Site-Specific Bioavailability for Lead at Small Arms Firing Ranges and the Development of an Air Force Protocol Document

Loren Lund, Ph.D. (PARSONS)

DoD POC: Glenn Anderson (TRAVIS AFB)

***ESTCP In Vitro* Soil Metal Bioavailability Workshop**

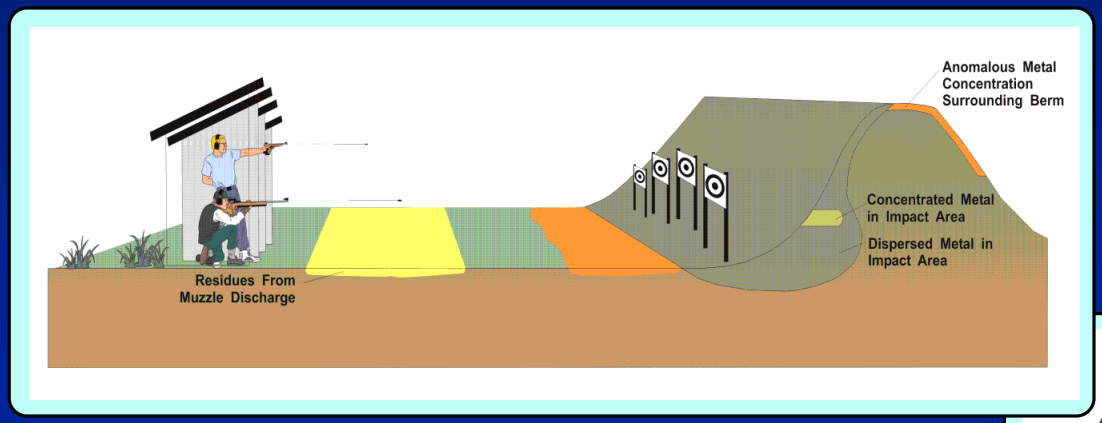
San Diego, CA September 2005

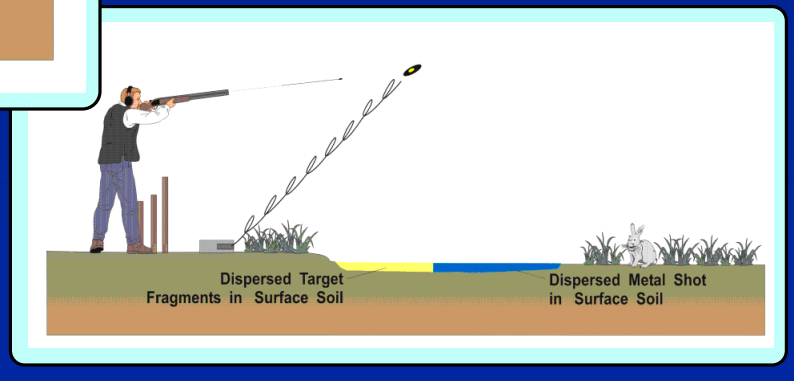
Outline of Presentation

- **Background information** on the protocol document (Parsons, 2000) and demonstration sites
- Summary of **results**
  - ➔Soil particle size and lead concentrations in soil
  - ➔*In Vitro* bioavailability of lead
  - ➔Speciation of lead in soils
- Overall **conclusions**
- **Lessons learned**, positive feedback, and success story

Objective of Protocol Document

- **Establish a cost-effective, site-specific, technically sound, and unified approach**
  - ➔ **Used results and "lessons learned" from four sites in CA, TX, and Alaska**





Investigation Timeframe and Guidance Documents/Issue Papers

- **Investigations and protocol development: 1998-2000**
- **USEPA (1994) *Guidance Manual for IEUBK Model***
- **USEPA (1996) *TRW Interim Adult Soil Lead Methodology***

  Default $RBF_{soil/soluble}$ = 60%; Site-specific data "are highly desirable as variation in relative bioavailability is expected for different species of lead and different particle sizes"

- **USEPA (1999) *Short Sheet: IEUBK Model Bioavailability Variable***

  "Until such time that fully validated *in vitro* techniques become generally accepted, the recommended approach to demonstrating site-specific bioavailability will need to be supported by an appropriate animal bioassay."

