to Lake Superior; voluntary industrial reporting is just not working
- \$15M Torch Lake Superfund Program covered interior stamp mill sites with soil layer; benthos not remediated (800+ years); Hg methylation
- Mine tailings & smelter sites continue to contaminate many Lake Superior watersheds (U.S. & Canadian sides)
- Gay Site was not included in Torch Lake Project; tailings piles are currently contaminating miles of the Keweenaw Peninsula shoreline