Mercury analysis from biological and environmental samples

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outline

- Burkina Faso
  - hair samples from AGM area (miners and controls)
- Pakistan
  - hair samples from workers in two chlor alkali factories
  - hair samples from dental practices and controls
- Chile
  - soil samples from one waste dump in a gold mine area including two controls
- Cambodia
  - hair and nail samples from two AGM areas
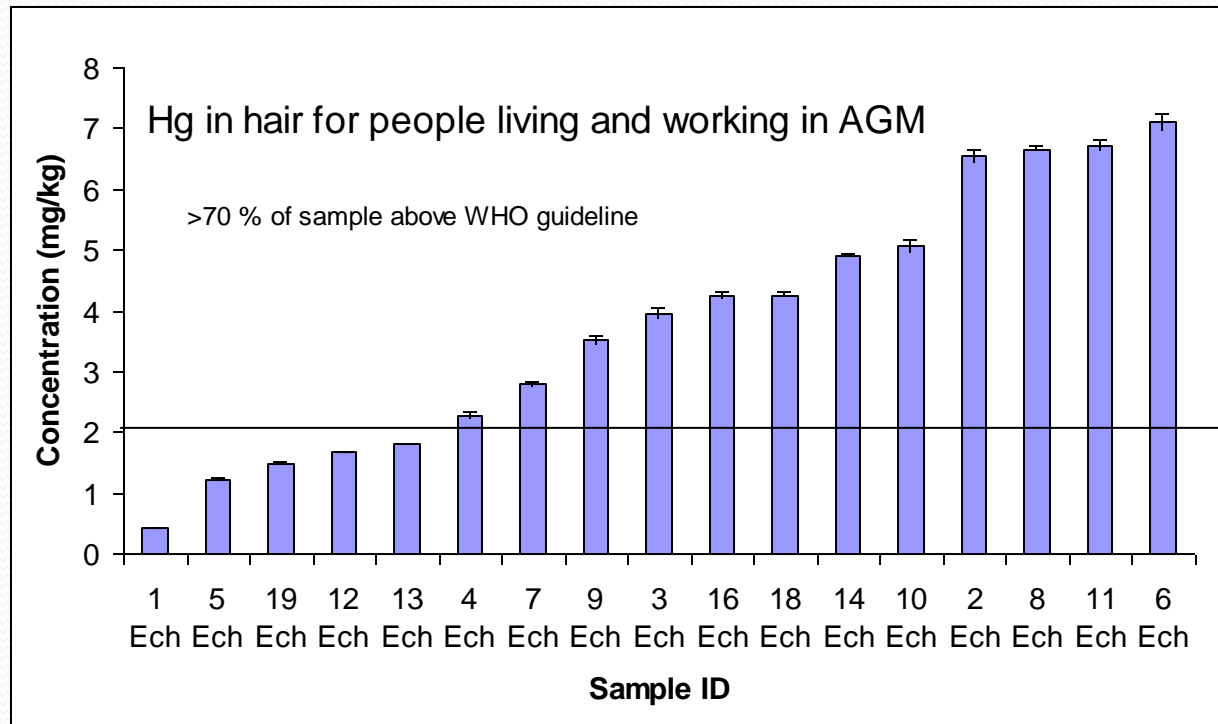 - soil and sludge samples from hospitals and waste dumps
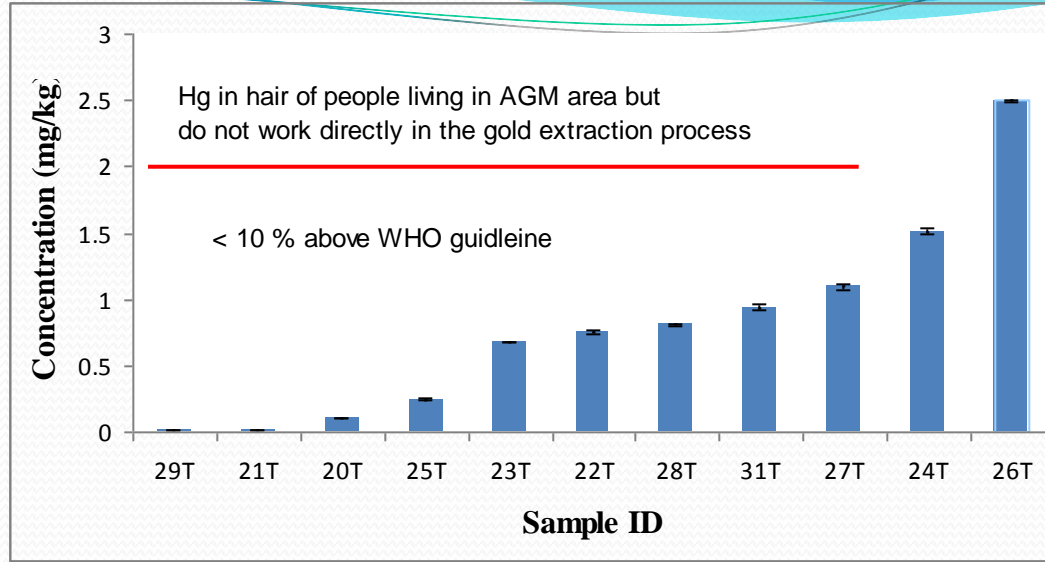
Quality Controls

- Certified references materials used
  - NIES 13
  - IAEA 085
  - both contain methylmercury and inorganic mercury
  - recovery > 97 %
- Spiked soil samples with
  - methyl mercury and inorganic mercury
  - recovery > 95 %

Burkina Faso

- 31 Hair samples in plastic bags were sent to TESLA
- mass was very limited (often less than 30 mg)
- Information given
  - group of gold miners
  - group of people living in the vicinity of AGM area
- washing followed by oxidative acid digestion
- total Hg analysis was carried out in duplicates each one analysed three times using AFS

Burkina Faso

AGM

Hg in hair of people living in AGM area but do not work directly in the gold extraction process

< 10 % above WHO guidleine

Hg in hair for people living and working in AGM

>70 % of sample above WHO guideline

Burkina Faso (summary)

- some samples too low in mass to conduct an analysis
- exposure to mercury minimal in AGM area
  - hair (median: 0.75 mg/kg)
  - min/max: 0.01 – 2.50 mg/Kg)
- exposure to mercury for miners significant
  - hair (median: 3.95 mg/Kg)
  - min/max: 0.01 – 7.10 mg/Kg)

t-test: p < 0.0001
F-test: p < 0.01

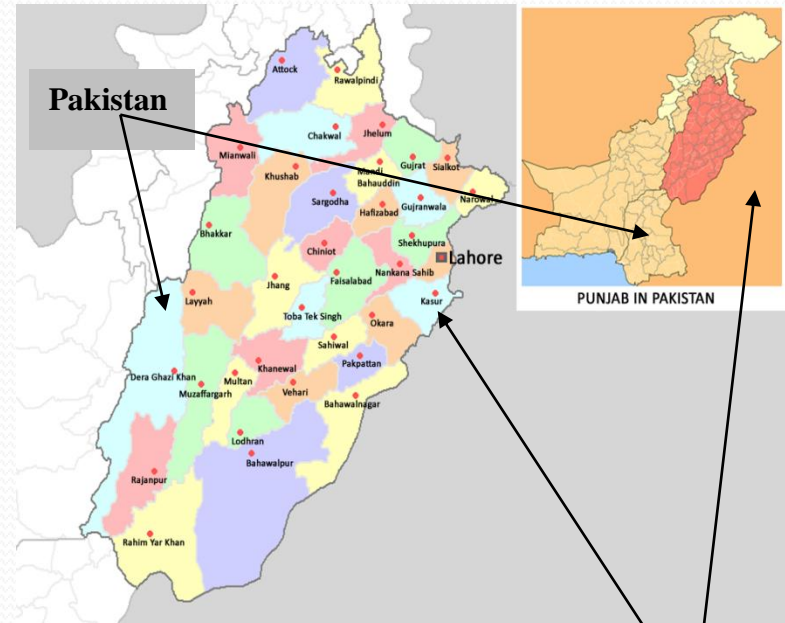UNEP project :Mercury in waste management
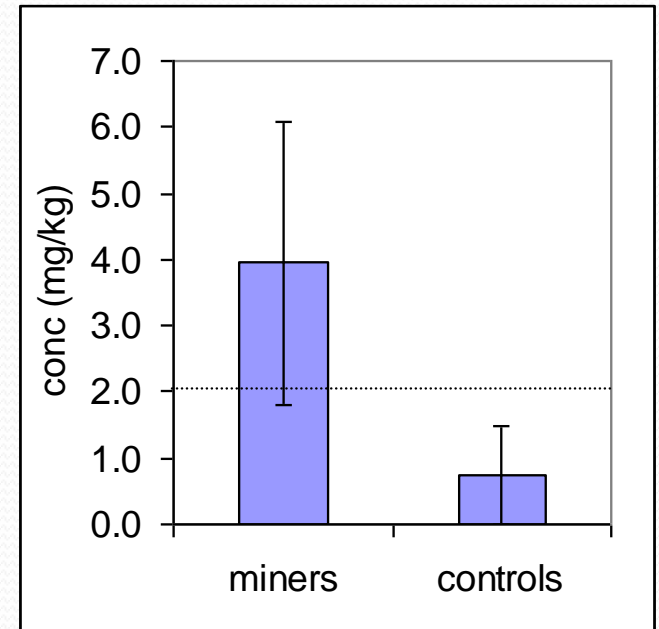
Pakistan