Guidance Documents/Issue Papers (cont'd)

- US Navy (2000) *Guide for Bioavailability Adjustments*

  Contains SOPs for soil speciation and *in vitro* tests (*in vitro* methods based on Ruby *et al.* [1996] modified by Drexler [Univ of CO at Boulder])

- NEPI (2000) *Assessing the Bioavailability of Metals in Soil*

  Correlation studies indicate Drexler's "*in vitro* test is predictive of relative lead bioavailability in two animal models"

- ITRC (2003) *Characterization and Remediation of Soils at Closed Small Arms Firing Ranges*. January

- USEPA (2003) *TRW Recommendations for Performing Human Health Risk Analysis on Small Arms Shooting Ranges*. March

  "The TRW does not recommend changing the default value for bioavailability without collection and TRW review of good site-specific data to support such a change"

Guidance Documents/Issue Papers (cont'd)

- Drexler (2003) *Bioassays: Past and Future*. Presented at USEPA Bioavailability Workshop. Tampa, FL. April

  Presented results for: 1) *In Vivo – In Vitro* Correlation; 2) Method Validation; 3) QA/QC; and 4) Sensitivity Analysis

- NRC (2003) *Bioavailability of Contaminants in Soils and Sediments: Processes, Tools, and Applications*

  "Replacing default values with site-specific information should be encouraged… There is no clear regulatory guidance or scientific consensus about the level and lines of evidence needed for comprehensive bioavailability process assessment"

- US DoD (2003) *Guide for Bioavailability Adjustments*
- USEPA (2004) *Lead Bioavailability in WTC Dust*. Appendix 7. Health-Risk Report. May 12.

  Used *in vitro* bioavailability and mineralogical analyses

Guidance Documents/Issue Papers (cont'd)

- Drexler, *et al.* (2003) *Issue Paper on the Bioavailability and Bioaccumulation of Metals*. Submitted to USEPA. August.
- USEPA (2004) *Framework for Inorganic Metals Risk Assessment*. Draft. November.

  "When validated, *in vitro* methods for determining lead relative bioavailability in soils may be used in place of animal studies"

- Multiple Papers on Bioavailability and Risk Assessment (2004) *Human and Ecological Risk Assessment* journal. Volume 10.
- USEPA SAB (2005) *Review of EPA's Draft Framework for Inorganic Metals Risk Assessment*. Internal Dft. March.
- CalEPA "*Bioavailability of Lead and Arsenic: Using in vivo and in vitro Measurements*" workshop. September 13, 2005.

Objectives for Collecting Site-Specific Bioavailability Data

- Incorporate site-specific bioavailability data into the overall risk-based approach
  - ➔**Soil particle size** and lead concentrations in soil
  - ➔***In Vitro* bioavailability** of lead
  - ➔**Speciation** of lead in soils
- Collect empirical data that could be used in **developing guidance** on the use of bioavailability adjustments in risk assessments

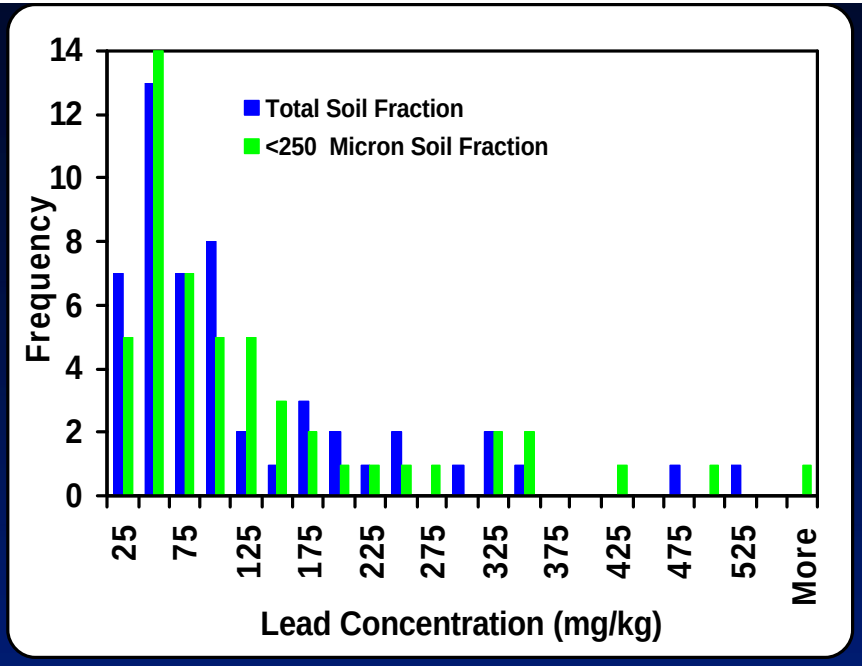
Background Information on CA & TX Demonstration Sites

Site	Description
Small-Arms Range, Travis AFB, CA	• 2.5 acres target range • Used between 1950s and 1970s • Backstop berm was removed by 1985 • Future industrial land use
Small-Arms Range, TX	• 5 acres target range in gravel pit • Used prior to 1984 • Backstop berm ~125 ft long X 15 ft high • Future industrial or open space land use • Range floor and berm covered with fly ash
Skeet Range, TX	• 25 acres recreational skeet range • Used from 1960s to 1980s • Flat terrain • Future industrial land use

