# Pathway Risk Assessment Approach for Metals Applied to Spent Foundry Sand


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# Beneficial Use of By-Products: Many Materials Considered.

- Spent Foundry Sand
- Manure/Compost
- Biosolids/Compost
- Heat dried Manure or Biosolids
- Yard Debris Composts
- MSW Composts
- Food Processing Byproducts/Composts
- Coal Combustion Byproducts
- Combined with other feedstocks to balance nutrients and fertility/Composts.

# Tailor-Made Soil Amendments

- Combine Organic Resources & Byproducts
  - Fertilizers or Soil Conditioners.
  - Manure, Biosolids, Food processing wastes
  - Yard debris composts
  - Agricultural organics (straw, spoiled hay, etc.)
- Inorganic Byproducts (to adsorb metals or $PO_4$)
  - Fe and Mn rich byproducts
  - Foundry Sands (steel, iron; not brass, Pb)
  - Wood ash; fly ash (variable with source)
- Process by anaerobic digestion or composting
  - Convert Fe and Mn to high surface area.
  - Compost to make soil conditioner products:
    - Reduce pathogens, stabilize carbon.
    - Slow N release.

# Concern About Utilization of Byproducts on Land?

- Cheap disposal of industrial wastes without significant benefit; Beneficial Use Designation
- Potential for contamination of soil, crops and livestock = Some are not safe.
  - K061 Steel mill fume waste as Zn fertilizer.
    - High in Zn, Cd, Pb, As; dioxin present.
  - "Fear in the Fields" (Seattle Times)
  - Smelter and mine waste toxic sites in many states.
- Potential to cause phytotoxicity if mishandled.
  - Steel byproduct limestone near Tifton, GA.
  - Often not mixed with $CaCO_3$; high in Zn, Cd, Pb, etc.
  - Peanuts were killed by excessive soluble Zn when soils became strongly acidic several years later.

# Pathways for Risk Assessment of Elements in Soils, and Highly Exposed Individuals-1.

| Pathway | Highly Exposed Individual |
| --- | --- |
| 1. Soil➔Plant➔Human | General markets; 2.5% of food. |
| 2. Soil➔Plant➔Human | Home gardens; 60% of garden foods for lifetime |
| 3. Soil➔Human | 200 mg/day soil/dust ingestion |
| 4. Sol ➔Plant➔Livestock➔Human | Farms; 45% home-grown meat. |
| 5. Soil➔Livestock➔Human | Grazing ruminants; soil is 2.5% of annual diet; 45% home-grown meat. |
| 6. Soil➔Plant➔Livestock | 100% of livestock feeds grown on soils |
| 7. Soil➔Livestock | Grazing ruminants; 2.5% soil in diet. |

# Pathways for Risk Assessment of Elements in Soils and Highly Exposed Individuals-2.

| Pathway | Highly Exposed Individual |
|---|---|
| 8. Soil➔Plant | Sensitive crops; strongly acidic. |
| 9. Soil➔Soil Biota | Earthworms; microbes; metabolic function of soil. |
| 10. Soil Biota➔Soil Biota Predator | Shrews; 1/3 of diet presumed to be earthwroms full of Soil. |
| 11. Soil➔Airborne Dust➔Human | Tractor operator. |
| 12. Soil➔Surface water➔Human | Subsistence fishers. |
| 13. Soil➔Air→Human | Farm households |
| 14. Soil➔groundwater➔Human | Well water on farms. |

# Factors Affecting Soil Metal Uptake and Phytotoxicity

- **Properties of Metal:**
  - Solubility in soil
  - Binding within plant root
- **Properties of Soil:**
  - pH
  - Adsorption properties (OM, Fe and Mn oxides)
- **Properties of Plant:**
  - Fe uptake mechanism
  - Uptake and susceptibility of species/cultivar
- **Interactions:**
  - Seldom even additive; not synergistic.

# Complex Equilibria of Metal Ions with Components of Soil Environments

Plant Shoots

Chelated to Organic Matter
Humics; fulvics

Plant Roots

Adsorbed on Fe/Mn

**Soil Solution**

$Ni^{2+} + L \Leftrightarrow NiL$

Soil Microbes

Occluded in Fe/Mn oxides

Inorganic Solids

$Ni(OH)_2$ Ni-Silicate
NiO Ni-Al-hydroxide

L = Ligands
Organic
Inorganic

# SOIL-PLANT BARRIER

## Processes in soils or plants which prevent excessive food-chain transfer of elements

- Insolubility or adsorption in soil or plants roots:
  - $Cr^{3+}$, Pb, Fe, Hg, Sn, Au, Ag, Zr, V, Al, F, Ti, etc.
- Phytotoxicity limits plant yield at levels which are not toxic for lifetime consumption by livestock:
  - Zn, Cu, Ni, As, Mn, B, F, etc.
- Exceptions to Soil-Plant Barrier:
  - Cd, Se possible risk to humans
  - Mo, Se, Co possible risk to livestock
- Barrier can be circumvented by direct ingestion of manure or biosolids on forages or soil surface:
  - Fe, F, Pb, Hg may comprise risk if high in surface soil.

