

# **Risk Assessment for Beneficial Use of FGD-Gypsum in Agriculture**

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# Alternative Beneficial Uses: FGD-Gypsum

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- Calcium fertilizer for peanuts, etc.
- Sulfate fertilizer for many crops.
- Improve water infiltration.
  - Reduce soil erosion/crusting.
- Reduce P runoff by Ca precipitation.
- Reduce Al toxicity in subsurface soil.
- Alleviate sodicity.

# **Risk Assessment Activities for FGDG**

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**With support from US-EPA, will analyze FGD-gypsum, poultry litter, amended soils, crops, and water/solids from runoff tests in GA and AL fields.**

**Cooperate with US-EPA, EPRI, and researchers to conduct risk assessment for contaminants in land applied “new” (post fly ash removal) FGD-Gypsum**

**Key issues include As, Hg, (Se).**

**Assess all pathways for exposure**

**Farm and garden crops**

**Soil Ingestion by children**

**Livestock exposure.**

**Leaching and runoff from amended fields**

# Potential Issues Expected in Risk Work

- Extreme risk assessment by US-EPA for As and  $\text{Cr}^{6+}$  would prohibit exposure to any US soils unrelated to use of FGD-Gypsum.
- As issues are being challenged by many industry scientists. Toxicologists at EPA appear to have used inappropriate data. But until the need for lower As limits is resolved, **all progress on other land application questions is on hold** (Spent Foundry Sand; FGD-Gypsum; compost; etc.)
- EPA  $\text{Cr}^{6+}$  proposal at  $0.02 \mu\text{g Cr}^{6+}/\text{L}$  drinking water limit is based on Nat. Toxicol. Prog. feeding test at Maximum Tolerated Dose of  $180 \text{ mg}/\text{L}$ . But other research shows that  $\text{Cr}^{6+}$  is reduced rapidly to  $\text{Cr}^{3+}$  in the stomach and precipitated, preventing any adverse effect of up to about  $10 \text{ mg}/\text{L}$ . EPA rule for extrapolation of high level data seems inappropriate. Cancer only seen at highest doses.

# Old vs. New FGD-Gypsum

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- **Old FGD-Byproduct** contained fly ash element residues, such that B, As, Se, etc. were a source of concern depending on the coal source.
  - Used at limestone rate for alfalfa, FGDB could supply B, Ca, alkalinity and Se that served as fertilizers without causing excessive transfer of toxics to crops.
- **New FGD-Gypsum** manufactured post fly ash removal contains low levels of all trace elements.
  - Difficult to find potential adverse effects of constituents of present high quality FGD-Gypsum.

# Composition of Old CCPs (mg/kg)

	MN	23 Fly Ash			59 FGDs		
	Dowdy	Furr et al., 1977			Kost et al., 2005		
		Mean	Min	Max	Mean	Min	Max
B	824.	255.	10.	600.	145.	68.	948.
Mo	7.4				8.6	<0.02	63.7
Se		8.4	1.2	17.	3.6	2.7	23.0
As		85.6	2.3	312.	75.	5.2	386.
Cd	<0.5				2.3	<0.5	40.7
Zn	33.9				119.	5.0	469.
Cu	52.4				177.	13.3	1490.
Ni	16.9				33.0	12.4	156.
Pb	22.7				11.3	5.0	139.
Cr	32.7				16.9	11.4	89.3

# Trace Elements in NEW Gypsum and Soils

Element	FGD-G-95%ile	Mined-G	95%ile-US Soil
As	10.1*	<2.6	12.
B	146.	<3.0	.
Cd	0.29	0.2	0.6
Co	<2.0	0.3	17.6
Cr	8.69	5.1	70.
Cu	2.52	<0.8	30.1
Mo	2.48	0.6	2.16
Ni	2.39	2.3	37.5
Pb	1.0	<1.5	38.0
Se	27.9	<4.6	1.0
Zn	15.0	4.3	103.

\*OSU/EPRI dataset.