- 72 Hair samples in plastic bags were sent to TESLA
- Questionnaire provided by TESLA was filled out and provided information about diet, age, amalgam fillings, working tasks, etc..
- Groupings:
  - workers at two chlor-alkali electrolysis
  - workers dental practices and hospital
  - control group (students and staff at university)
- washing followed by oxidative acid digestion
- total Hg analysis was carried out in triplicates and measured by ICPMS
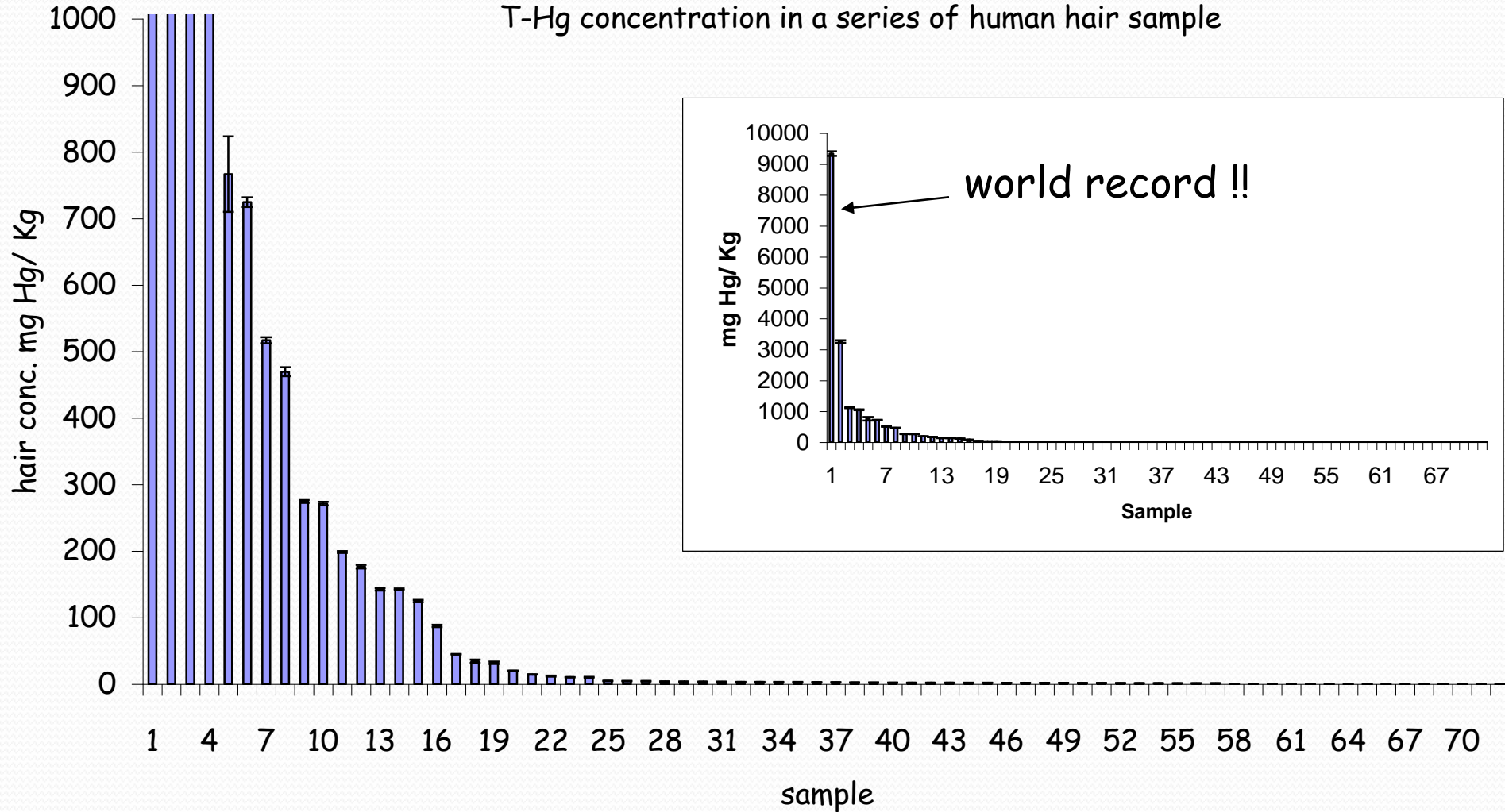
Hair analysis of workers in Pakistan's Hg hot spots

✓ 72 hair samples were obtained from Pakistan by UNEP from four (4) groups as follows:

- G. No (1): 23 Human hair samples were collected from Chlor-Alkali factory workers (Participants) by UNEP.

- G. No (2): 10 Human hair samples were collected from Chlor-Alkali factory workers (Participants) by UNEP.

- G. No (3): 21 Human hair samples were collected from dental and health workers (Participants) by UNEP.

- G. No (4): 18 Human hair samples were collected from Punjab University (Lahore / Pakistan) students and staffs (Participants) by UNEP.

- All the human hair samples were collected from the Lahore area of Pakistan as shown in this **Fig**.