# EPA 503 Limits for Land-Applied Biosolids Compared with U.S. Soils and Foundry Sand

| Element | APL | Attainable | BKG Soil(95%ile) | SFS |
|---|---|---|---|---|
| | mg/kg | mg/kg | mg/kg | mg/kg |
| As | 41. | <25. | 12. | 1.0 |
| Cd | 39. | <5.-10 | 0.60 | <5.9 |
| Cd/Zn, % | (1.5) | <0.8 | 0.33 | . |
| Pb | 300. | <100. | 38.8 | <7.7-25.7 |
| Hg | 17. | <5. | 0.09 | . |
| Mo | 35. | <40. | 2.16 | <4.4 |
| Se | 36. | <15. | 1.00 | . |
| Cr | 1200. | . | 70. | 3.0-85.5 |
| Cu | 1500. | <500.-750 | 30.1 | <23.1-48.5 |
| Ni | 420. | <100. | 37.5 | <0.12-2328 |
| Zn | 2800. | <1000.-1500 | 103. | <33.4-83.6 |

# Most Limiting Potential Adverse Effects of Elements in Soil Amendments-1

| Element | Most Limiting Adverse Effect |
|---|---|
| N | Nitrate leaching or plant accumulation. |
| P | Phosphate leaching or runoff causing eutrophication of surface waters. |
| K | Grass tetany or fat necrosis in cattle. |
| Ca | Mg deficiency/milk fever in cows. |
| Mg | None observed from livestock manures |
| BOD | Phytotoxicity from ethylene, etc. |
| S | Malodor when anaerobic; excessive sulfate can cause induced Cu deficiency in ruminant livestock. |

# Most Limiting Potential Adverse Effects of Elements in Soil Amendments-2

| Element | Most Limiting Adverse Effect |
|---|---|
| Cu | Phytotoxicity to sensitive plants–Acid soils. |
| Zn | Phytotoxicity to sensitive plants–Acid soils. |
| Mn | Phytotoxicity to sensitive plants–Acid soils. |
| Ni | Phytotoxicity to sensitive plants-Acid soils. |
| Se | Leaching in alkaline soils; causing toxicity to predators in aquatic ecosystems. |
| Mo | Alkaline soils; forage crops accumulate Mo; high Mo induces Cu deficiency in ruminants. |
| Fe | Induced Mn deficiency in sensitive crops. Livestock ingestion of excessive $Fe^{2+}$ can cause direct toxicity and induced Cu deficiency. |

# Most Limiting Potential Adverse Effects of Elements in Soil Amendments-3.

| Element | Most Limiting Adverse Effect |
|---|---|
| Al | Phytotoxicity to sensitive plants–Acid soils. |
| B | None in humid regions; leaches rapidly. |
| Cd | None; low Cd:Zn prevents adverse Cd effects. |
| Pb | Ingestion of high Pb soil risk to children; But BBPNPs may make soil Pb non-bioavailable |
| F | Brittle bones in grazing livestock--soil ingestion |
| As | Soil Ingestion: Toxic to children/livestock. |
| Al | Phytotoxicity to sensitive plants–Acid soils. |
| $Cr^{3+}$ | In manure, $Cr^{6+}$ reduced to $Cr^{3+}$; not toxic; not a useful Cr fertilizer; plants don't absorb. |

## Comparison of EPA Soil Screening Limit with Element Levels in Spent Foundry Sand and US Background Soils

| Element | SSL | Elements in SFS | | | 95%ile |
|---|---|---|---|---|---|
| | | Min. | Med. | Max. | |
| | ------------------------- mg/kg DW ----------------------- | | | | |
| Ag | 391 | . | . | . | . |
| Al | 78200 | 190. | 5130. | 11700. | 74600. |
| As | 0.426 | 0.04 | 0.83 | 4.8 | 12. |
| B | 15600 | . | . | . | . |
| Ba | 15600 | 5.0 | 5.0 | 141. | 840. |
| Be | 156 | 0.05 | 0.15 | 0.60 | 2.3 |
| Cd | 78.2 | 0.02 | 0.06 | 0.36 | 0.6 |
| Co | 1560 | 0.25 | 0.88 | 6.62 | 17.6 |
| Cr | 235 | 0.25 | 4.93 | 134. | 70. |
| Cu | | 0.25 | 7.04 | 88.2 | 30.1 |

# Comparison of EPA Soil Screening Limit with Element Levels in Spent Foundry Sand and US Background Soils

| Element | SSL | Elements in SFS | | | 95%ile |
|---|---|---|---|---|---|
| | | Min. | Med. | Max. | |
| | ------------------------- mg/kg DW ------------------------ | | | | |
| Fe | | 540. | 4260 | 64000. | 42600. |
| Mg | | 50 | 1310 | 3200. | 18800. |
| Mn | 3600 | 5.56 | 54.5 | 707. | 1630. |
| Mo | 391 | 0.11 | 1.03 | 21. | 2.16 |
| Ni | 1560 | 1.02 | 3.47 | 117. | 37.5 |
| Pb | 400 | 0.50 | 3.63 | 22.9 | 38.8 |
| Sb | 31.3 | 0.02 | 0.17 | 1.7 | 1.39 |
| Se | | 0.06 | 0.20 | 0.44 | 1.0 |
| Tl | | 0.02 | 0.02 | 0.10 | 0.7 |
| V | 548 | 0. 5 | 2.88 | 11.3 | 119. |
| Zn | 23500 | 5.0 | 5.0 | 245. | 103. |

# Conservative Aspects of the Soil Screening Limit (Pathway 3)

Daily ingestion of 200 mg of soil/dust

(95%ile is 100 mg/day at age 1-4)

Ingest soil daily from age 1 to age 7

(Ingestion peaks at age 1.5-2)