# Considerations of Se in new FGDG

- Some FGDG is higher in Se than background US soils. But most US soils are naturally Se-deficient for animal life. Animal feeds are Se supplemented.
- FGDG ( $\text{CaSO}_4$ ) is always very high in sulfate.
- Sulfate inhibits selenate uptake by plants (except hyperaccumulators).
- At most, plants would be slightly higher in Se, which would comprise a benefit because most US crops are low in Se.
- Other nations are working to increase Se in staple foods to improve national Se nutrition.
- It is likely that the high sulfate supply along with small increase in environmental Se would also prevent any adverse effects of FGDG-Se on ecosystems as well as agriculture.

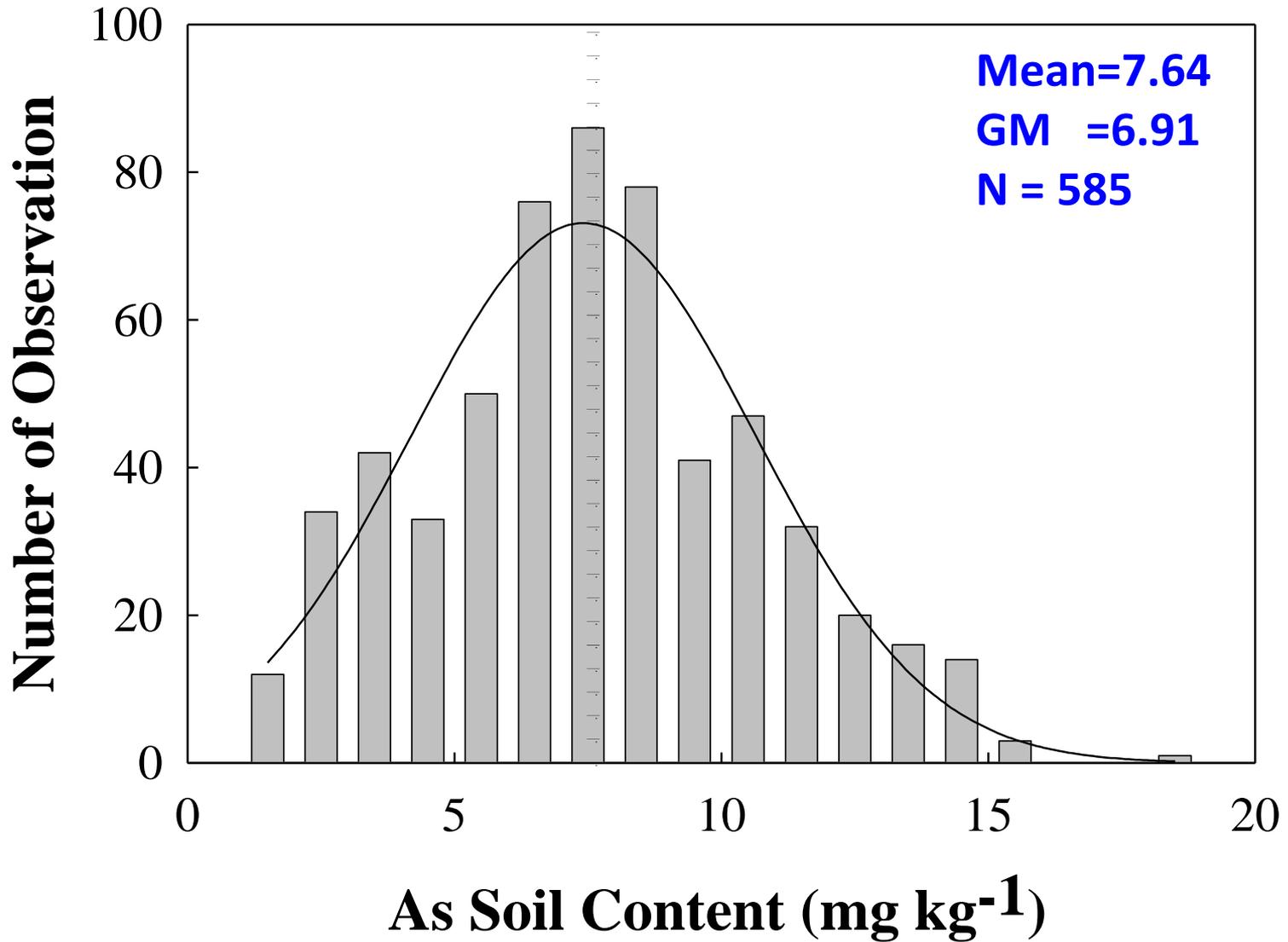
# Present Considerations of As Limit

- EPA concludes that soil may not exceed **0.43 mg As/kg** without risk thru soil/dust ingestion by children.
- **This concentration is below As in normal US soils.**
  - 5 to 95 %ile range for As in US soils is 2-12 mg/kg.
- Many question the validity of the 0.43 mg kg<sup>-1</sup> limit for soil As (10<sup>-6</sup> lifetime cancer risk).
- EPA considering 17-fold increase in As cancer slope.
- Public Comment period on change in As cancer slope factor for IRIS has been continued; Science Advisory Board comment period remains open.
- Many problems with new slope factor reported.
- Questions about use of the Taiwan dataset led to lawsuit against the IRIS proposed cancer slope factor based on the “Data Quality Act”.

# Concentrations of As in US Soils

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

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)**

# Distribution of Soil As Concentrations in Recent USGS Transects of USA (Smith et al., 2005) [N=256].

<b>Statistic</b>	<b>mg kg<sup>-1</sup> DW</b>
<b>Mean</b>	<b>5.8</b>
<b>Minimum</b>	<b>1.0</b>
<b>Maximum</b>	<b>18.0</b>
<b>Median</b>	<b>5.0</b>
<b>90<sup>th</sup></b>	<b>10.0</b>
<b>95<sup>th</sup></b>	<b>11.4</b>
<b>99<sup>th</sup></b>	<b>13.0</b>
<b>EPA-SSL</b>	<b>0.43</b>

