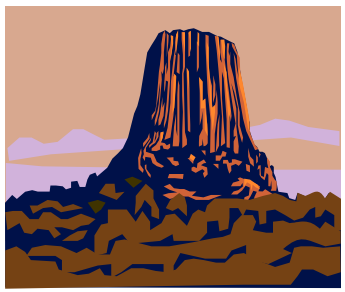
Air Toxics Analysis—Particularly Metals

17th International Emission Inventory Conference
Portland, OR
June 2-5, 2008

Karen Hagelstein, Ph.D., CIH
TIMES Limited
Sheridan, WY USA
aircaredoc@aol.com

John Heinze, Ph.D.
Environmental Health Research Foundation, Chantilly, VA USA
jheinze@ehrf.info



Particulate Metal Emissions

Sources

Industry Inventories

Metal Industry Assessments

Worker Exposures

Health Hazard Rankings

Biomonitoring

Recommendations

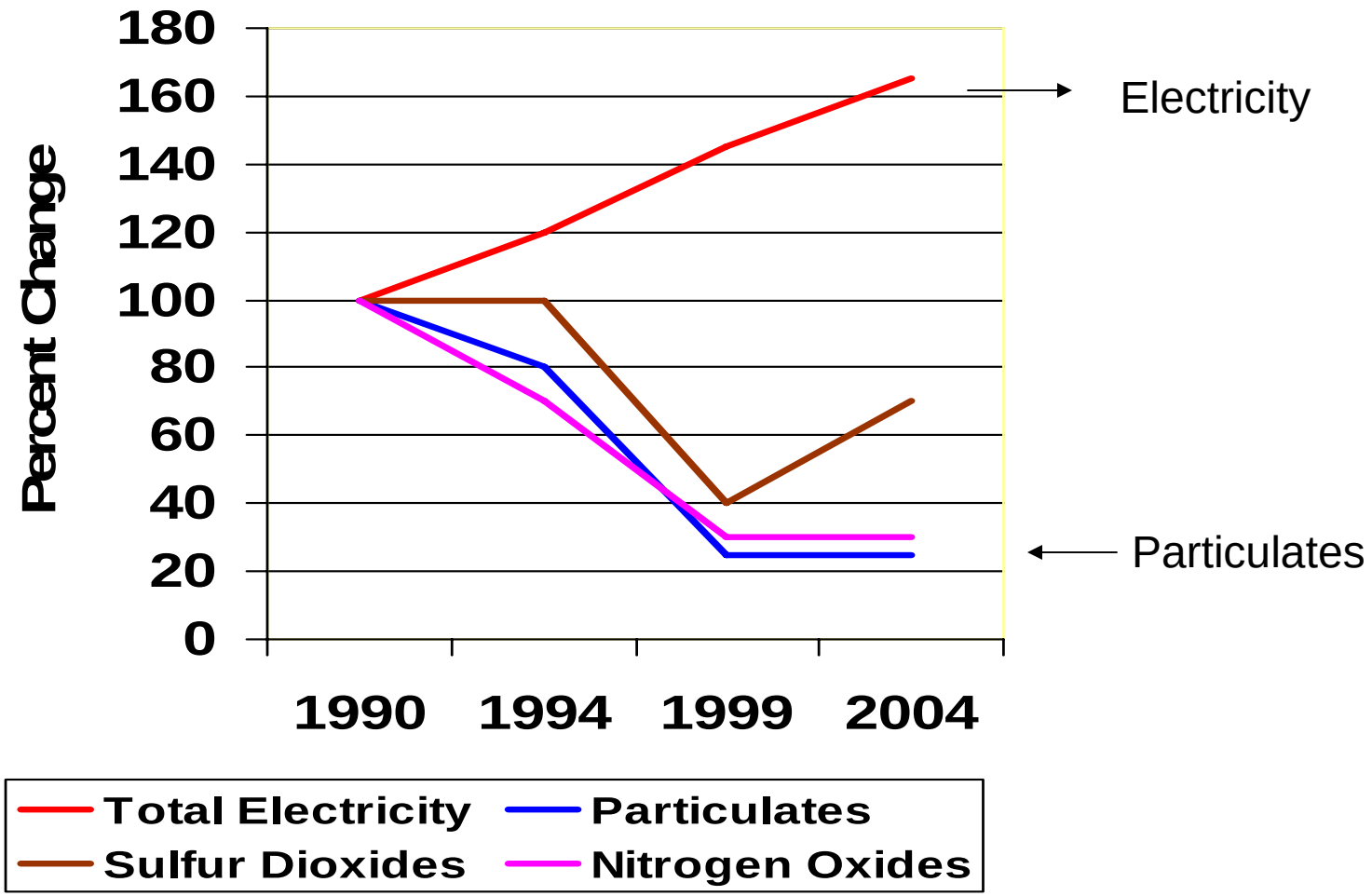
Air Pollution Sources—Including Particulates

AREA/NATURAL = 25%

MAJOR INDUSTRIAL/POINT = 25%
(10 to 25 HAPs tons/year)