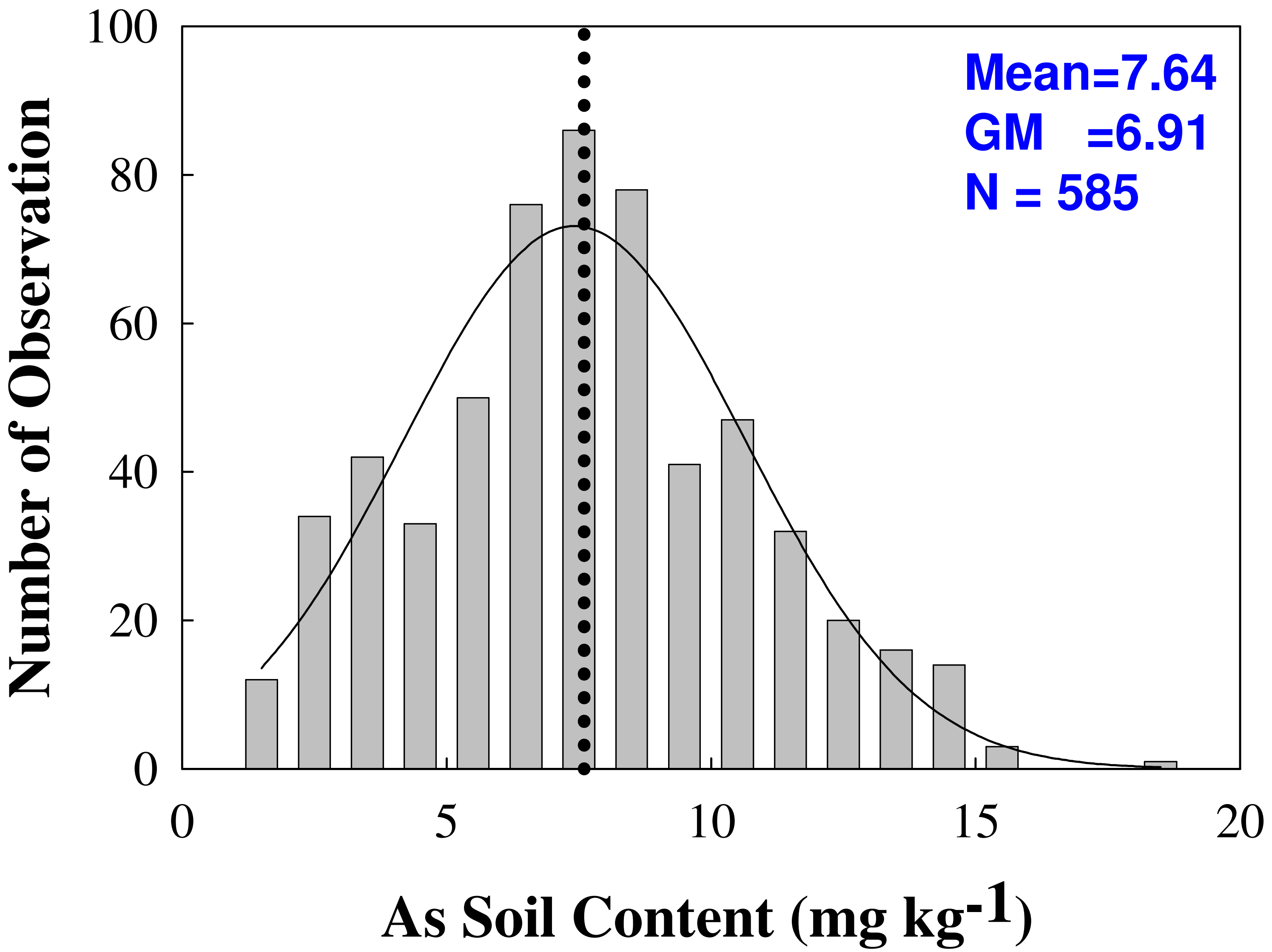
100% bioavailable as Na-arsensate on fasting

(Monkey feeding indicated 5-10% absorbed)