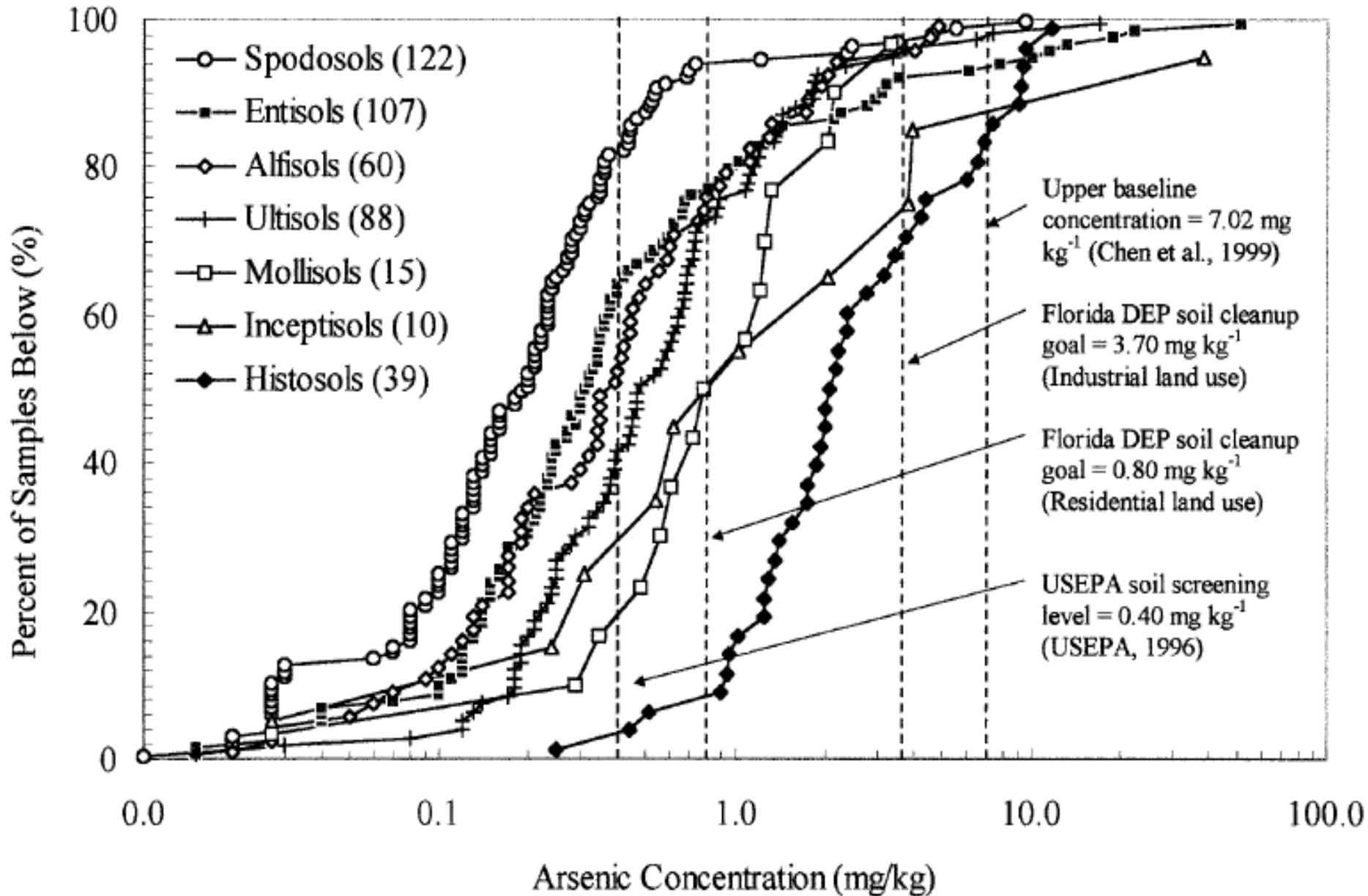