Location of study area (Lahore) in Punjab Province, Pakistan

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Pakistan

T-Hg concentration in a series of human hair sample

world record !!
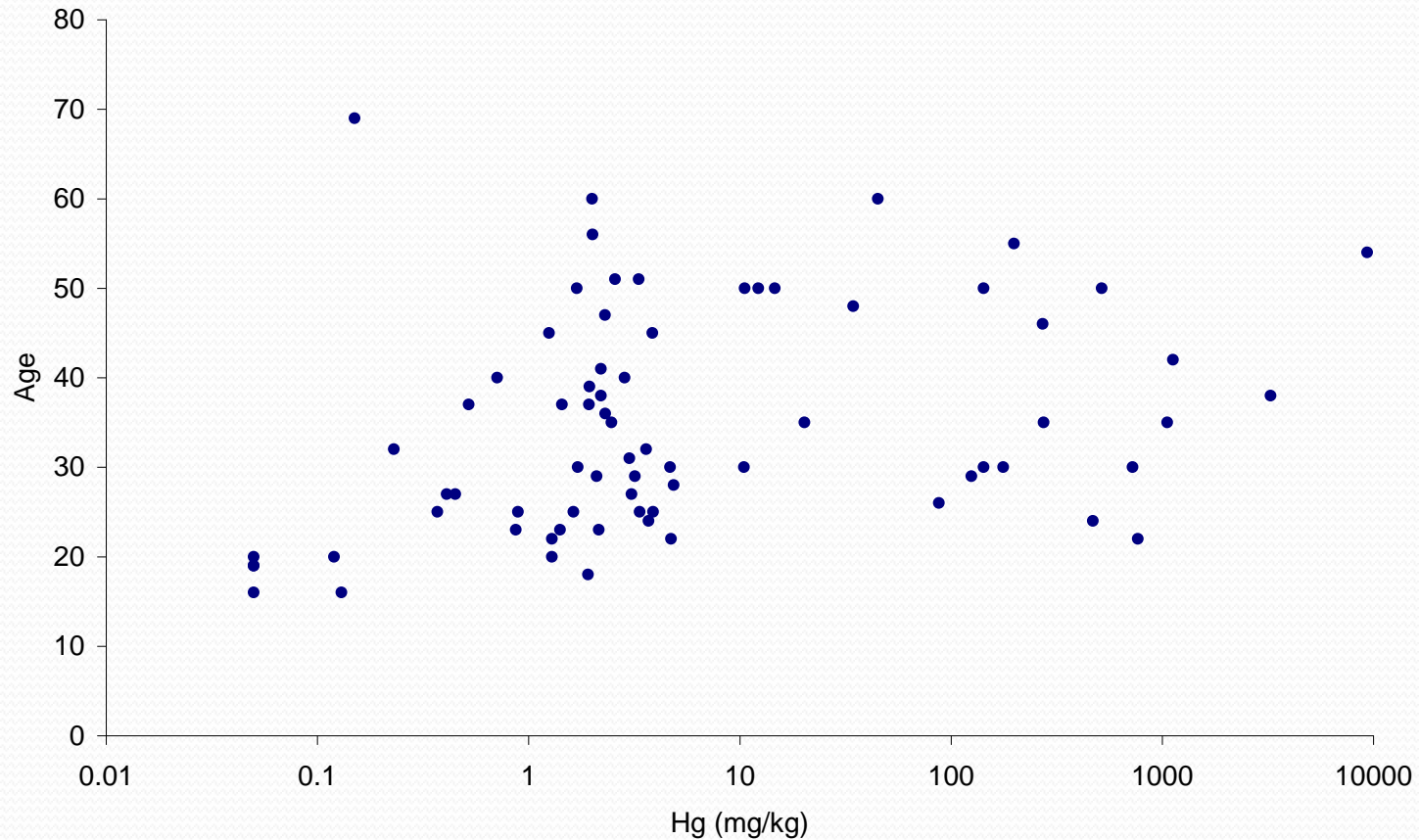
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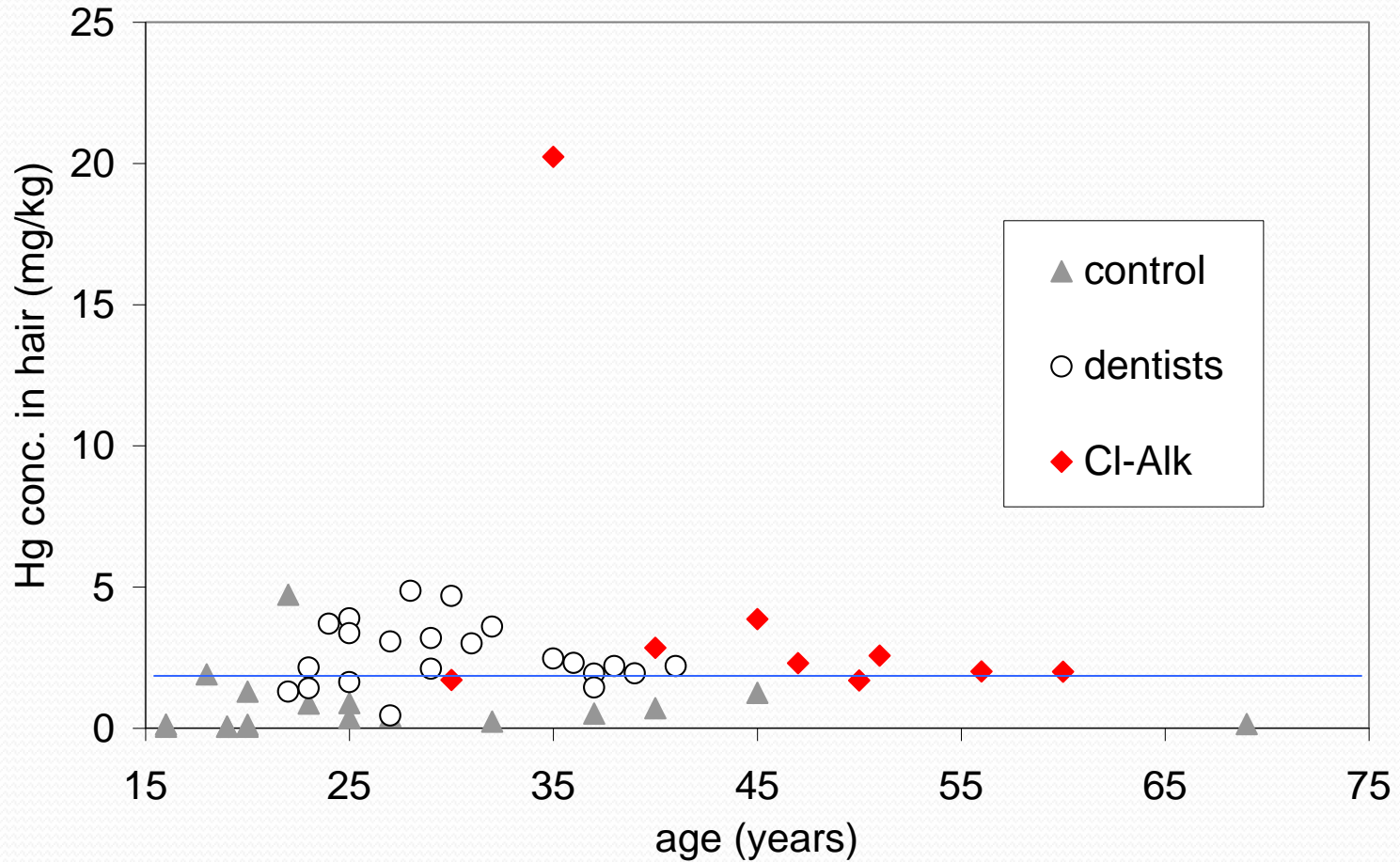Highest ever measured [Hg] in hair of 1st chloro-alk. plant
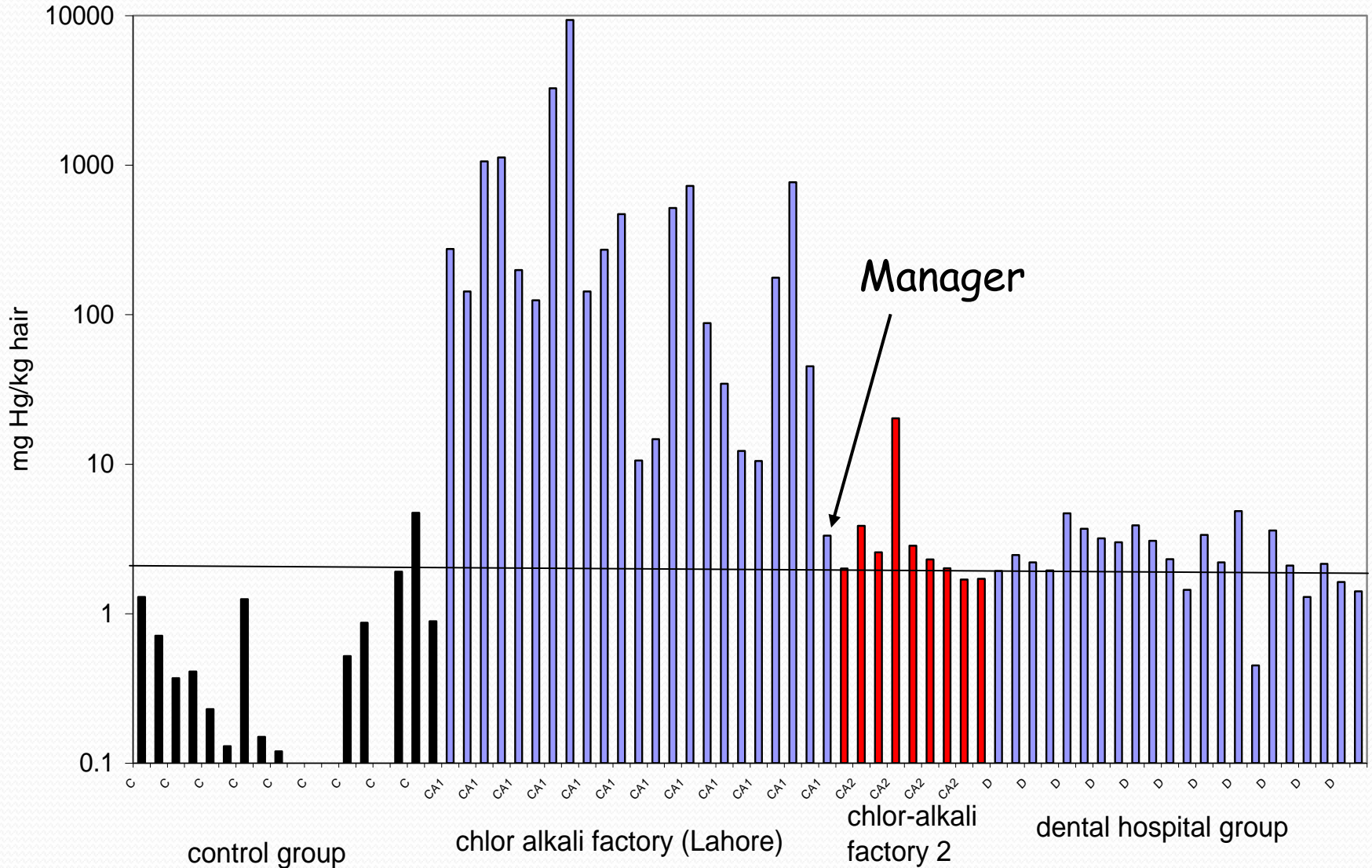
Manager