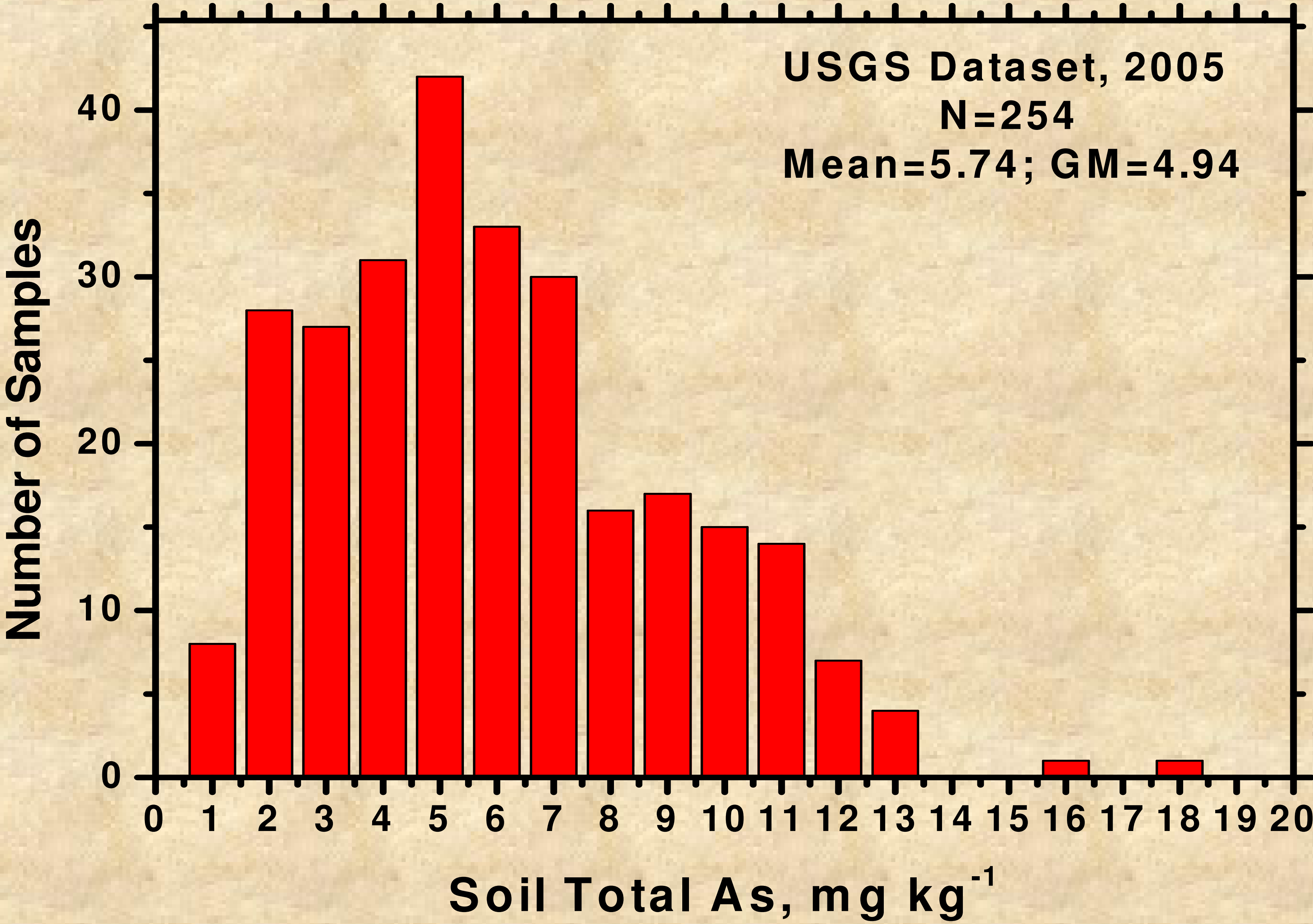
# Concentrations of As in US Soils

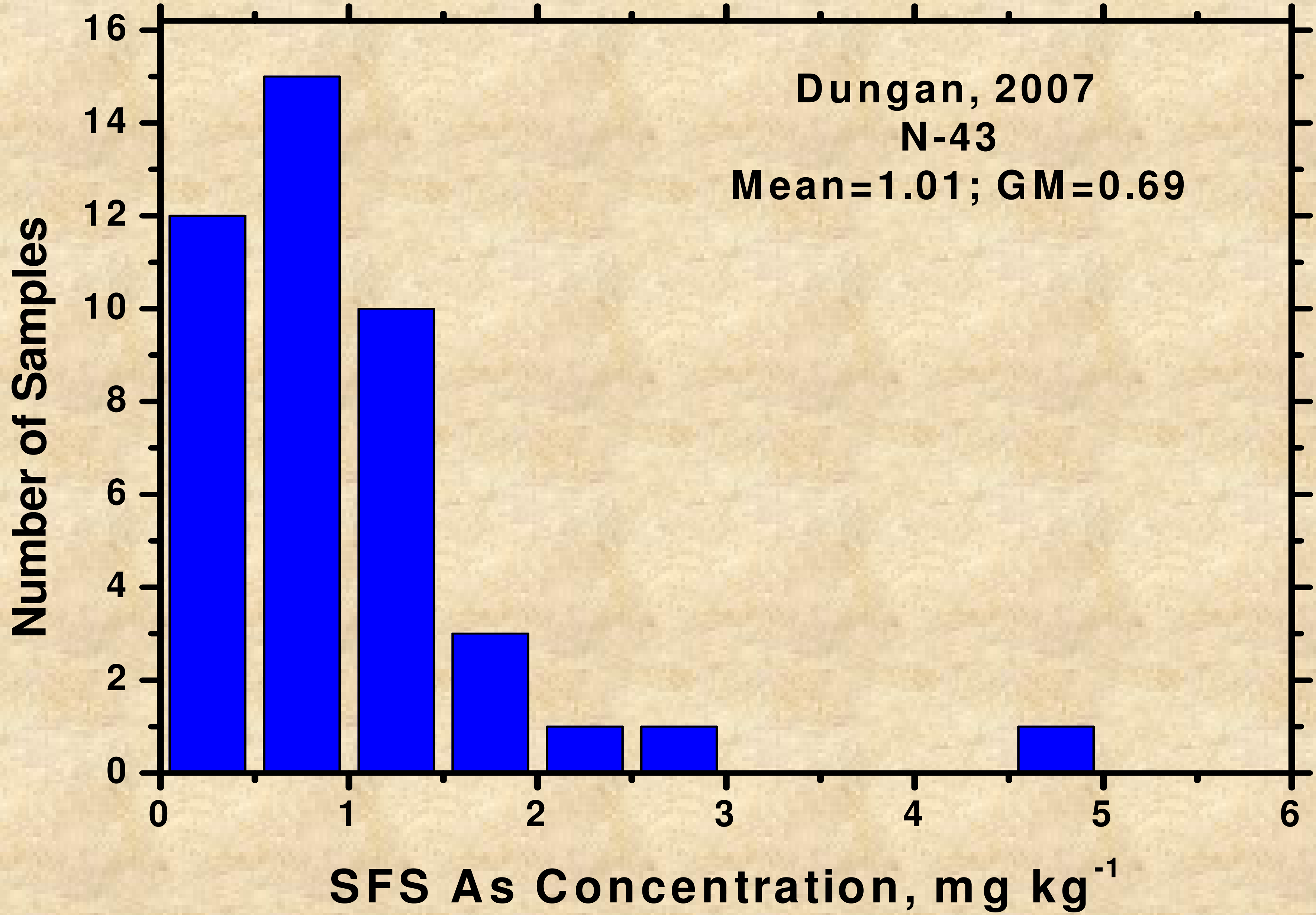
| Mean | Range | N | Reference |
|---|---|---|---|
| 7.2 | <0.1-97 | 1318 | **US**: Shacklette & Boerngen, 1984 |
| 11.3 | 0.1-194 | >3000 | **World**: Ure and Berrow, 1982 |
| 0.42 | 0.1-50.6 | 441 | **FL**: Chen, Ma & Harris, 2002 |
| 5.8 | 1.0-18.0 | 254 | **US(USGS)**: Smith et al., 2005 |
| 7.6 | 1.2-18.4 | 585 | **CA**: Chang et al. (2006) |
| 0.69 | 0.04-4.8 | 43 | **SFS**: Dungan (2007) |