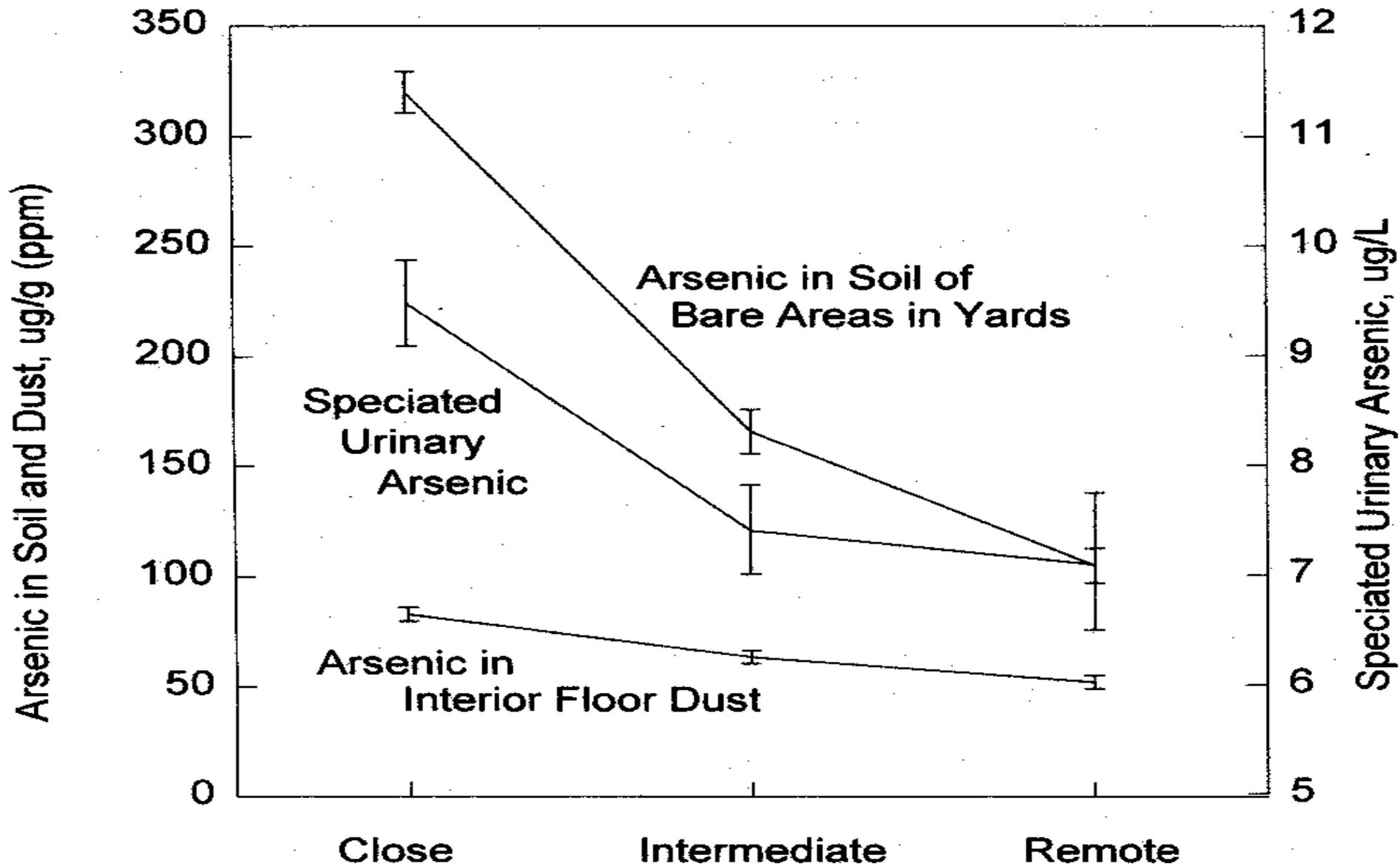