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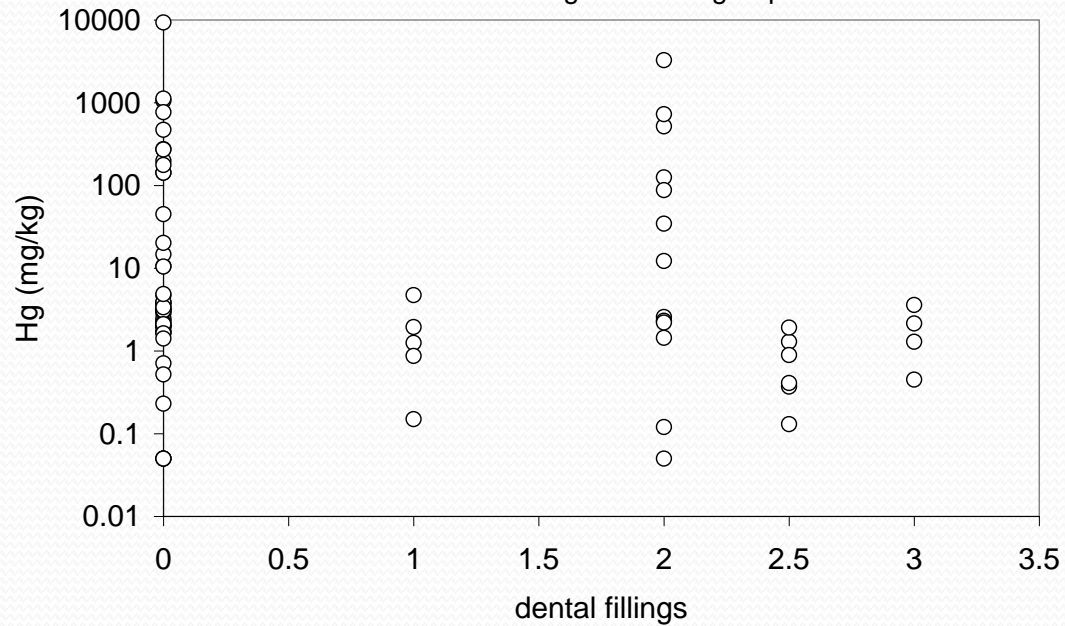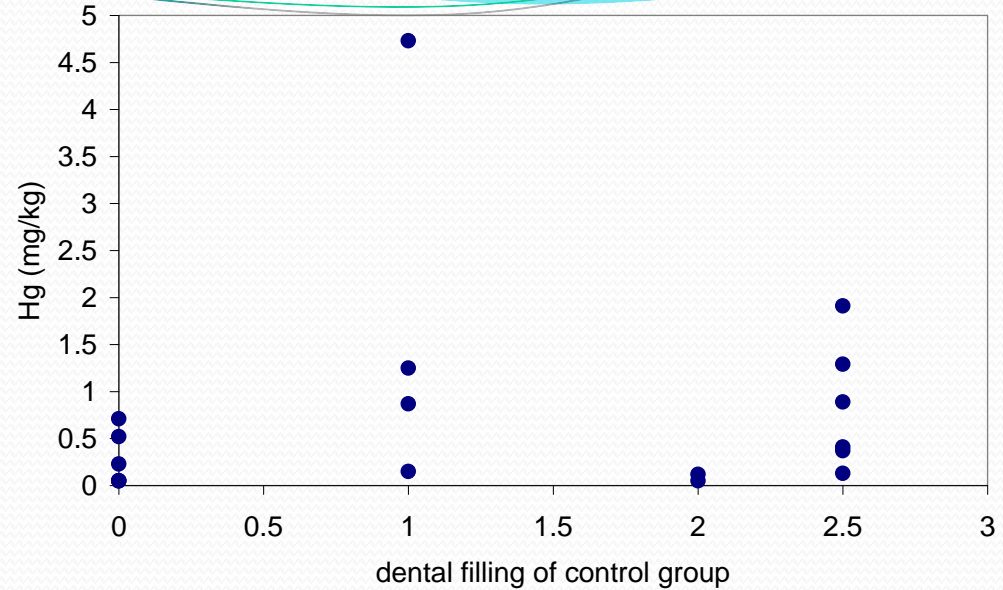
… Hg (hair) shows no trend with age …
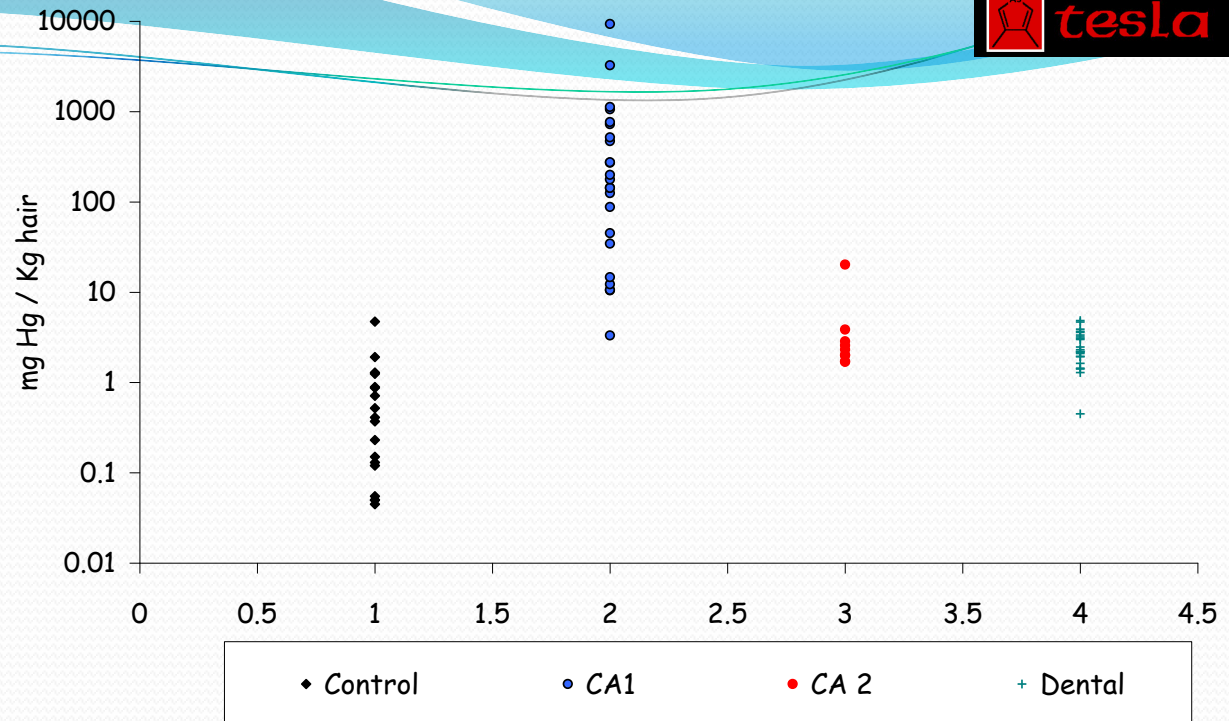

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… Hg (hair) shows no trend with age …

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No correlation of mercury in hair and number of dental fillings

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Pakistan (Summary)

- workers at dental clinics & hospitals show elevated levels of Hg in hair compared to control group although max level higher in some controls
- workers at chlor-alkali plant exposed to extremely high levels of mercury
- results from one plant cannot be extrapolated to the another plant

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| Location	n	Mean ± SD (µg/g)	Range (µg/g)	Comments	References
Tucurui, Para, Brazil	125	35.0	0.9-240	Fishermen	Leino and Lodenius (1995) [2]
Palawan Philippines	130	3.7	0.1 – 18.5	Hg mining impacted area	Williams et al. (2000) [3]
Kuwait	100	4.181	-	Fishermen	Al-Majed and Preston (2000) [4]
Diwalwal, Philippines	316	4.14	0.03-37.8	Gold amalgamation area	Drasch et al. (2001) [5]
Rio Branco, Brazil	2318	2.418 ± 0.850	-	Urban population	De Oliveira Santos et al (2002) [6]
Jacareacanga, Para, Brazil	205	8.6	0.3-83.2	Brazilian Amazon riverine community	Crompton et al. (2002) [7]
Ten cities in Japan	8665	1.82 (GM*)	0.02 – 29.4		Yasutake et al. (2004) [8]
Cambodia	94	3.1 (GM) 7.3 (GM)	0.54-190	A source other than fish may be responsible for high Hg in some Cambodians	Tetsuro, A. et al .(2005) [9]
Madeira River B., Amazon , Brazil	713	15.22 ± 9.60	5.99-150	Riverside population	Bastos et al. (2006)[10]
Wujiazhan town, northeast China	108	3.44 (AM**) 0.648 (GM*)	0.16-199	The river was polluted with Me-Hg by industrial wastewater discharge	Zhang and Wang (2006) [11]
DSX, Wanshan	49	5.5 ± 2.7	1.5-16	Mercury mining area	Ping Li (2009) [12]
XCX, Wanshan	36	3.3 ± 1.4	1.6-9.4	Mercury mining area	Ping Li (2009) [12]
Chlor-Alkali / Pakistan (SCL)	9	Mean 4.36 Median 2.30	1.69 – 20.2	Pakistani Chlor-Alkali factory	This study
Chlor-Alkali / Pakistan (ICL)	23	Mean 818 Median 177	3.3 - 9341	Pakistani Chlor-Alkali factory (Lahore)	This study
Pakistani Health worker/ Pakistan	22	Mean 2.59 Median 2.26	0.45- 4.86	Dental Hospital (Pakistan /Lahore)	This study
Punjab University (Lahore /Pakistan)	18	Mean 0.76* Median 0.39*	<0.03-4.73	Pakistani Control group (student population)	This study

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Pakistan (open questions)

- problems at CA in Lahore needs to be addressed
- ethical issues with information
  - extremely high Hg concentrations
- bioavailability of Hg (speciation)
  - Hg^o adsorption
  - transformation to $Me\text{-}Hg^+$
  - Hg^{2+} ??