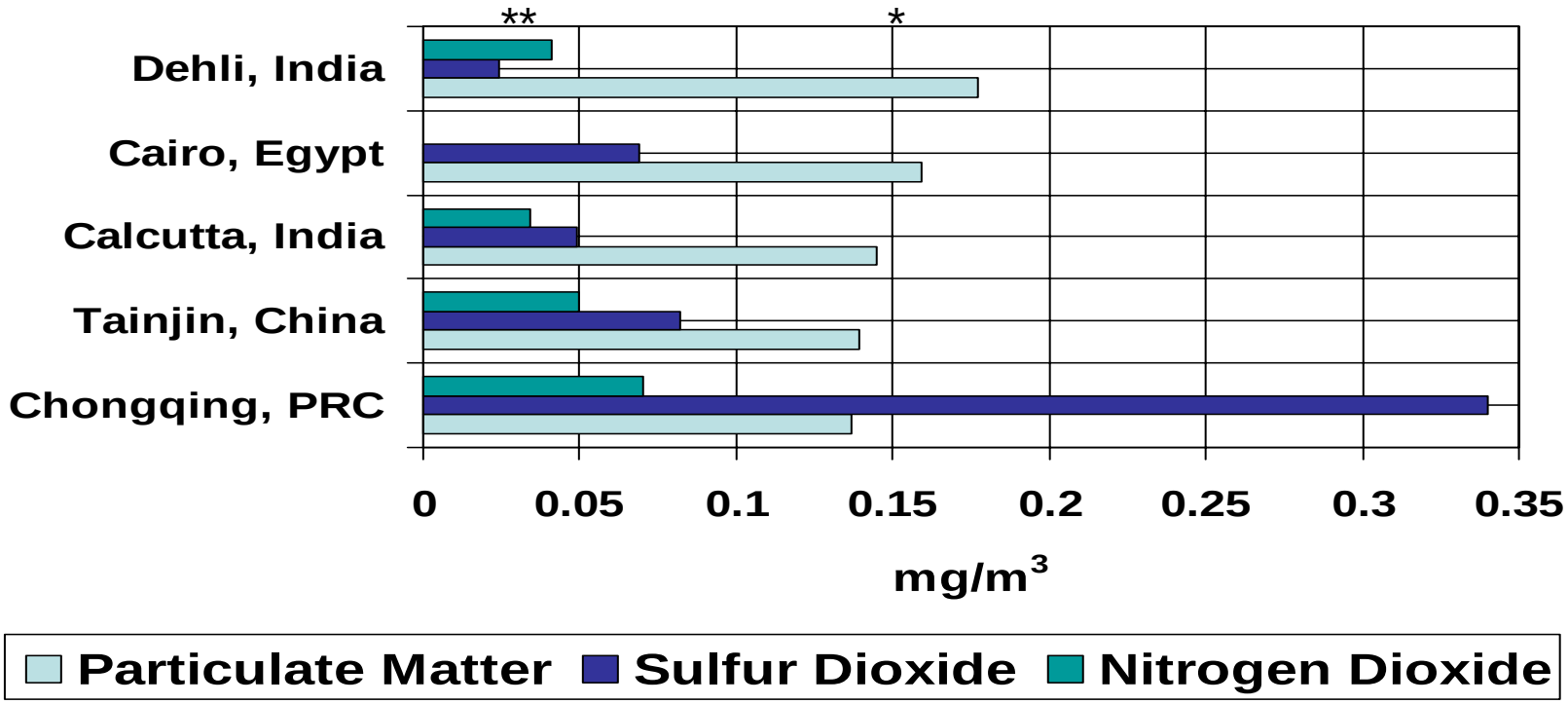
ALL MOBILE = 50% AIR POLLUTION

Urban Air Is Improving



www.epd.gov.hk

Particulate Standards Differ



***EPA PM10 = 0.15 mg/m^3**

****WHO PM10 = 0.03 mg/m^3**

<u>WORKER EXPOSURE LIMITS (ACGIH and OSHA):</u>

Respirable Particulates = 3.0 to 5.0 mg/m^3

Total Inhalable Particulates = 10 to 15 mg/m^3

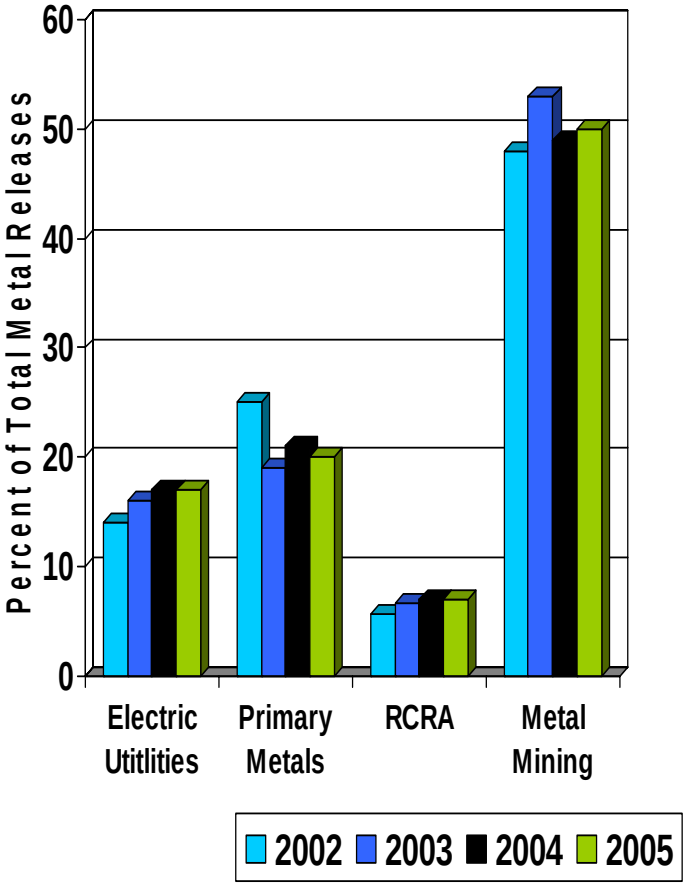
Controlling Particulate Metals-Additive

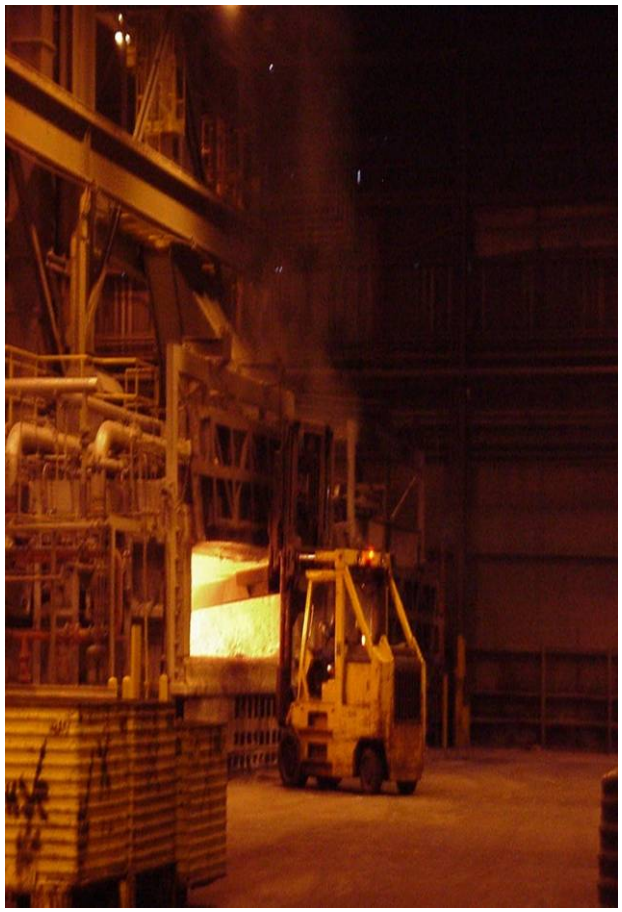
- Cyclone/Scrubber
- Fabric Filters
- Electrostatic Precipitation