Fig. 1. Cumulative probability curves for As concentrations in Florida surface soils. Numbers in parentheses are sample sizes of individual soil orders.

**As in Florida soils (Chen et al., 2002)**

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

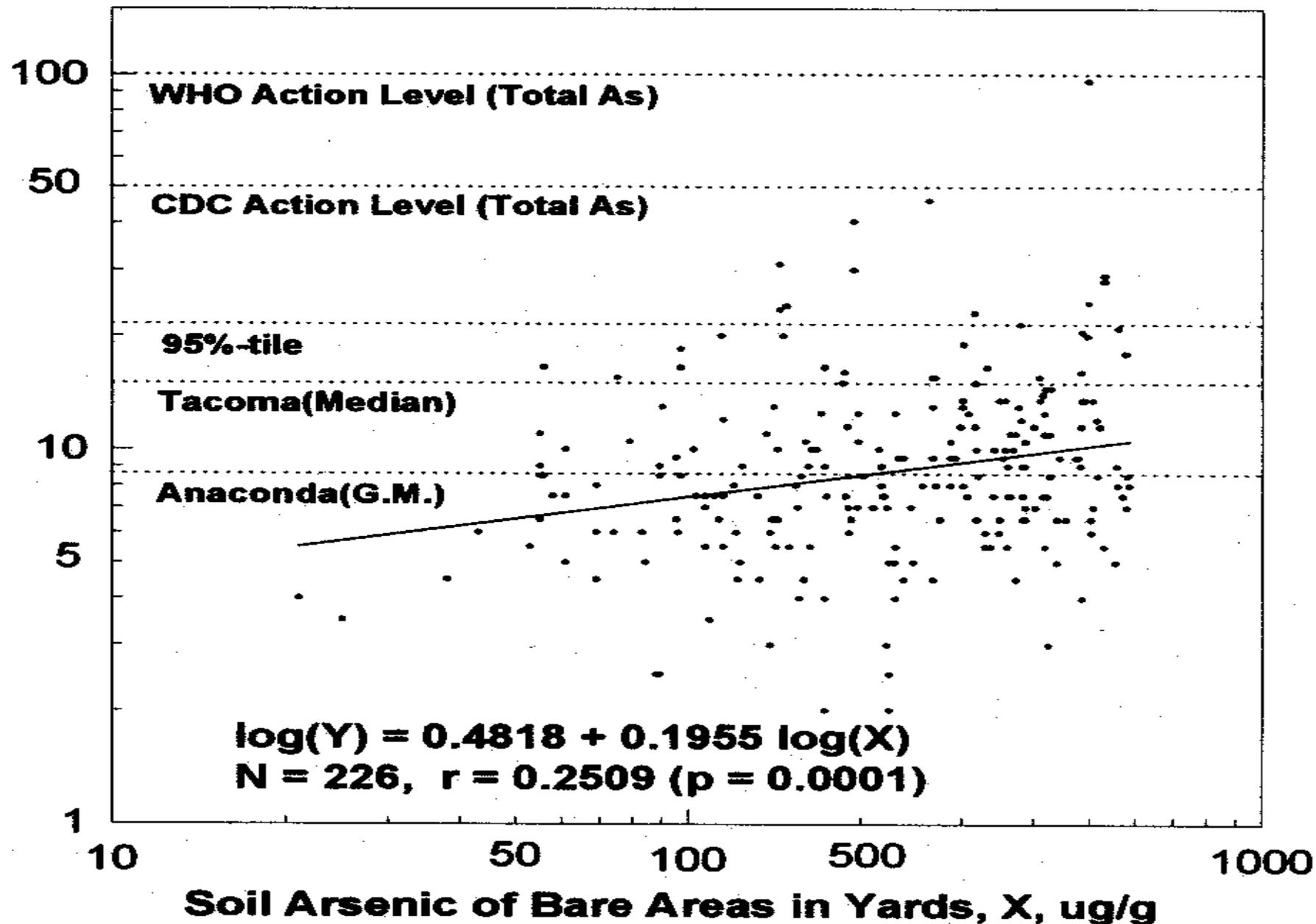
- Soil As above 40-100 mg kg<sup>-1</sup> soil may comprise risk to children by soil ingestion based on increased urinary As levels from inorganic As sources in exposed children.
- Risk from ingested soil As is expected to be greater for soils which have little As sorption capacity (low Fe sands).
- High Fe oxides in soil significantly reduce soil As bioavailability to primates and pigs.
- 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 0.43 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.