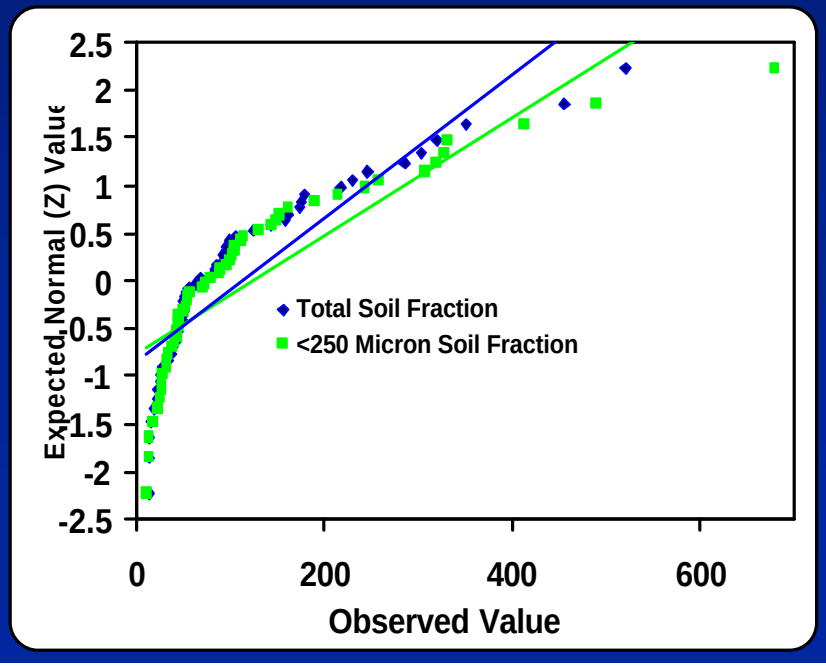
Soil Particle Size and Lead Concentrations in Soil

- Soil particles <100-250 µm **adhere to skin** and thought to be size fraction available for **incidental ingestion**
- Samples sieved using #10 mesh (2.0 mm [hereafter referred to as "**total**" soil fraction]) to remove large metal fragments and compared with results from samples sieved using #60 mesh (**<250 µm**)
- **Distribution and correlation analyses** conducted on lead concentrations in total and <250 µm fractions