- Wet Flue Gas Desulfurization

Air Pollution Controls

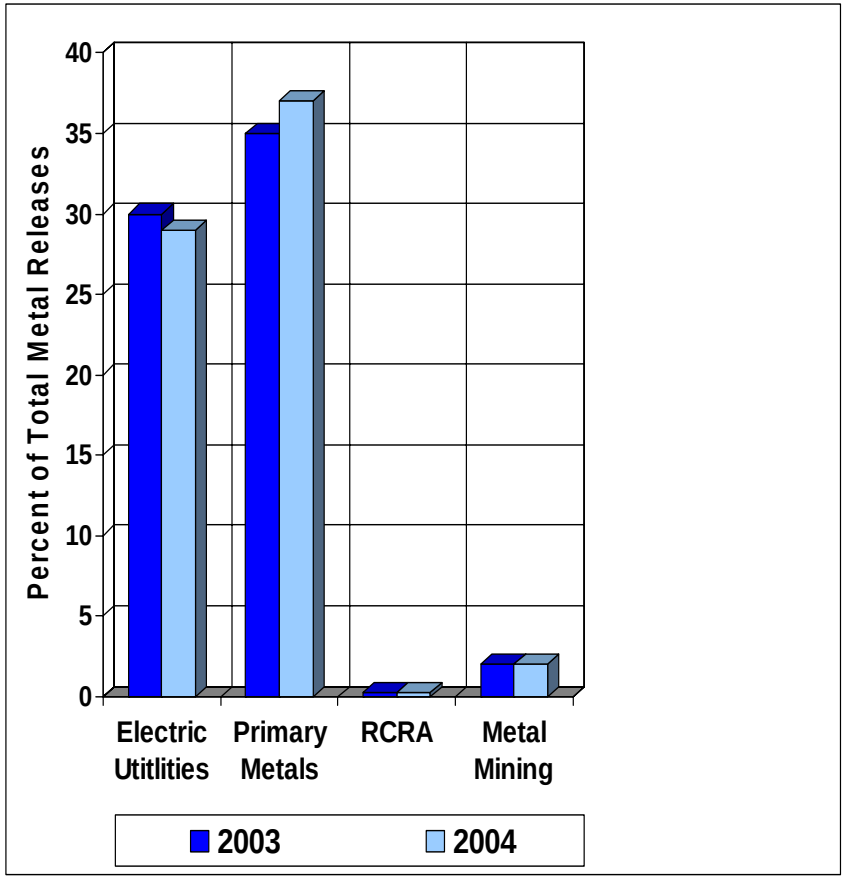
Dependent on Coal Type	% MERCURY Capture
<u>Particulate Matter</u>	
Electrostatic Precipitator: Cold-Side (ESP:CS)	2-63%
Electrostatic Precipitator: Hot-Side	27-48%
Fabric Filter (FF)	87-93%
<u>Particulate Matter/SO_2</u>	
ESP:CS + Wet Flue-Gas Desulfurization (FGD)	56-74%
FF + Wet FGD	89%
<u>Particulate Matter/SO_2/NO_X</u>	
Selective Catalytic Reduction + ESP:CS + Wet FGD	>90%
Selective Catalytic Reduction + Spray Dryer + FF	47-99%