Proximity Index of Residence to the Smelter Site

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).

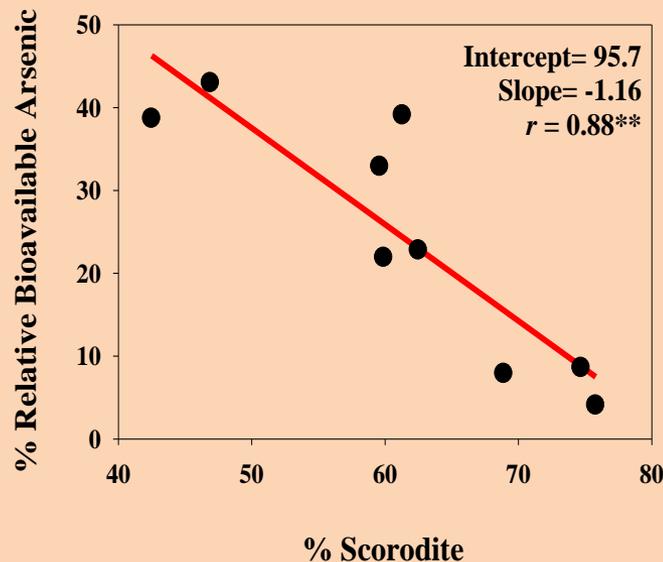
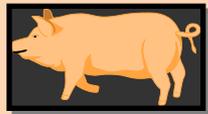
Speciated Urinary Arsenic, Y, ug/L



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

# Speciation of As vs. Bioavailability

- Metal speciation is best characterized by in situ spectroscopic methods.
- Pb speciation by SEM/EDAX for smelter-contaminated soil  
Identified bioavailability of Pb species: high ( $\text{PbCO}_3$ ) and low ( $\text{PbS}$ ; pyromorphite)
- Most authoritative approach: X-Ray Absorption Spectroscopy with synchrotron source (XANES, EXAFS)



**Arsenic bound to Fe in soil is inversely related to oral Bioavailability to pigs.**

**There are Very Few Studies of Metal Speciation vs. Human Bioavailability Due to Animal Model Limitations: Access, Expertise and Expense**

# Important Sources of Soil As Enrichment

- **Poultry and swine manure ( $\geq 25$  mg As/kg DW).**
  - Persistent in soils with much Fe and Al oxides.
  - High  $\text{PO}_4$  in litter inhibits retention of As in Coastal Plain soils.
  - Some producers have ceased adding arsenicals to poultry and swine feed.
- **Historic use of Pb-arsenate as pesticide.**
  - Apples, pears, cherries, etc.
- **Historic use of arsenic herbicides and defoliants.**
  - Cotton, potato, etc.
  - Railway right-of-way weed control.
- **Historic use of As in livestock tick dips.**
- **Gold mine wastes; usually rich in As, Hg and Fe.**
  - High Fe in gold mine wastes lowers As bioavailability.
- **Acid sulfate soils rich in As collected on Fe oxides.**

# Important Sources of Dietary As

- **Rice (staple food with highest inorganic As.**
  - US rice As somewhat higher than Japanese rice.
  - Much of As in US rice is organic form; lower risk.
  - Some US rice is produced on As enriched soils.
  - Flooded soils form arsenite; promotes rice uptake.
- **Some fish and shellfish rich in organic As, but also contain some inorganic As.**
  - Fish commonly contain non-risk arsenobetaine.
- **Seaweed foods commonly rich in As.**
- **Organic As in manure and biosolids is rapidly converted to inorganic arsenate.**
- **Plants accumulate As weakly, and translocate little As to grain and fruits.**
  - Apple on contaminated orchard soils remains low in As.