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Chile

- 33 soil samples in plastic bags were sent to TESLA
- milled and very homogenise
- Information given
  - waste dump from a gold mine (?)
  - surface and core samples (information limited)
- oxidative acid digestion
- total Hg analysis was carried out in duplicates each one analysed three times using AFS
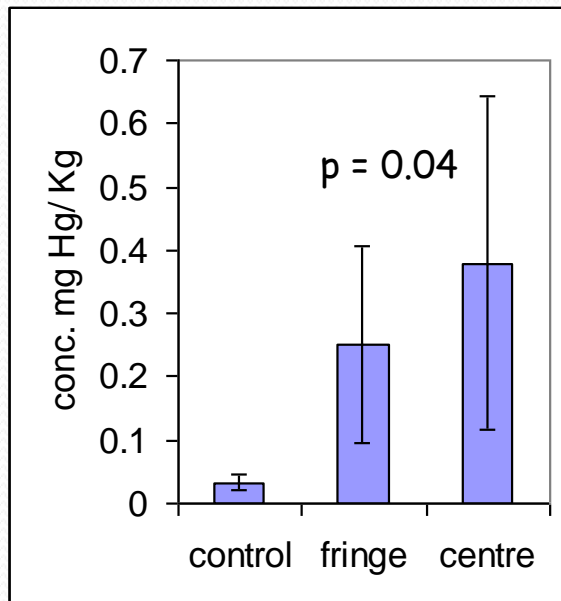
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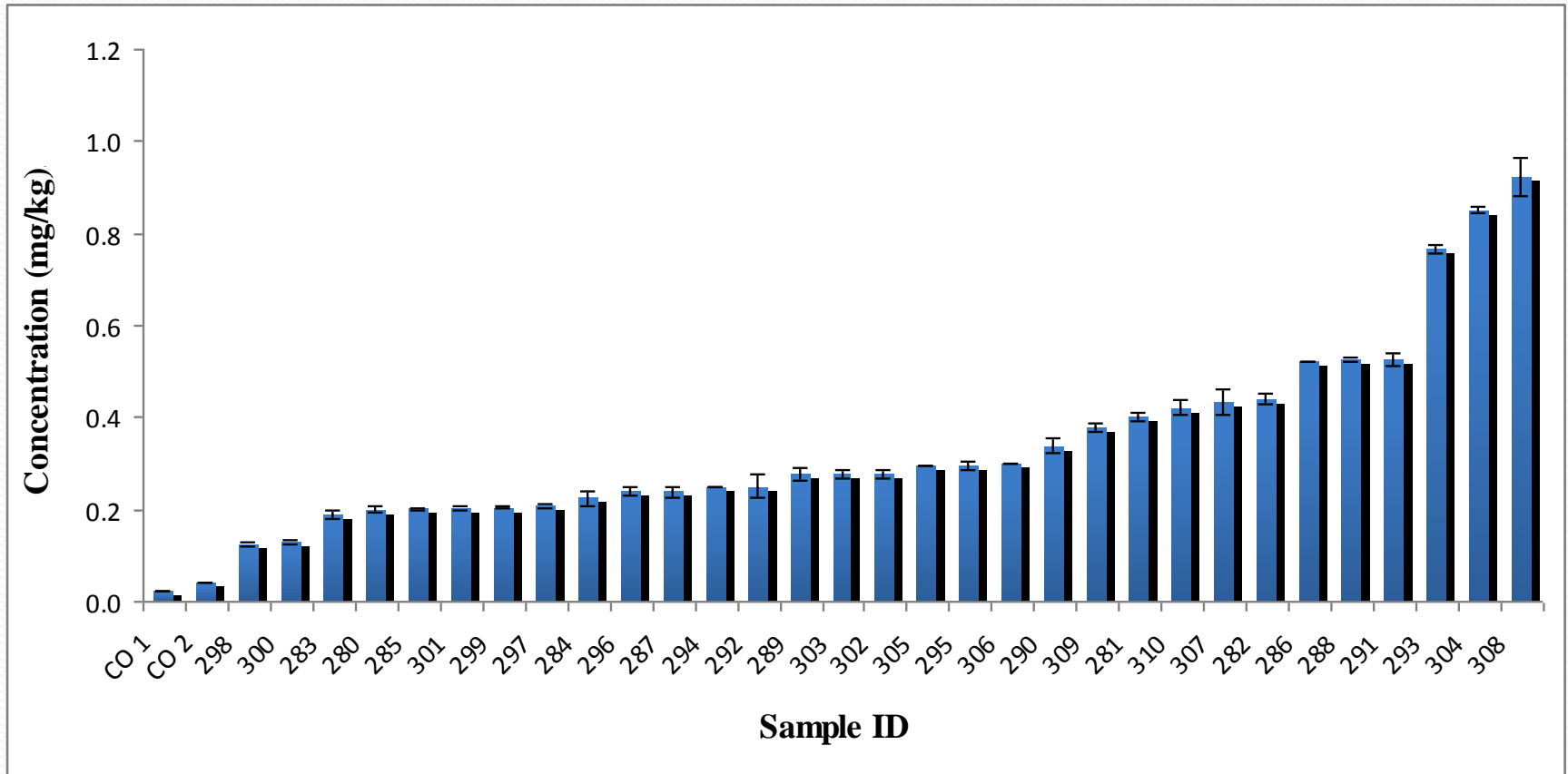
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Homogeneity of soil samples

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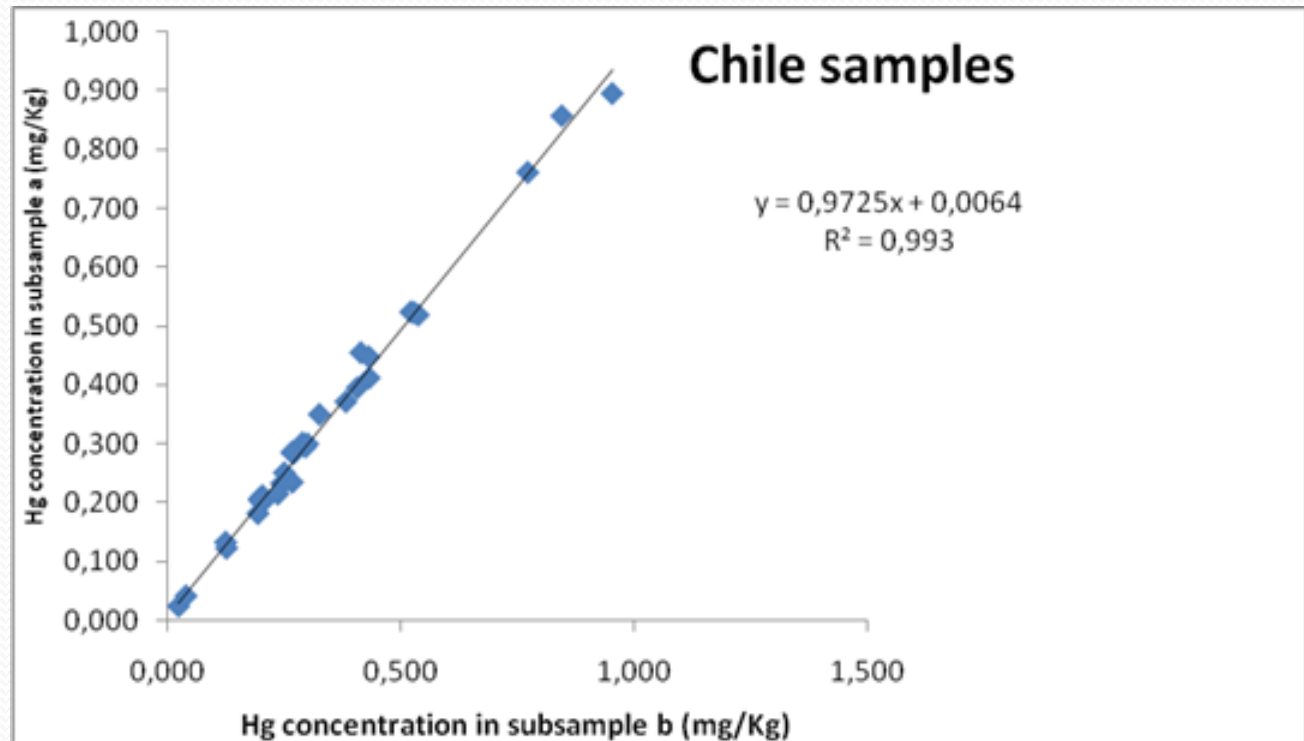
Chile (summary)

- all soil samples elevated Hg
- overall no extreme concentrations
- highest conc < 1 mg/Kg
- centre of waste dump higher than at the fringes

0.85

0.92

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Cambodia

- hair and nail samples
  - from miners and family members who assist in the AGM from two areas (together 24 samples)
- soil and sludge from sewage near
  - the two AGM areas (each 3 samples)
  - public drainage system from four areas (each 3 samples)
  - two hospitals together 7 samples
  - two dental clinics (each 3 samples)
  - two dumping sites together 9 samples
- detailed information about the sample location was given

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Cambodia (AGM)

→ elevated Hg in hair
→ similar Hg (hair) samples for miners and family members
→ nail Hg lower ?