**How should the US deal with background soil As which varies with parent rock As levels and soil formation processes, as well as historic agricultural and industrial practices?**

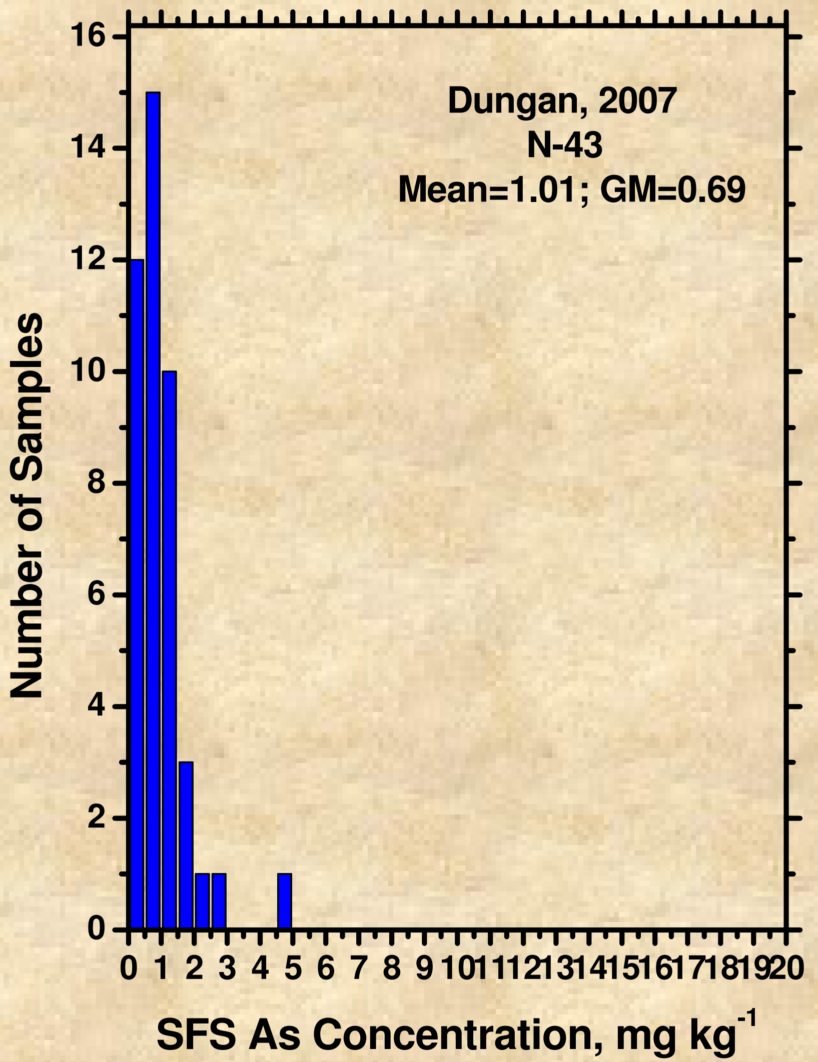



Distribution of Soil As Concentration in California Soils (Chang et al, 2007)


USGS Dataset, 2005
N=254
Mean=5.74; GM=4.94
Number of Samples
0
10
20
30
40
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Soil Total As, mg kg-1



Dungan, 2007
N-43
Mean=1.01; GM=0.69
Number of Samples
0
2
4
6
8
10
12
14
16
0
1
2
3
4
5
6
SFS As Concentration, mg kg-1