EPA TRI Total Metal Releases Industry Trends



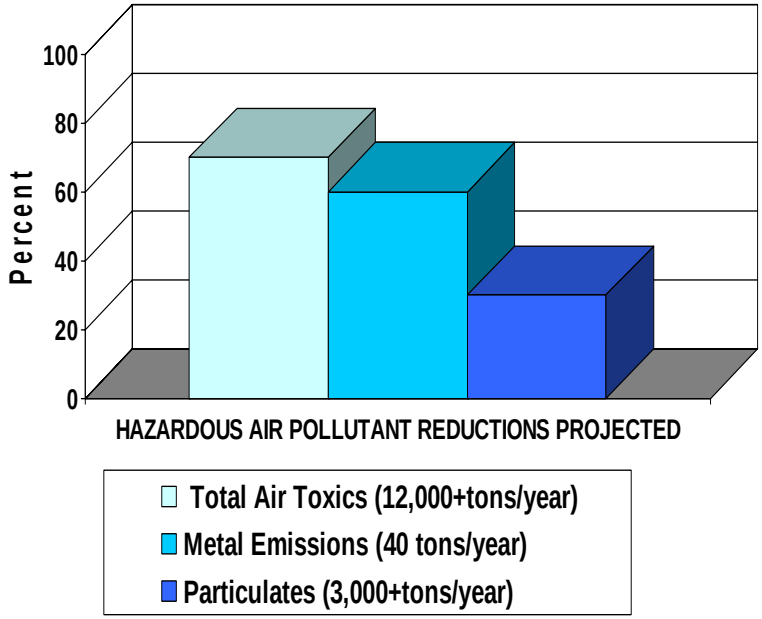


Industry Airborne Metal Releases

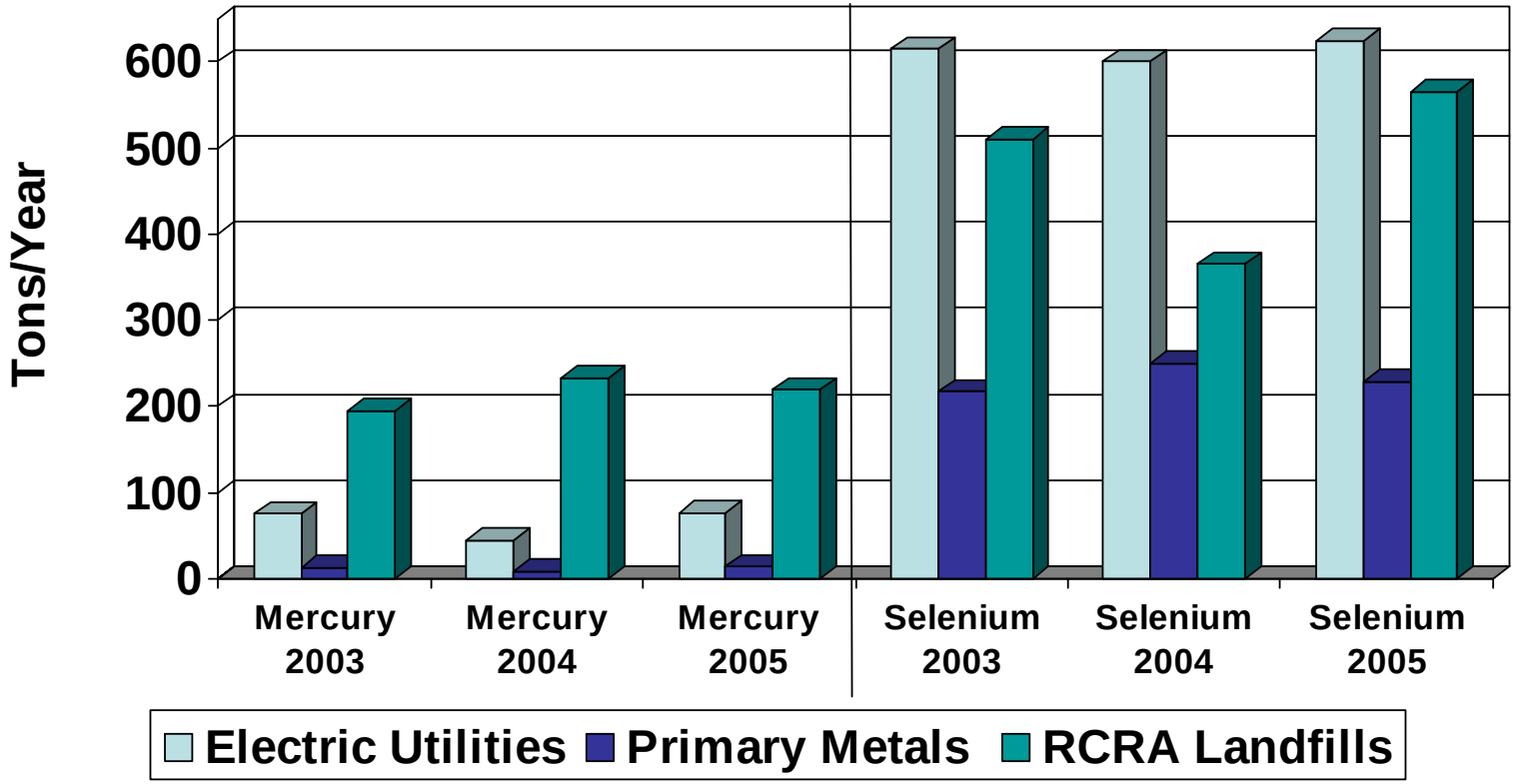


Projected Reductions Not Verified:

Secondary Aluminum Plants (Primary Metals) USEPA 40 CFR Part 63, 2000



EPA TRI Industry
Total Mercury & Selenium Releases



2005 EPA TRI
Total Metal Emissions
(Million Pounds)

METALS	ALL Industries	Electric Utilities	Primary Metals	RCRA	Metal Mining
Arsenic	185	6.45	5.25	1.77	172
Cadmium	3.33	No Data	1.14	1.56	0.52
Lead	470	8.27	34.0	19.7	394
Mercury	4.40	0.15	0.03	0.44	3.67
Selenium	3.47	1.25	0.43	1.13	0.46
TOTAL (18 Metals)	2,310	384 17% Total	470 20% Total	168 7.3% Total	1,160 50% Total

Summary: EPA TRI 2005 Metal Emissions

TOTAL METALS (18 Metals)

Metals Industry > Electric Utilities Releases

Decreasing Total Emissions from 2000 to 2005

Majority (77%) Total Metal Releases Offsite

AIRBORNE METALS

Onsite Total Metals Released to Air ~7%

Majority (>70%) Are Point Sources

Metals Industry Is Largest Source (35%)

Selenium>Mercury Emissions

CASE STUDY 2003—Environmental Samples at Three Aluminum Facilities