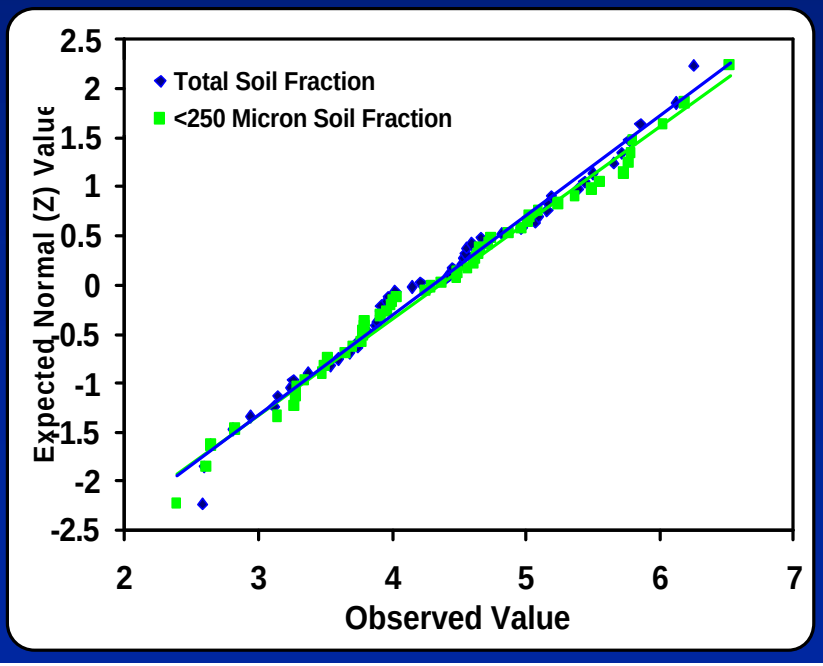
Skeet Range



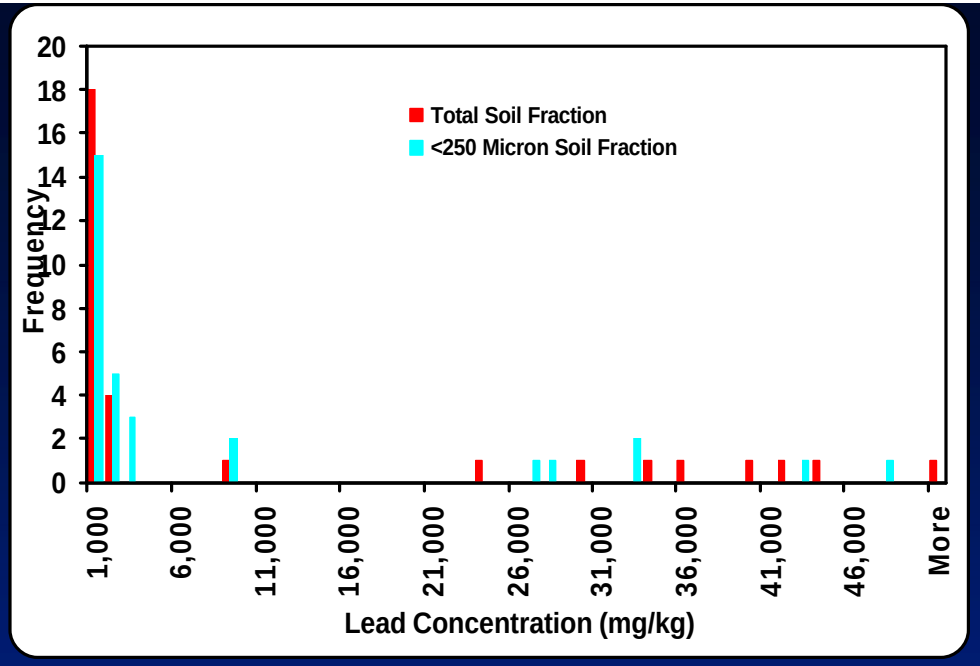
Probability Plot of Untransformed Data



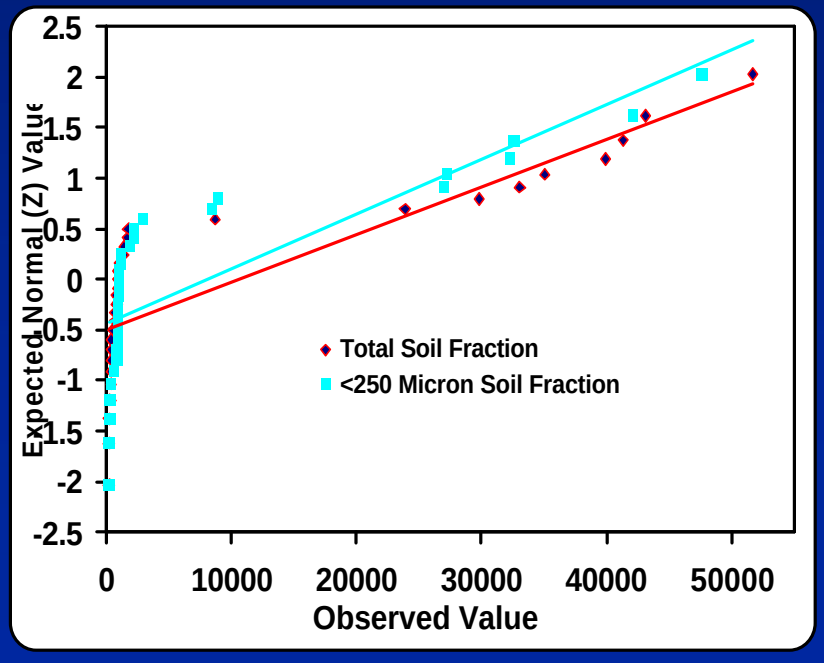
Probability Plot of Ln-Transformed Data



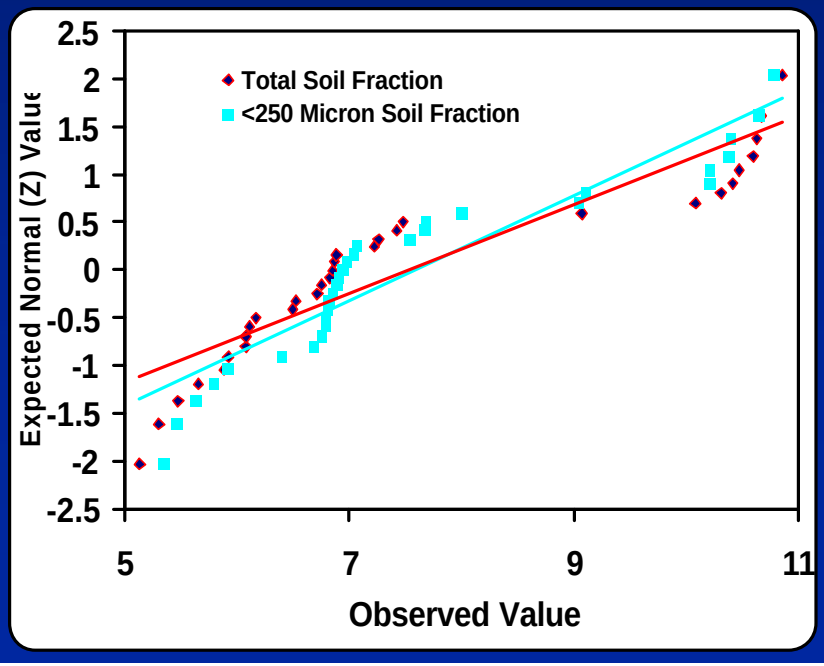
Rifle/ Pistol Ranges



Probability Plot of Untransformed Data



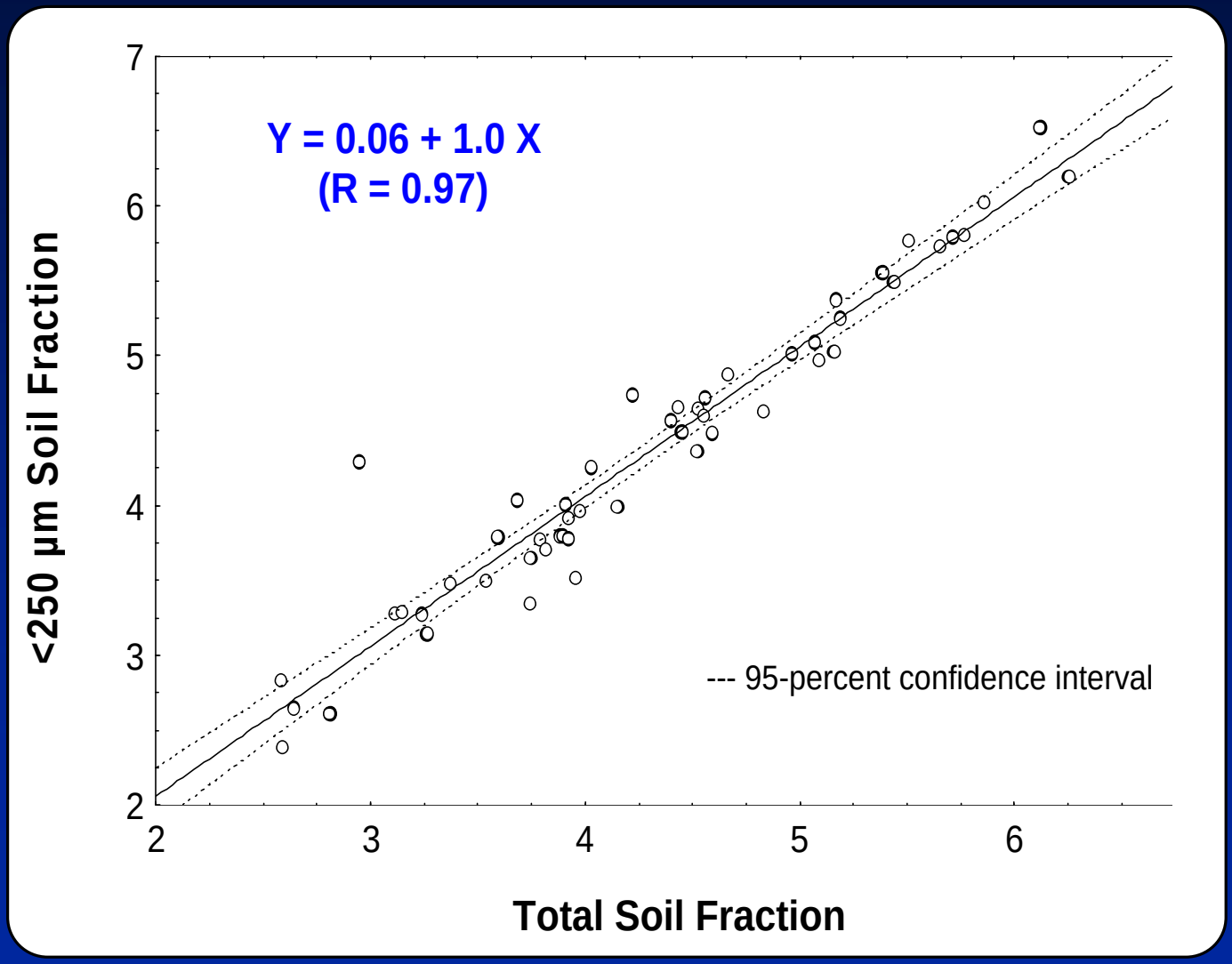
Probability Plot of Ln-Transformed Data



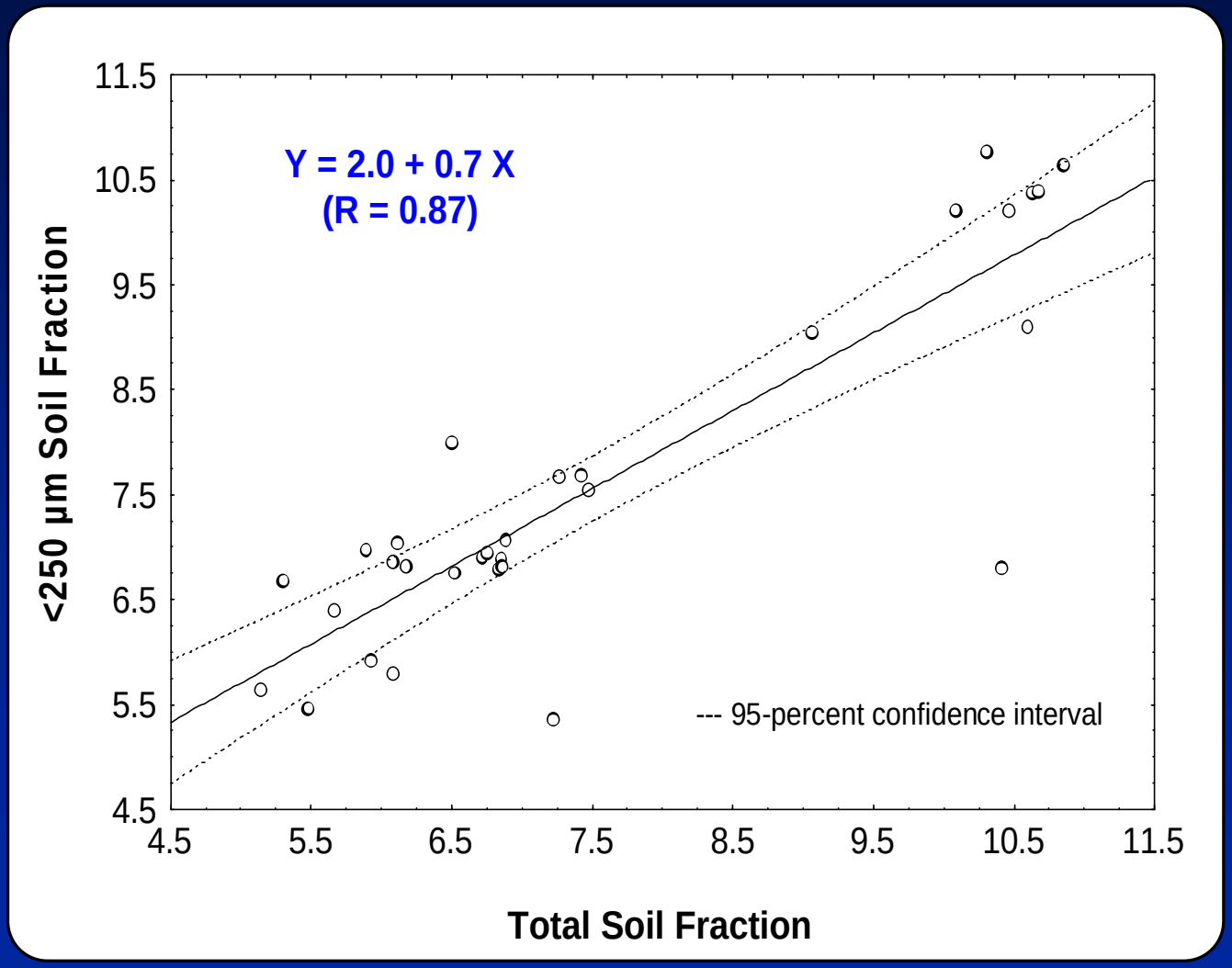
Conclusions of Distribution Analysis