Dungan, 2007
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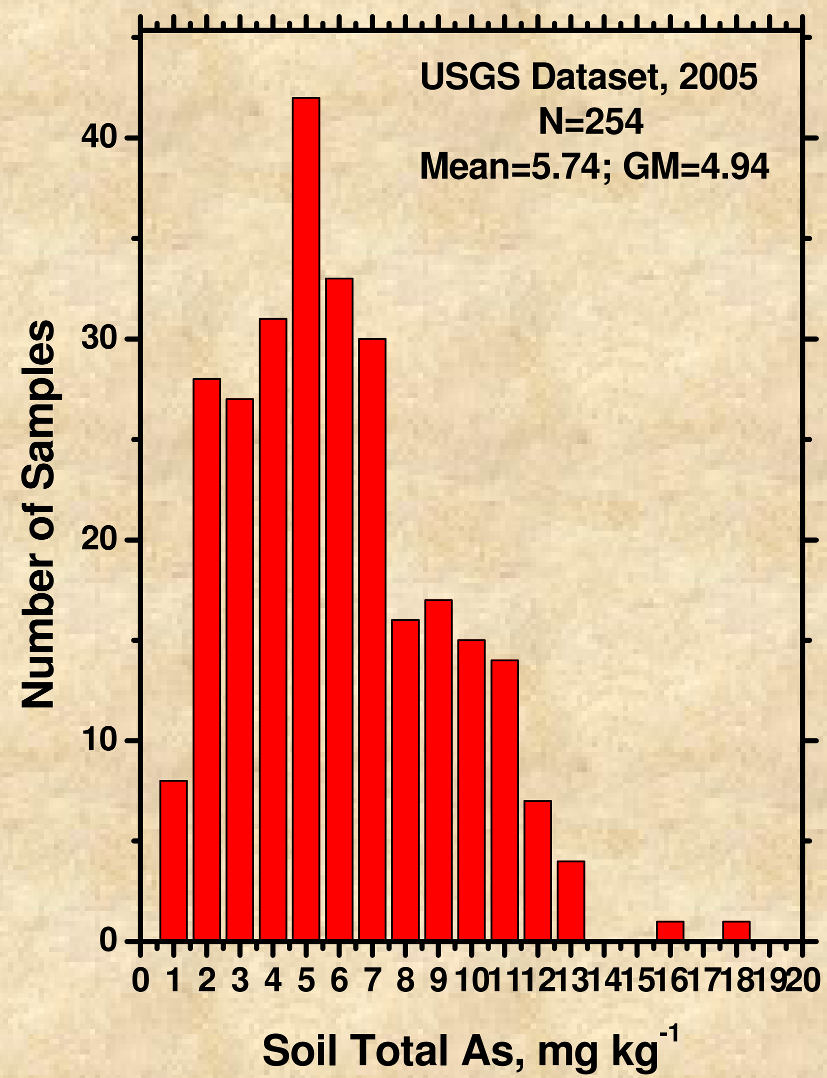
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Mean=5.74; GM=4.94