# Problems With New As Cancer Slope Factor

- **Based on Taiwan farm families highly exposed to As in water and food.**
  - High daily intake of high As water if artesian deep wells.
  - Cooking water added more As to rice (dietary staple).
  - Rice in Taiwan diet gave ~50  $\mu\text{g As/d}$ , not 10  $\mu\text{g/d}$  assumed by EPA.
  - Tropical climate caused higher water intake than EPA assumed.
  - Some families had high As artesian wells, but others had low As shallow wells. Epidemiological study used median village well As.
    - This miss-classified villagers with low or high As wells.
  - Epidemiologists used huge control population causing statistical artifact.
- **Some western US populations drank water with somewhat high As for decades, 50-150  $\mu\text{g/L}$ , without increase in cancer incidence (Lamm et al.; Meliker et al. in Michigan).**
- **Many researchers support threshold cancer model for inorganic As exposure.**

# Potential Risk to Livestock From Gypsum SO<sub>4</sub>

- Possible adverse effect in cattle which grazed FGD-gypsum amended fields in IN.
- Requested to look for information about whether FGD-gypsum would be able to cause adverse effects on cattle.
- Examined literature and contacted animal scientists regarding issue, and sought details on rates of dissolution.
  - Learned that amounts of FGD-gypsum which could be ingested from surface piles could be expected to cause PEM (Polioencephalomalacia) in ruminants. High dietary sulfate can be toxic (destroys part of brain).
  - Disclosed to industry; advised industry to prevent access to piles of gypsum in the field. Industry already developed warning to applicators and farmers with grazing livestock.
  - Provided reprints and literature summary to EPA, EPRI, and ARS Cooperators.
- Best avoided by Management Practices: prevent livestock exposure to piles of FGD-Gypsum or freshly amended pastures until rainfall.

# Summary/Conclusions: FGD-Gypsum

- New **FGD-Gypsum** is low in trace elements and other problem contaminants compared to background soils.
- Presuming **new FGD-Gypsum**, trace element levels will be below the 95<sup>th</sup> %-ile of background US soils.
- The Spent Foundry Sand Risk Assessment found no risk to humans or the environment (all Pathways) when elements were below the 95<sup>th</sup> %-ile of US soils.
- Dioxins, PAHs, and other xenobiotics were also subjected to risk assessment; all low in **new FGD-Gypsum**.
- Questions about Hg emissions remain, but it seems difficult to conclude it would be such a new and significant hazard to prohibit beneficial use of **FGD-Gypsum** in Agriculture and Horticulture.

# Summary/Conclusions: As Risk Assessment

- As in the New **FGD-Gypsum** is as low as in background US soils.
- Present IRIS risk assessment for As would lower present limits by 17-fold (**from 0.43 mg As/kg to 0.025 mg As/kg**).
- If the proposed IRIS change in cancer slope factor for As is adopted, **there will be no food, water, or soil** that US citizens could be exposed to without violating EPA guidance.
- The **IRIS change would apply directly only to drinking water and the As MCL-Goal**, but the actual MCL is set based on application of technology with a cost effective limit.
- Application to food would require cessation of consuming rice, seaweed, and many fish and shellfish.
- Application to all soil simply absurd; all US soil would be deemed hazardous!

# Steps in Risk Assessment for FGDG

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- **Collect appropriate data from field trials**
  - Cooperative tests – ARS, EPA and EPRI.
  - EPRI sponsored other tests with useful data.
- **Full characteristics of FGD-Gypsum**
- **Screening Assessment (against very conservative Soil Screening Limits and Eco-SSLs).**
- **For those that fail screening assessment, do modeling (Monte Carlo) assessments.**
- **Determine whether NEW FGD-Gypsum requires any regulations and prepare report to aid states.**
- **External peer review (start Apr. 4, 2012).**

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