- **Process Materials**

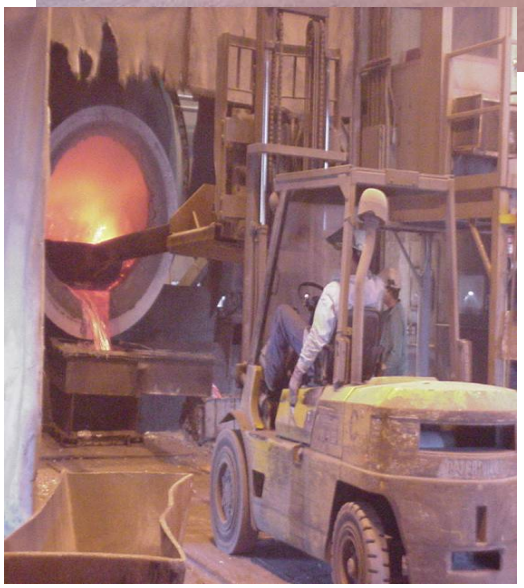
  Aluminum Melt, Alloy, & Dross
- **Solid Wastes**

  Baghouse Dust

  Salt Cake
- **Air Quality**

  Stack Emissions

  Workplace--Area & Personal Samples



Worker Monitoring—Particulate Metals

Worst Case Exposures

- Respirable Particulates
- Pumps/Cassettes/Filter Metals—ICAP-AES, XRD
- Real Time Particulate Infrared Sensors
- Colorimetric Detector Tubes for Gases (AsH_3)
- Area/Breathing Zones

Hazardous Metal Wastes

Ranking Solid Wastes: EPA TCLP Values

Mercury = 0.2 mg/L

Selenium = 1.0 mg/L

Cadmium = 1.0 mg/L

Lead = 5.0 mg/L

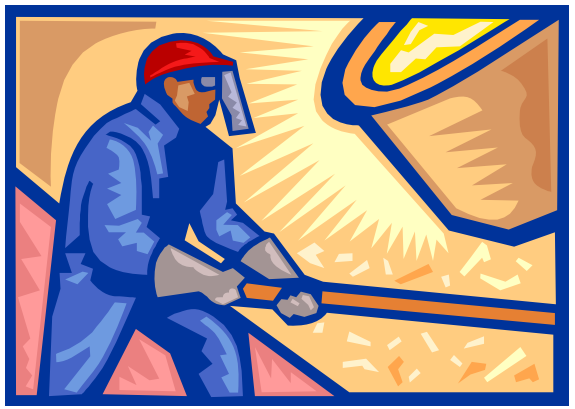
Chromium = 5.0 mg/L

Arsenic = 5.0 mg/L

INDUSTRIAL EXPERIENCES: USA $$

SELENIUM Contaminant of Concern	Ground Water Impacts	Surface Water Impacts	USEPA Fish Advisories	Bird Impacts	Mammal Impacts	Hazardous Waste Impacts
Coal Fly Ash Disposal	X	X	X	X		X
Oil Refinery Wastewater		X	X	X		X
Copper Mining Wetlands	X	X	X	X		X
Phosphate Waste Shale Disposal	X	X	X	X	X	
Gold Mining Heap Leach	X	X	X			
Aluminum Recycling Facility						X
U.S. Five States 1993/1998			X			