- Review of histograms and probability plots suggested the total and <250 µm soil fractions had lead concentrations that were **lognormally distributed**
- Correlation analyses should be based on **log-transformed** data

Regression Curve of Log-Transformed Lead Data from Skeet Range



Regression Curve of Log-Transformed Lead Data from Rifle/Pistol Ranges



Results/Conclusions of Correlation Analyses

- **Regression correlation coefficients** for log-transformed lead concentrations at the skeet and rifle/pistol ranges were 0.97 and 0.87, respectively
- Lead concentrations were **similar** in the total versus <250 µm soil fractions
- Lead predominantly **present in <250 µm soil fraction** likely to be ingested

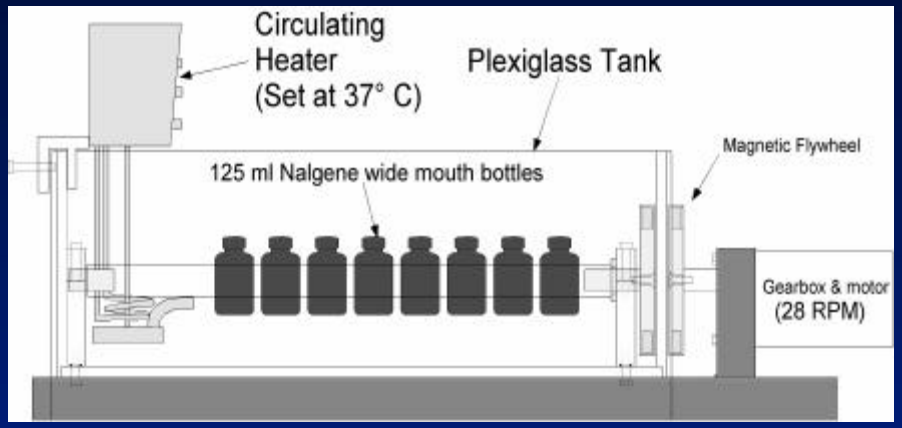
In Vitro Bioavailability of Lead

$$AF_s = AF_{soluble} \times RBF_{soil/soluble}$$

AFs	=	Fraction of lead absorbed by GI tract
$AF_{soluble}$	=	Absorption factor for soluble lead
$AF_{soil/soluble}$	=	Relative bioavailability in soil versus soluble