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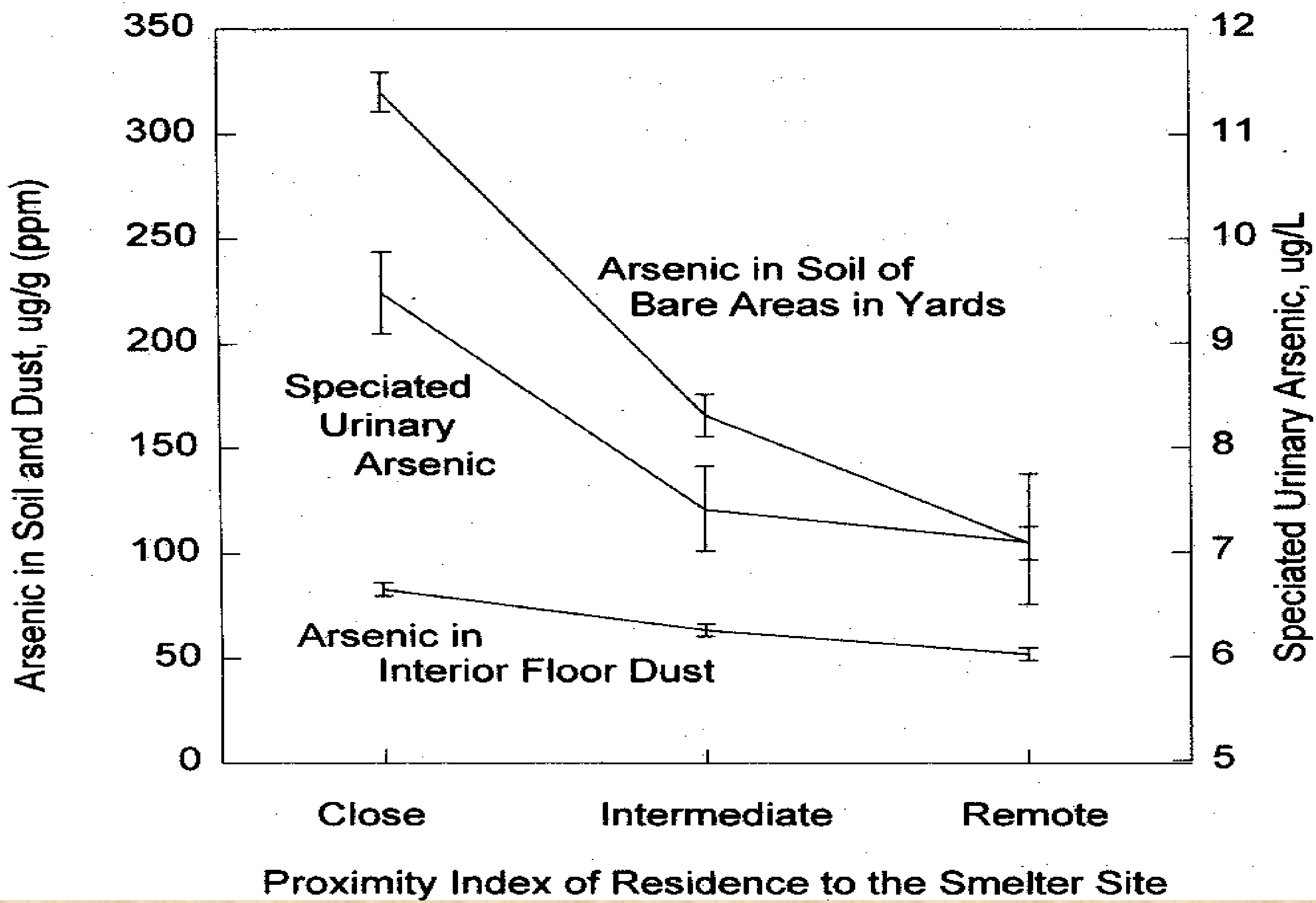
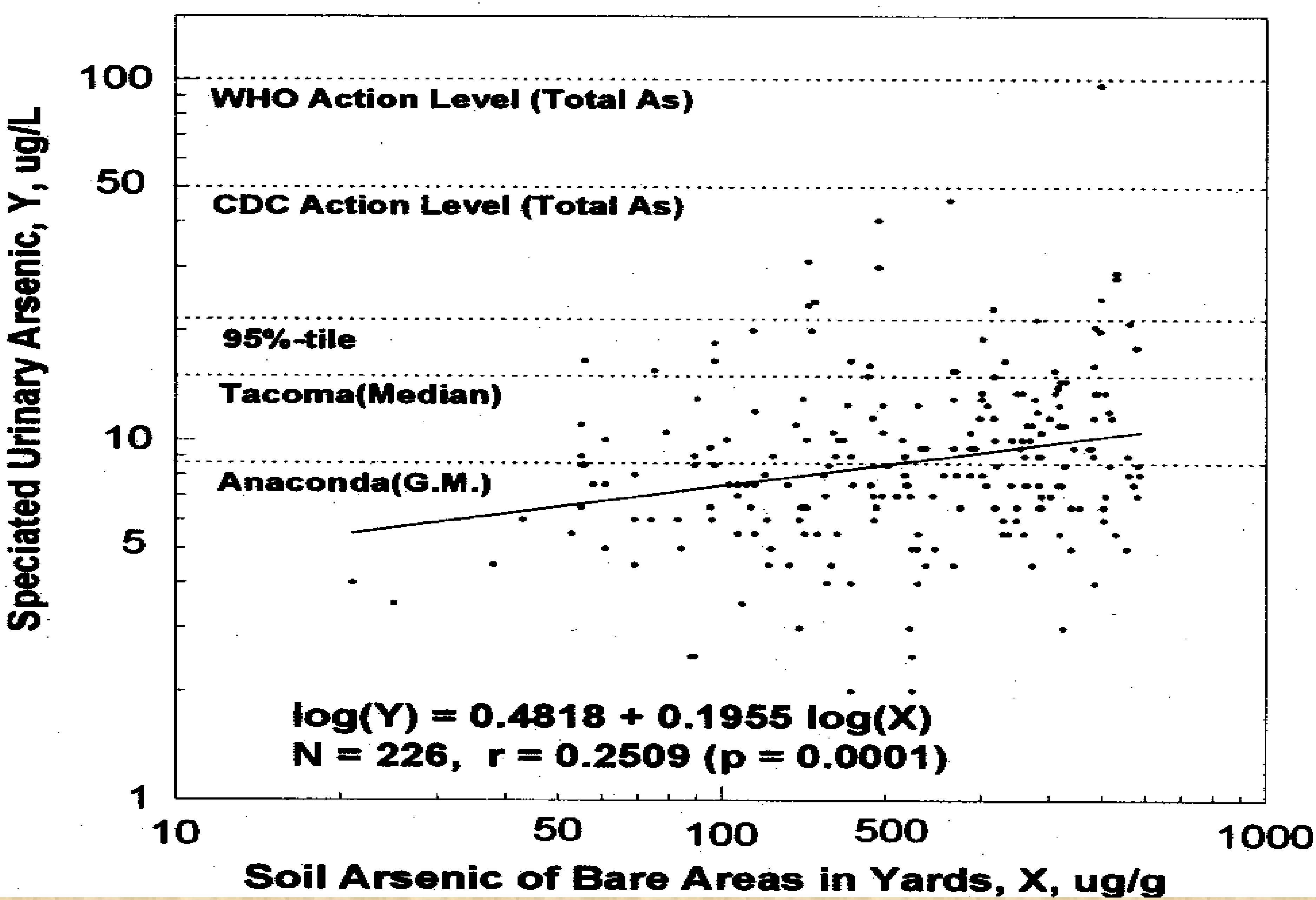
Soil Total As, mg kg-1