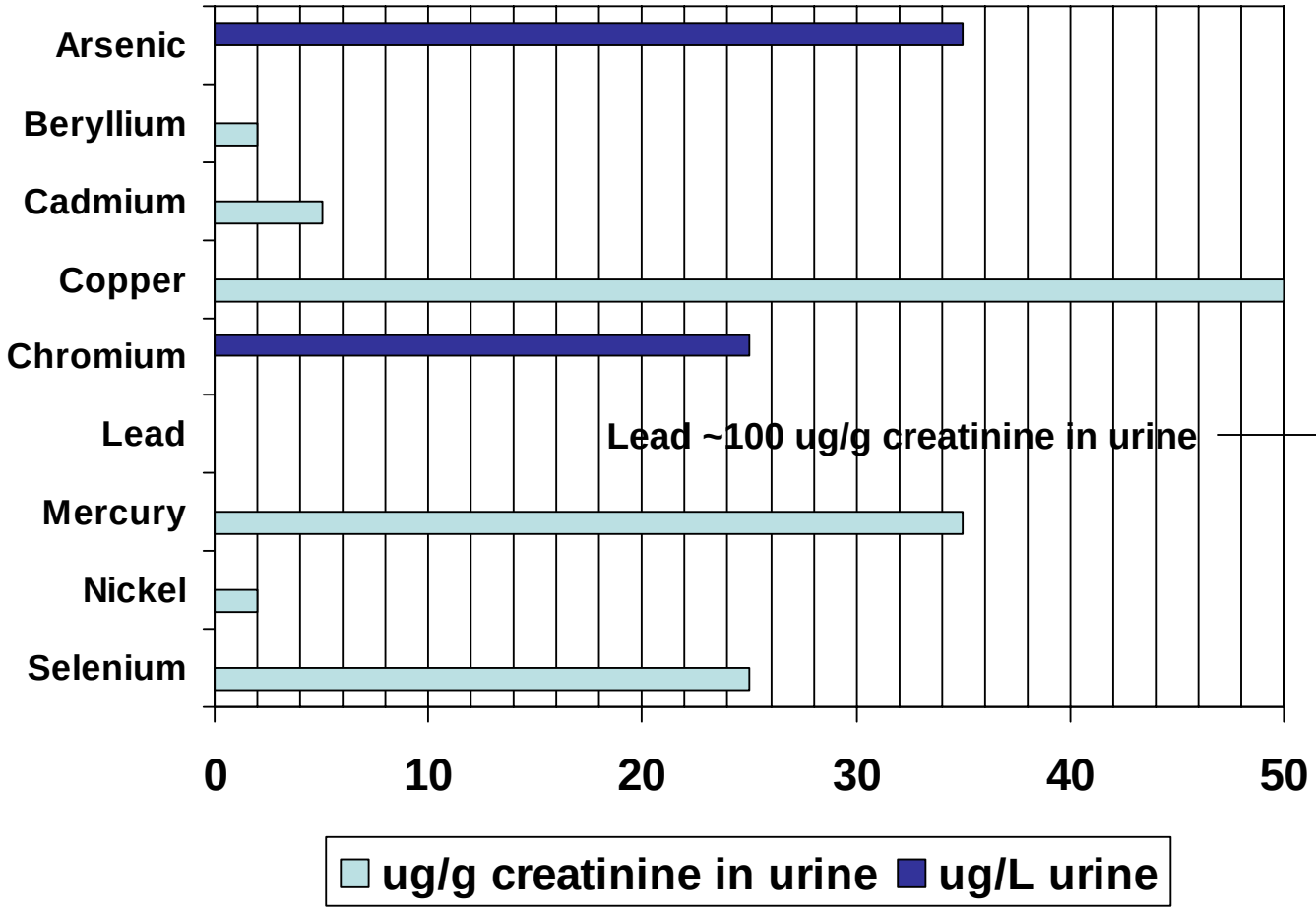
Worker Health & Particulate Metals



- **<u>OSHA Exceedences (2000-2005):</u>**
  Noise, Dust, Fumes (SIC 33XX)
  Test Substances = 1-75 (No Selenium Compounds)
  Maximum Number of Tests ~ 300/Year
- **<u>2007 NIOSH Chromium Exposures ~30% Industries Had</u>**:
  No Exposure Data (i.e. Noise)
  No Air Monitoring for 3 Years
- **<u>2007 Aluminum Alloy Welding Study</u>**:
  Alloys with Lower Melting & Boiling Points are More Reactive = Higher Particulate Emissions
- **<u>Boiler Maintenance Workers</u>:** Cr, Cu, Mn, Ni, Pb, Ni Exposures and Increased Autonomic Cardiac Dysfunction
- **<u>Battery Assembly Workers:</u>** Cadmium Dust Exposures and Increased Kidney Failure, Lung Cancer, Bone Disease

Worker Biological Exposure Indices (BEIs, ACGIH, 2005)

Taiwan Steel Worker Overexposures (As, Be, Se)