- Used *in vitro* method by Dr. John Drexler of Colorado University (CU) in Boulder, CO to estimate $RBF_{soil/soluble}$
- Method has been shown to correlate well with *in vivo* swine studies (Medlin, 1997); subsequent validation studies conducted (refer to Drexler presentation from USEPA 2003 bioavailability workshop and also, his presentation at CalEPA's workshop this week)

Drexler *et al.* (2003) *In Vitro* Bioavailability Method



Picture from Drexler '03 EPA wkshp talk

- 100 mL of simulated stomach solution (37 ºC) added to 1 g dried/sieved (<250 µm) sample
  - ➔ Solution: 0.4 M glycine in DI water & pH to 1.5 using HCl
- Argon gas over surface; after 10 min, began stirring (60 rpm)
- 5 mL samples collected and filtered (<0.45 µm) 60 min after simulated stomach solution added to sample
- Filtrate analyzed via ICP spectroscopy and EPA Method 6010B
- $RBF_{soil/soluble}$ estimated as percent *in-vitro* bioavailability

In Vitro Bioavailability Results

Site	N [a/]	$RBF_{soil/soluble}$ (Percent)		
		Range	Mean	SD [b/]
Skeet Range	7	49-65	60	5.2
Rifle/Pistol Range 1	5	75-96	85	10.3
Rifle/Pistol Range 2	15	55-108	81	14.8

[a/] N = Total number of samples
[b/] SD = Standard deviation

CONCLUSIONS:

- Average *in vitro* $RBF_{soil/soluble}$ at skeet range equivalent to default value (60%) recommended by TRW (USEPA, 1996)
- Average *in vitro* $RBF_{soil/soluble}$ at rifle/pistol ranges greater than TRW (USEPA, 1996) default value

Lead Speciation

- $RBF_{soil/soluble}$ is expected to vary significantly with particle sizes and **lead speciation**
- Speciation analysis conducted using an **electron microprobe** at University of Colorado, Boulder, CO
  - ➔Method used by USEPA Region 8 on mining waste soils (Casteel *et al.*, 1997)

Picture from Drexler '03 EPA wkshp talk

- **Speciation and Bioavailability**: Pb carbonate (most bioavailable) > Pb oxides > native/elemental Pb > Mn/Pb or Fe/Pb oxides and Pb phosphate (least bioavailable)

Lead Speciation Results: Surface Soils at Skeet Range

	Surface Soil Sample		
	A	**B**	**C**
In-Vitro bioavailability	61%	63%	59%
Total lead concentration	517 mg/kg	905 mg/kg	61 mg/kg
Lead Species (percent occurrence) [a/]			
Lead Carbonate (Cerussite)	<1	2	-- [b/]
Native Lead	--	--	--
Lead"M"Oxide [c/]	<1	2	--
Lead Oxide	--	2	--
Iron-Lead Oxide	11	13	39
Manganese Lead Oxide	82	60	61
$PbSiO_4$	<1	16	--

[a/] Number of particles counted: 65, 102, and 5 for samples A, B, and C, respectively. Uncertainty with speciation data for sample C was relatively high because of the low particle count.

[b/] "--" = not observed.

[c/] "M" = one or more other metals (e.g., antimony and copper).

- **Presence of least bioavailable forms (MnPb & FePb oxides) correlated with lower *in vitro* results versus rifle/pistol range**

Lead Speciation Results: Surface Soils at Rifle/Pistol Range

	Surface Soil Sample		
	A	**B**	**C**
In-Vitro bioavailability	79%	96%	79%
Total lead concentration	2,085 mg/kg	8,119 mg/kg	1,076 mg/kg
Lead species (percent occurrence) [a/]			
Lead Carbonate (Cerussite)	22	52	<1
Native Lead	<1	3	<1
Lead"M"Oxide [b/]	41	16	33
Lead Oxide	16	-- [c/]	--
Iron-Lead Oxide	18	6	55
Manganese-Lead Oxide	--	11	5

[a/] Number of particles counted: 97, 219, and 62 for samples A, B, and C, respectively. The following compounds, which may contain trace amounts of lead, also were detected: titaniun dioxide, barium sulfate (barite), brass, and clays.

[b/] "M" = one or more other metals (e.g., antimony and copper).