Ratanakiri

Kratie

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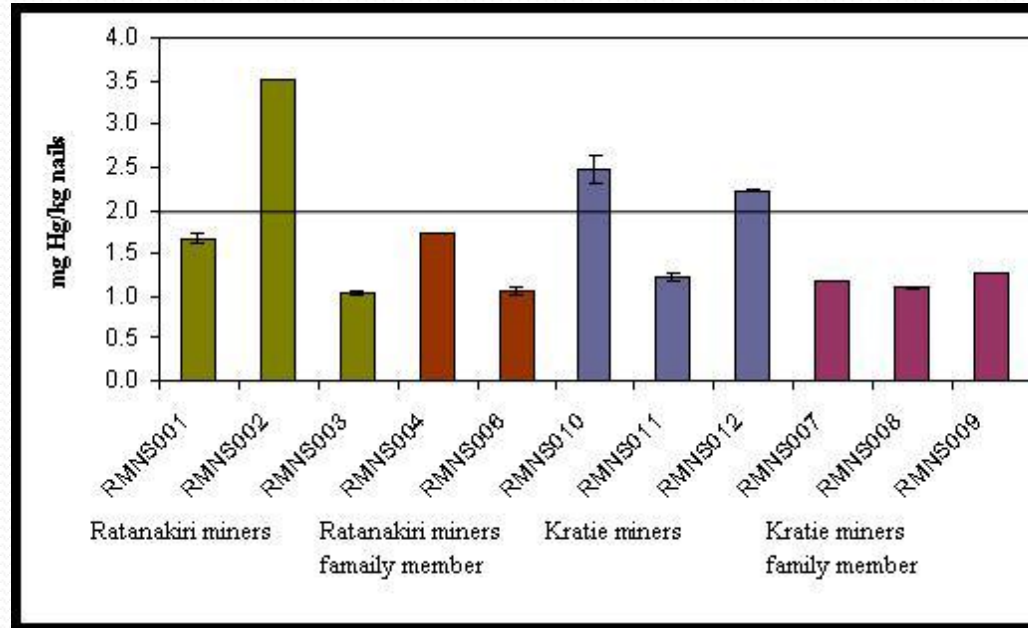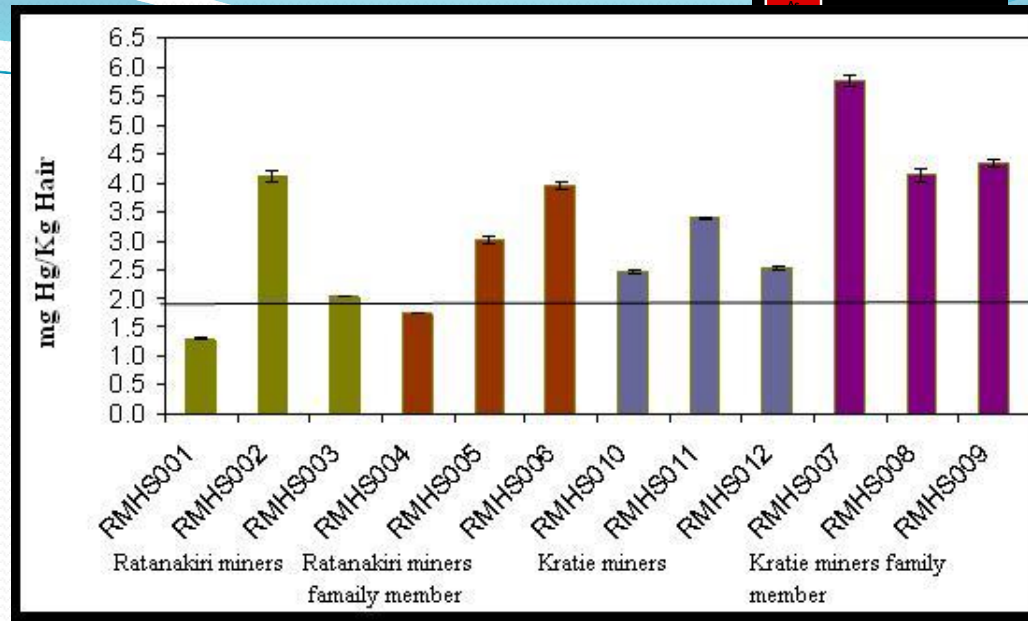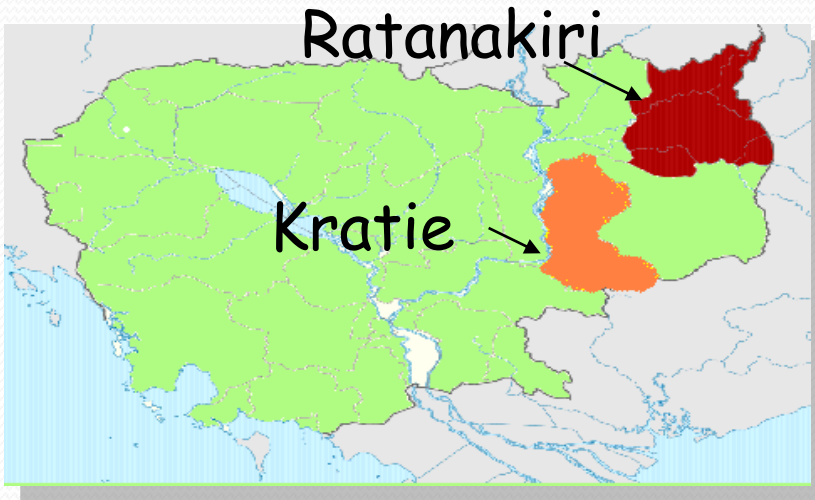
Cambodia (AGM)

→larger concentrations in the sludge surrounding the tailing points than the ore.