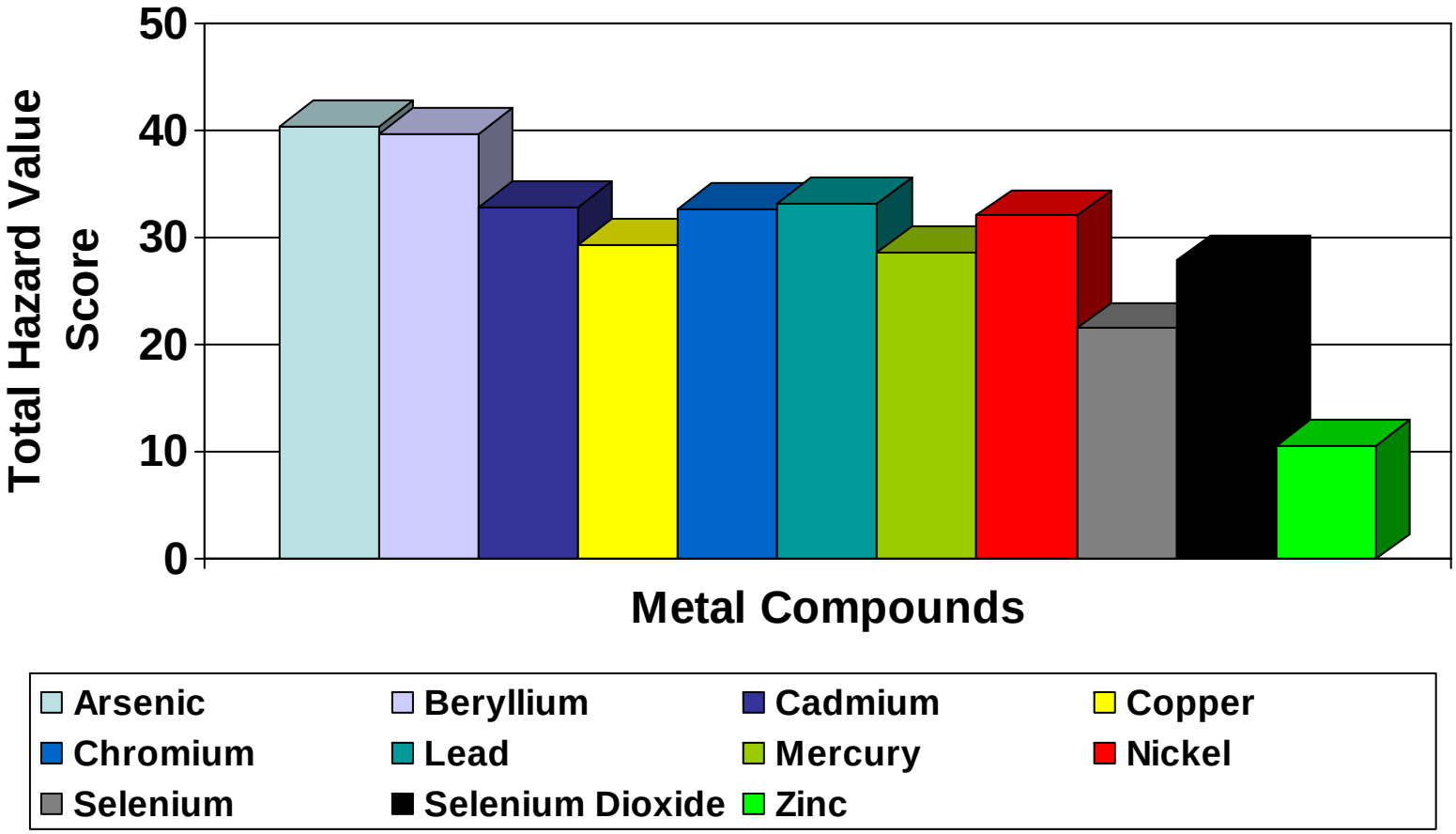
Metal BEIs: Hair/Nails

Health-Based Metal Concentrations

METALS (10)	As	Be	Cd	Cu	Cr	Pd	Hg	Ni	Se	Zn
OSHA PEL RANK (mg/m³) CANCER	3 0.01 X	1 0.002 X	2 0.005 X	6 0.10	8 0.50	5 0.05	6 0.10	4 0.015 X	7 0.20	9 5.0 Dust
EPA Ambient Air Risk-Based Conc. (mg/m³)	4.1E-7	7.5E-7	9.9E-7	1.5E-1	5.5	3.7E-7 TetraethylPb	3.1E-4	7.3E-2	1.8E-2	1.1
EPA Hazardous Air Pollutant RANK Total = 189 HAPS Detection Limit (mg/m³) High Analytical Confidence	17 3.1E-3	56 8.0E-5	13 3.0E-5		5 (Cr+6) 2.0E-4	42 8.0E-4 X	4 4.9E-4	36 3.0E-5 X	126 4.0E-5	
IFC Metal Mining Standards (mg/m³)	0.002	0.007		0.10		0.05	0.05		0.20	
EPA Hazardous Solid Waste TCLP (mg/L)	5.0	0.007	1.0		5.0	5.0	0.2	70.0	1.0	
EPA Drinking Water MCL (mg/L)	0.05	0.004	0.005	1.0	0.1	0.015	0.002		0.05	5.0
Biological Exposure Indices Taiwan Steel Worker Overexposures	35 ug/L Urine	2 ug/g creat. Urine	5 ug/g creat. Urine	50 ug/g creat. Urine	25 ug/L Urine	30 ug/100 ml Blood	35 ug/g creat. Urine	2 ug/g creat. Urine	25 ug/g creat. Urine	
Total Chemical Hazard Score (1-100 IRCHS)	40.4	39.7	32.9	29.4	32.7	33.3	28.7	32.1	21.6	10.6
Ecosystem Bioaccumulation Lichen Studies (120)	X			X	X	X	X	X	X	