# Soil Arsenic Risks: Biosolids, Composts, Ash, and Poultry Litter?

- Soil As above 40-100 mg/kg soil may comprise risk to children by soil ingestion based on urinary As levels in exposed children.
- Risk from ingested soil As is expected to be greater for soils which have little As sorption capacity.
- Soil feeding study with monkeys showed that soil As was about 5-10% as bioavailable as Na arsenate.
- Some in EPA think soil As limit should be 0.426 mg/kg, but this is at or below background level in the US.
- As may be essential to animals, and zero allowable As based on cancer observation may have to be revised.




**Effect of distance from Cu smelter on As in soil and housedust, and in speciated As (inorganic) in urine of children (Hwang et al., 1997).**




Relationship of As in bare soils in yards vs. speciated inorganic As in Urine of children living at samples homes (Hwang et al., 1997).

# Why Beneficial Use Guidelines are Needed

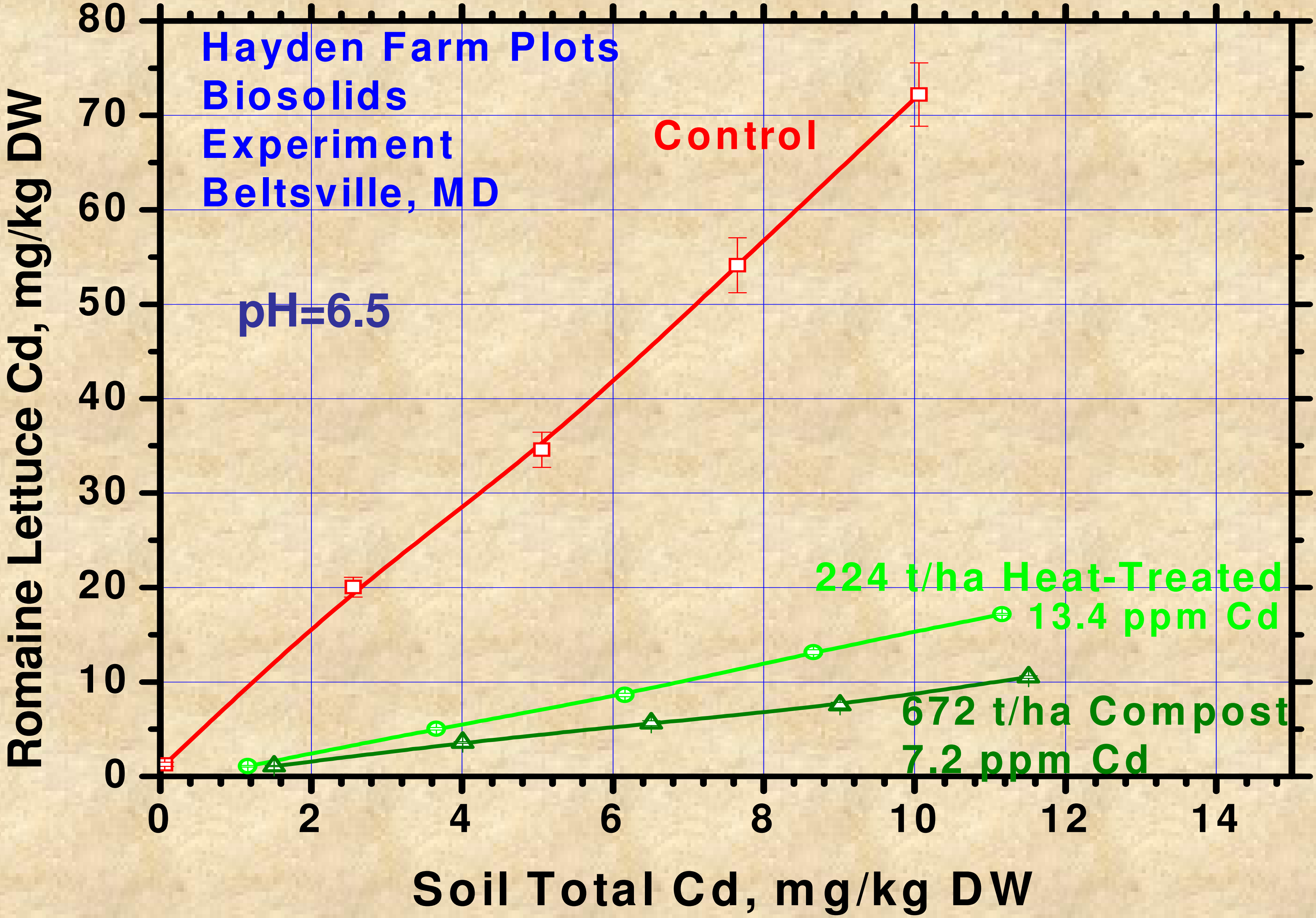
- Many states are not currently supporting beneficial uses of foundry sands.
- No comprehensive beneficial use documents available.
- Lack of understanding about foundry sands and their chemical composition.
- Regulators reluctant to issue permits because proprietary information is being withheld by foundries.
- Foundries with limited resources need support.

# Summary of ARS Research-1

- Heavy metal concentrations are similar or lower than levels in US topsoils.
- PAH and phenolic concentrations in waste foundry sands are relatively low.
- Iron and aluminum waste sands did not impact earthworm viability or soil microbial activity.
- Earthworms, spinach leaves and radish globes did not accumulate excessive amounts of toxic trace elements.
- We conclude that iron, aluminum and steel spent foundry sands present little risk to humans, either through dietary or dust exposure or direct soil ingestion.

# Summary of ARS Research-2

- We conclude that the principles identified during development of guidance for spent foundry sands may be useful for other byproducts
  - Demonstrate benefit when used in agriculture.
  - If trace elements are no higher than the 95%ile of the USGS dataset, conclude no identified risk.
  - If elements are higher than 95%ile, does not demonstrate risk, only need for further evaluation.
  - If testing shows potential risk to some part of the environment, work out limit based on practical phytoavailability and bioavailability in amended soils with high cumulative application in the field.




Phytoavailability of Cd added to Long-Term Biosolids-Amended Soils