→ore at Kratie higher than Ratanakiri whereas the sludge is lower at Kratie

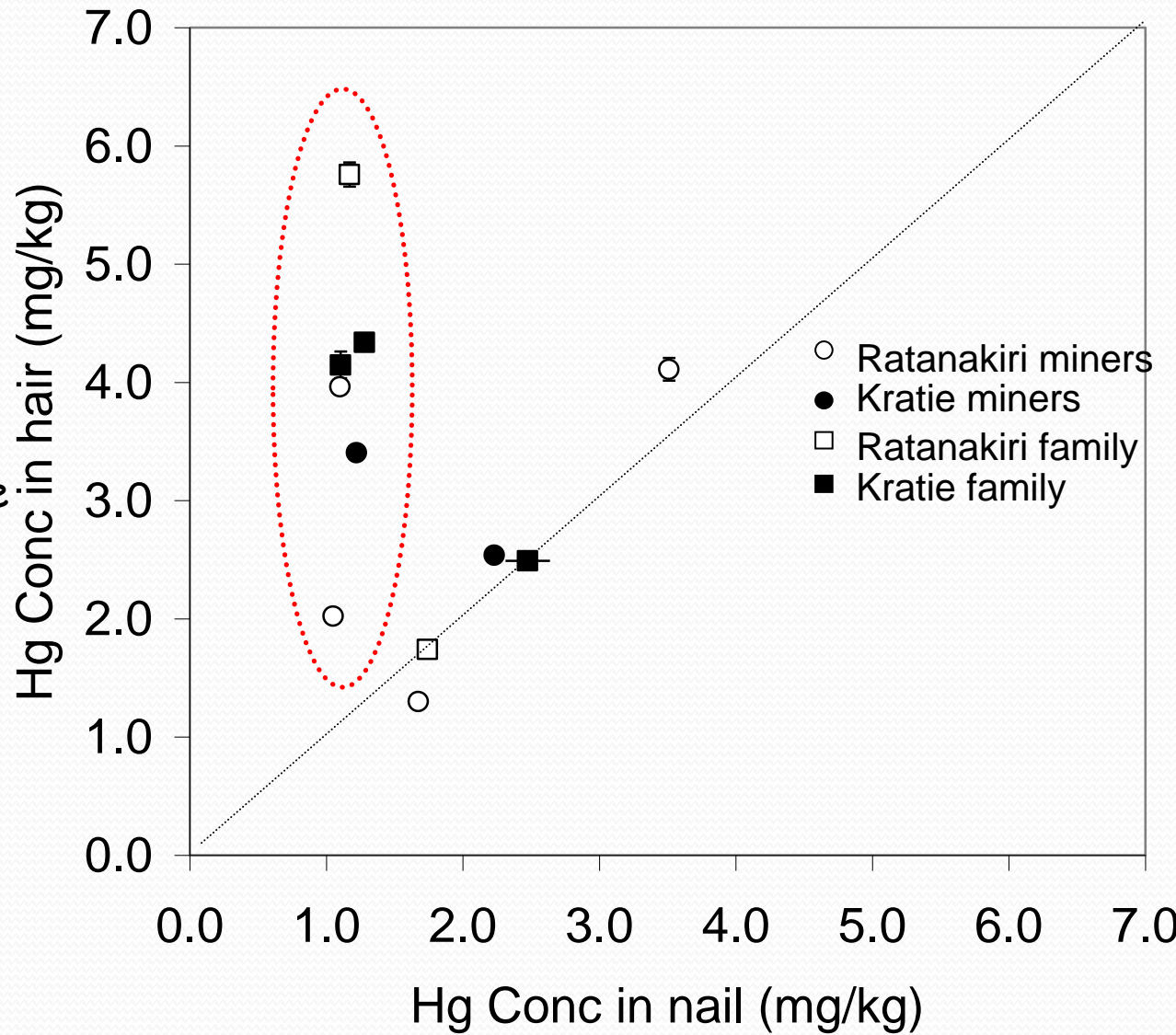UNEP project :Mercury in waste management
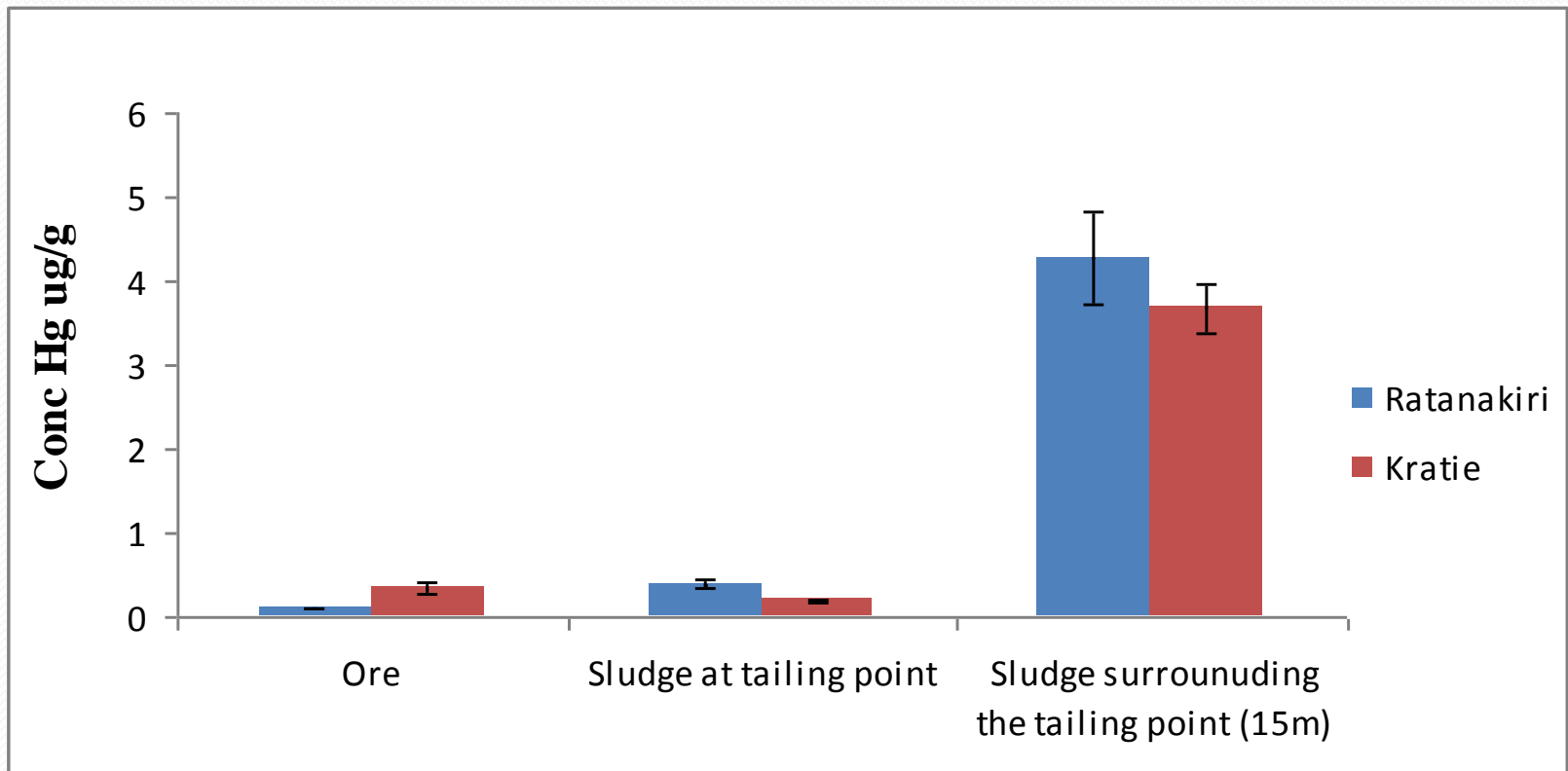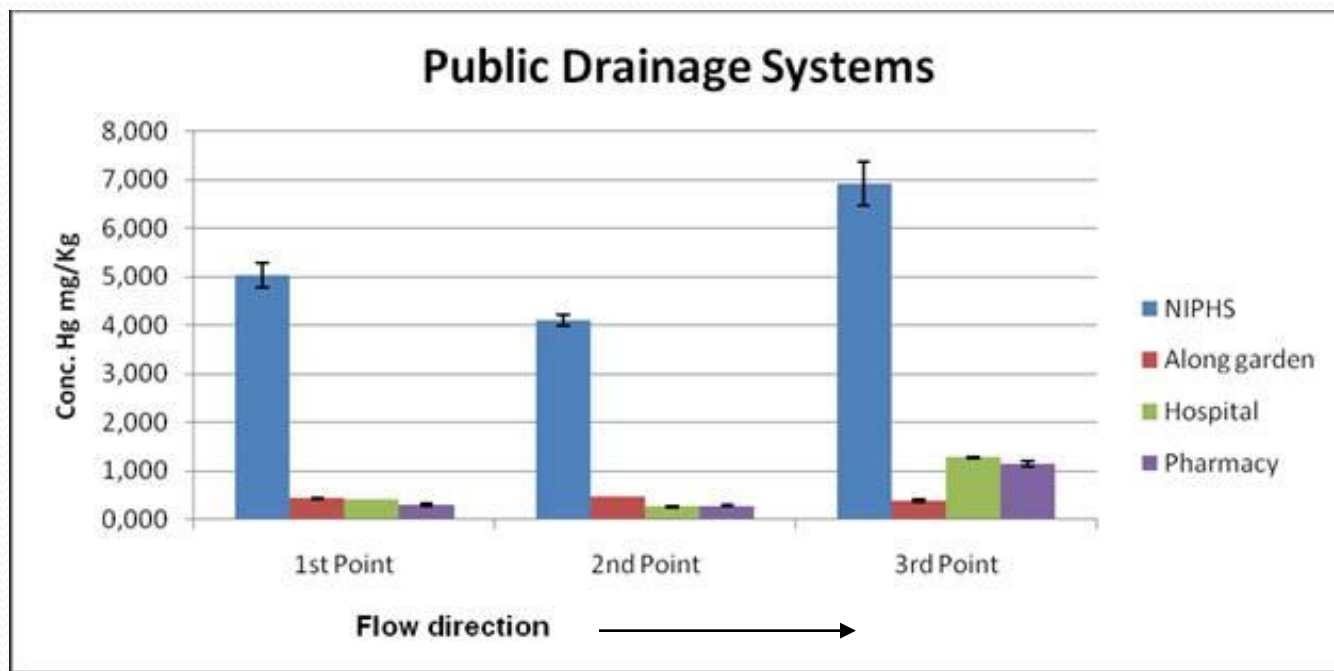
Cambodia (AGM)

→no pattern for miners /family members or region

→two groups of samples indicate different exposure

→high Hg in hair and low in nail indicates expsoure to volatile Hg (needs confirmation)

Scatter plot: Hg Conc in hair (mg/kg) vs Hg Conc in nail (mg/kg)

Legend:
- ○ Ratanakiri miners
- ● Kratie miners
- □ Ratanakiri family
- ■ Kratie family

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Cambodia (public drainage systems)

Public Drainage Systems

- in most cases higher Hg conc with distance from source
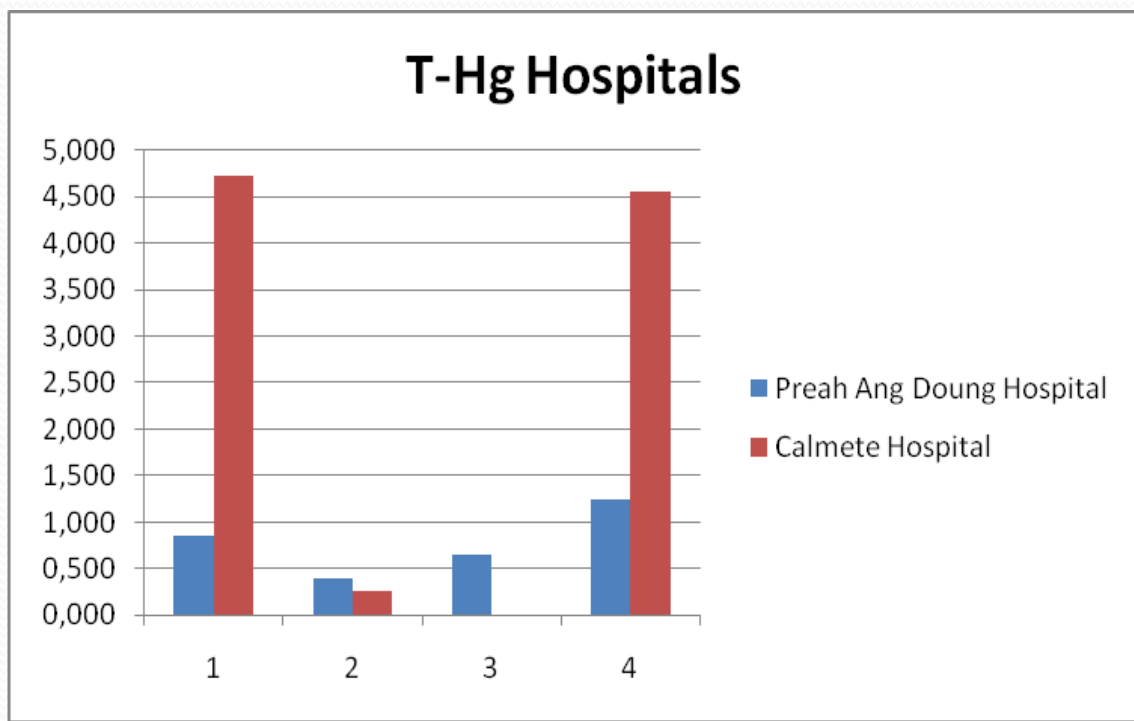- high level at the lake Boeung Kak near NIPHS (max. 6.9 mg/kg)