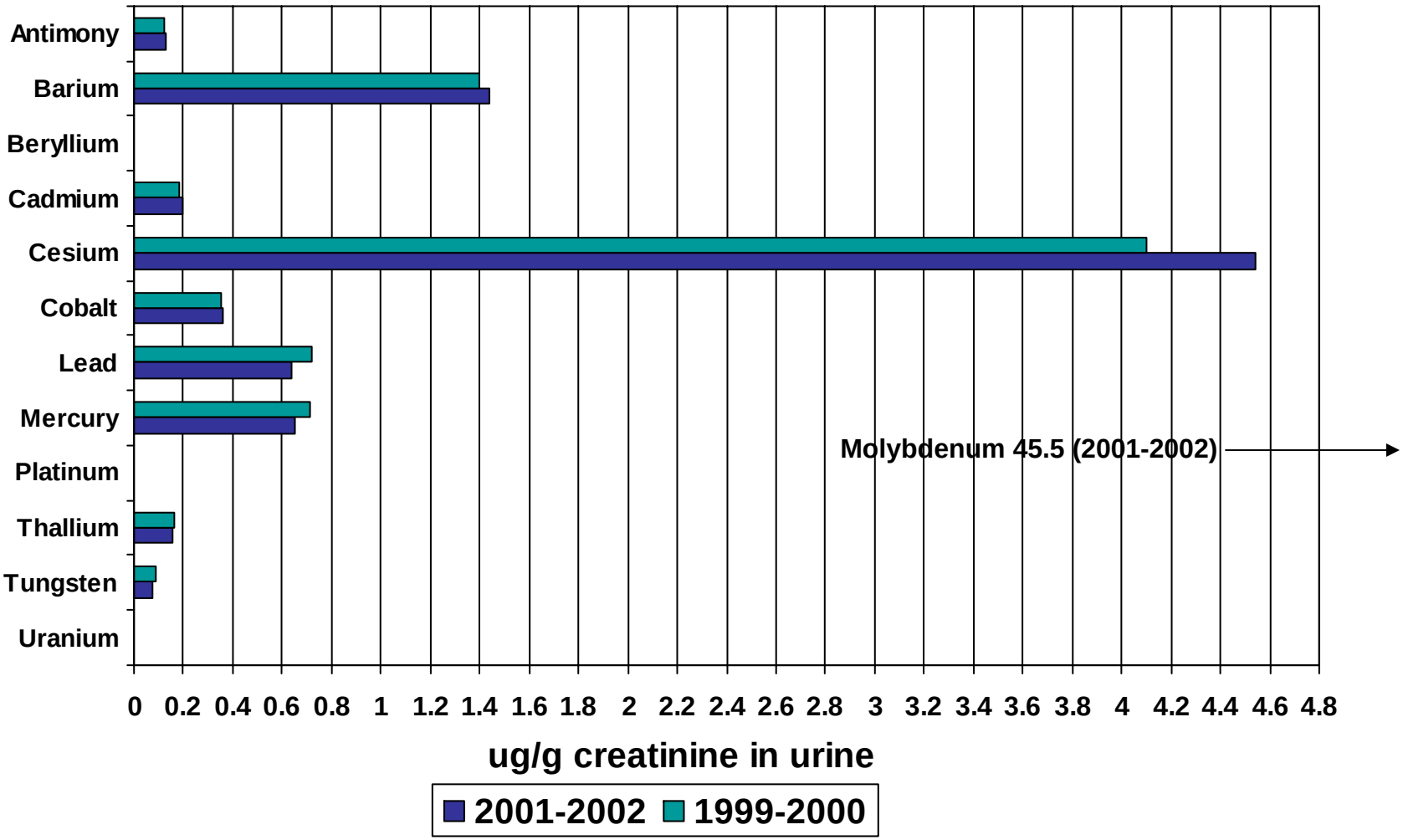
Total Environmental Hazard Scores

Indiana Relative Chemical Hazard Scores (1-100)



Biological Monitoring—Background Urinary Metals

Human Exposure to Environmental Chemicals (CDC Third Report July, 2005)



Metal Biological Benchmarks (1999 to 2005)

- USA blood lead levels have decreased.
- All USA women & children monitored have non toxic & decreasing levels of mercury.
- However, global mercury levels increasing.
- Cadmium levels are increasing (smokers).
- Cesium levels high due to medical testing.
- **Five Metal Health Hazards Not Monitored by CDC: As, Cu, Cr, Ni, Se.**

Airborne Metals Management

- **Major USA Sources--Metals Industry & Electric Utilities**
- **Recycling Industry Increasing**
- **Selenium Emissions Are Increasing**

  Component of Coal & Manganese Metals
- **Particulates & Metal Indicators:**

  Arsenic, Cadmium, Chromium,

  Lead, Mercury, Selenium
- **Biomonitoring Recommended**
- **Air Pollution Controls Effective But Emissions & Factors Uncertain**

THANK YOU FOR YOUR TIME