[c/] "--" = not observed.

- **Pb carbonate (highly bioavailable) predominant form in sample B, which correlated with highest *in vitro* bioavailability**

Particle Size, *In Vitro* Bioavailability, and Speciation Conclusions

- Total and <250 µm lead concentrations at firing range sites were **lognormally distributed**
- Lead concentrations were **similar** in the total versus <250 µm soil fractions
- Lead predominantly **present in <250 µm soil fraction** likely to be ingested
- ***In vitro* estimates** of $RBF_{soil/soluble}$ equivalent to or greater-than USEPA TRW (1996) default value of 60%
- Lead speciation results and expected bioavailability **correlated** with *in vitro* bioavailability results

Examples of "Lessons Learned"

- Encountered reviewers that were **"uncomfortable"** with the science
  - ➔ **Educate**, particularly during the work plan stage
  - ➔ **Provide examples** of other sites where approach used
  - ➔ Emphasize, per NRC (2003), site-specific data may result in **increase or decrease** compared with default
- Some reviewers uncomfortable with remedial goals that **differ** from values typically used

Values Listed in ROD for Travis AFB

Chemical of Concern	Soil Cleanup Level (mg/kg) [a]	Residential (mg/kg)		Industrial (mg/kg)	
		10^{-6} Cancer Risk	Chronic HI=1	10^{-6} Cancer Risk	Chronic HI=1
Antimony	6	NA	31	NA	410
Copper	250	NA	3,100	NA	41,000
Lead	1,000	NA	400	NA	750

Cal-Modified PRG for Lead

150 mg/kg

*from CalEPA Leadspread & residential defaults

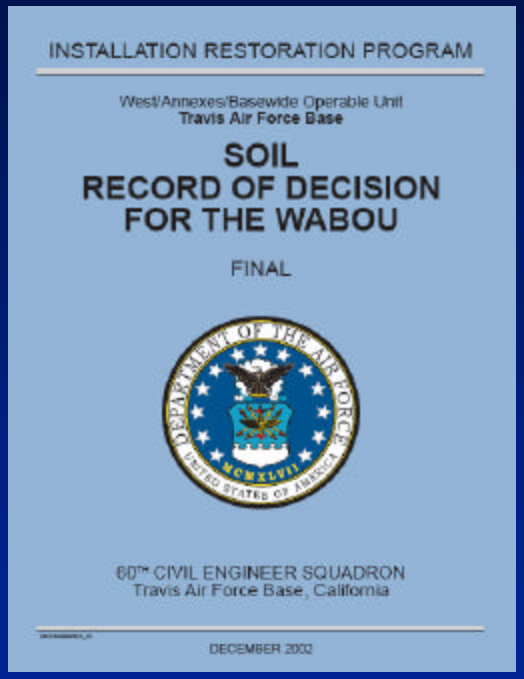
Examples of "Lessons Learned" (cont'd)

- At the time of the investigation, there was **no clear regulatory guidance** on the use of *in vitro* bioavailability results
  - ➔"**Mixed message**" via emerging guidance or informal policy
  - ➔In the absence of guidance, regulators that are "in the trench" reviewing methods/results were **uncertain of their agency's position**
- Important to proceed and collect technically defensible data in order to help **facilitate change**
  - ➔Practical constraints (e.g., resources, schedule, etc.) may limit amount and type of data – **not a good reason** to forgo collecting any data

Positive Feedback

- "Use of these analyses at the California demonstration site was **very well received** by USEPA" (Parsons, 2000)
  - ➔Reviewers said these data were very useful in helping them make **risk management decisions**
  - ➔USEPA Region 9 management recommended that these **data be collected at all** firing range sites
  - ➔Recommended that the Air Force **widely distribute** protocol document and suggested presenting at Tri-Services group meetings (presented in 2000)
- Use of site-specific bioavailability information (particle size, *in vitro*, and speciation results) provided **"comfort factor"** for regulators

Travis AFB Firing Range – Success Story



- **Site-specific bioavailability data were incorporated into derivation of cleanup goals in Remedial Action Plan (RAP) -- finalized in 2000 (Parsons, 2000)**
- **Record of Decision (ROD) finalized in Dec., 2002 (http://public.travis.amc.af.mil/pages/enviro/library)**

  ➔Value in RAP was selected as Pb final cleanup goal

Questions?

Contact Information:

Loren Lund, Ph.D.
Senior Toxicologist/Risk Assessor
PARSONS
787 E. 1500 N.
Shelley, ID 83274
(208) 357-5351 (phone/fax)
Loren.G.Lund@Parsons.com

DoD Contact: Glenn Anderson
Base Hydrologist
411 Airmen Drive
Building 570
Travis AFB CA 94535-2001
(707) 424-4359 (phone)
(707) 424-0833 (fax)
glenn.anderson1@travis.af.mil

Thank you for your time!