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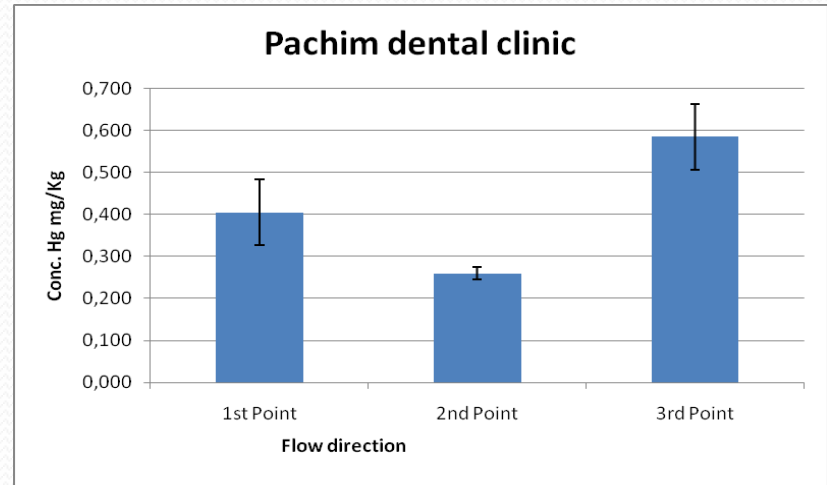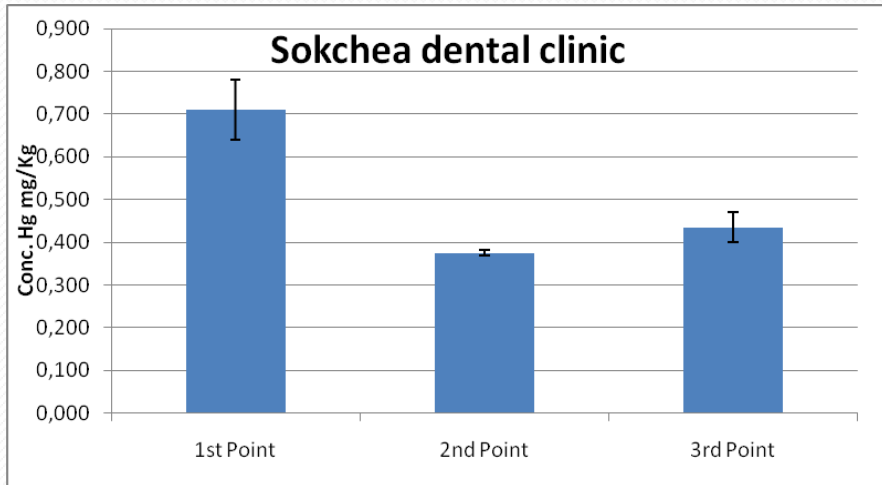# Cambodia

possible source
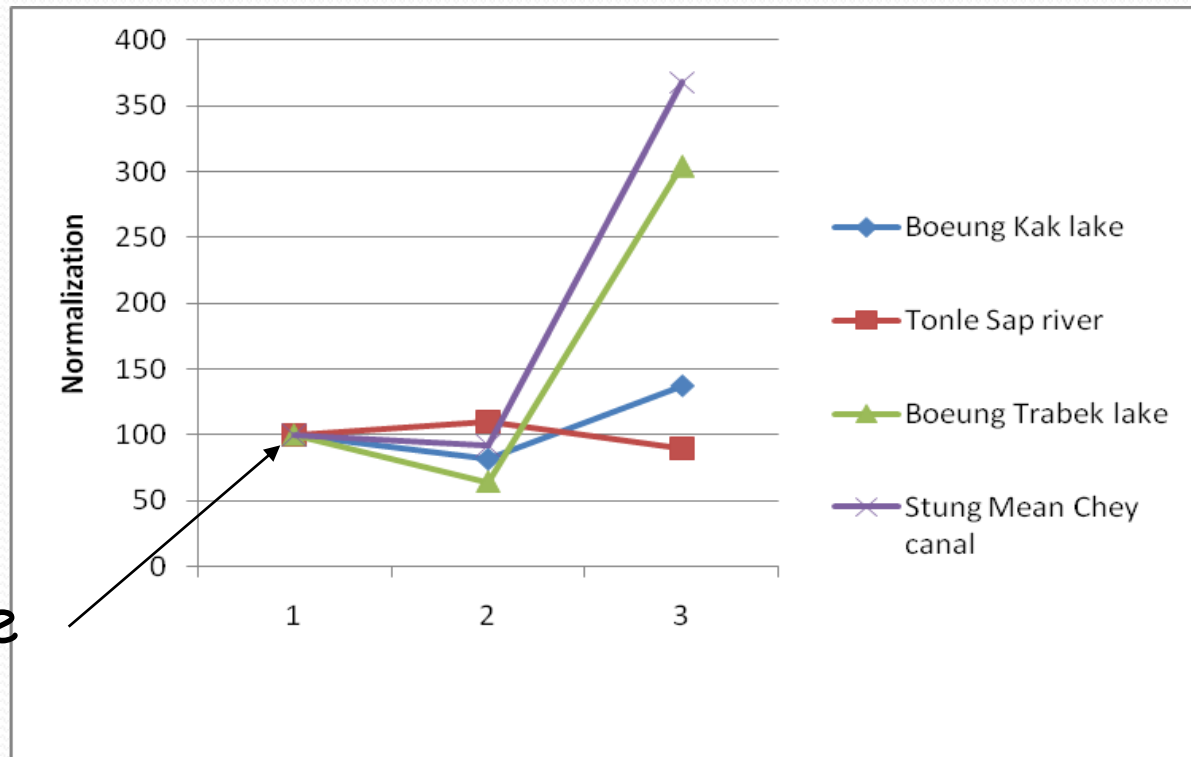
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Cambodia (hospitals)

- large differences in Hg concentrations.
- highest concentration in sludge similar to AGM tailing ponds

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Cambodia (dental clinics)

- similar Hg concentrations in sludge in public drainage near dental clinics
- generally low concentration (< 0.8 mg/Kg), lower than hospital sludge

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Cambodia (landfill sites)
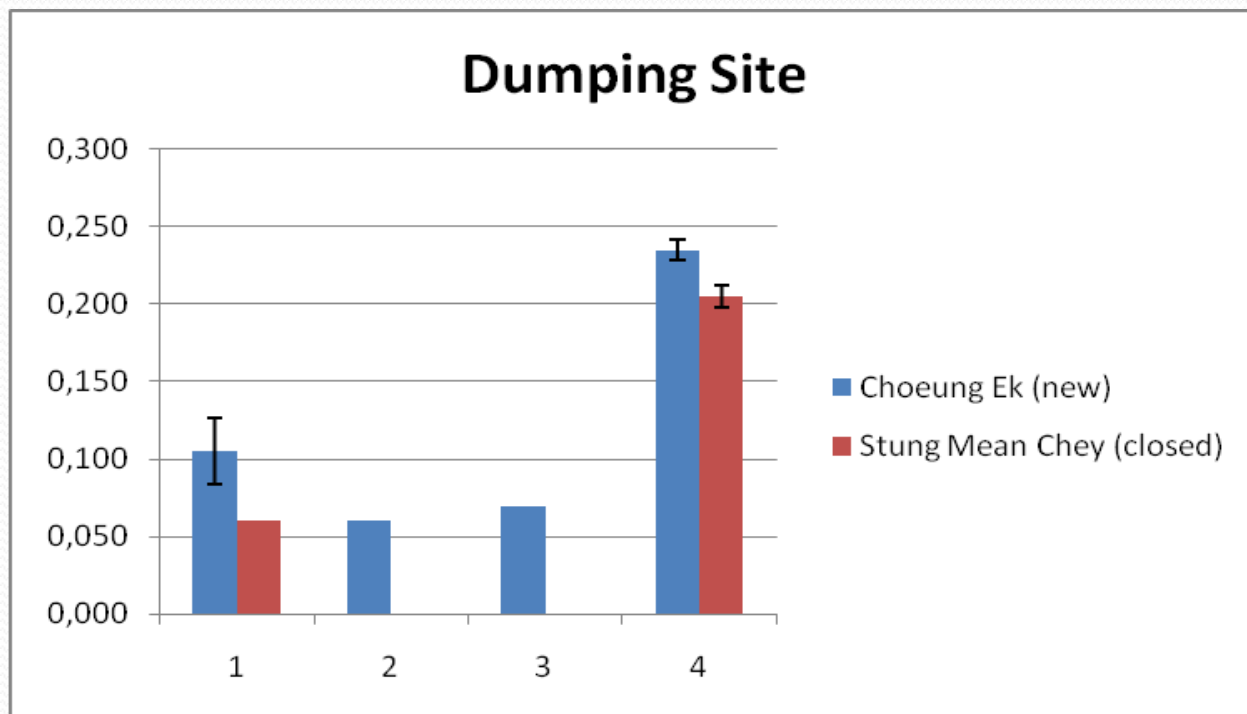
- similar Hg conc for new and old landfill site
- generally low Hg concentration, although probably elevated (compared to a general background level 0.075 – 0.28 mg/Kg)

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Cambodia (summary)

- landfill sites are the least contaminated Hg area
- AGM tailings ponds and sludge from hospital are highly elevated in Hg
- AGM workers are probably exposed to volatile Hg directly (needs confirmation)
- dental clinics are a source of Hg but not as high as expected