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Transient Phytoextraction Agents --- A New Class of Soil Amendments for Lead Phytoextraction

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2005 International Phytotechnologies Conference

April 21, 2005

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Lead-Contaminated Soils: Extent and Sources

- **Extent**
  - **Millions of acres at government and residential sites, Superfund sites, as well as areas surrounding smelter and mining sites**
- **Sources of Lead**
  - **Bullet fragments**
    - **Firing Ranges at Department of Defense facilities**
  - **Lead-based Paints**
    - **Drip zones surrounding pre-1978 homes**
    - **18% of existing housing in US**
  - **Leaded Gasoline**
  - **Smelter Fragments and Ore Minerals**

A cost-effective technology is required for remediation of these soils

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Remedial Alternatives for Pb-Contaminated Soils

- **Capping**
  - **Reduces or eliminates exposure to lead soil**
  - **Buries otherwise good topsoil**
  - **Does not remove lead from soil**
- **Electrokinetics**
  - **Removes lead via electrical current**
  - **Costs as much as $300 per ton for large areas**
  - **Large array needed for large areas**
- **Excavation and Disposal**
  - **Eliminates exposure to lead soil**
  - **Costly at $100 - $200 per ton for large areas**
  - **Removes otherwise good topsoil**

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Remedial Alternatives for Pb-Contaminated Soils

- **Soil Washing/Leaching**
  - **Removes lead via screening or extraction**
  - **Costs as high as $400 per ton, particularly for fine-grained soils**
  - **Destroys soil structure; creates phytotoxic conditions**
- **Stabilization**
  - **Reduces leachable lead concentrations and associated human health risk; does not remove lead from soil**
  - **Costs range from $110 to $205 per ton for *in situ* application**
  - **Requires adequate mixing with soil and continual monitoring.**

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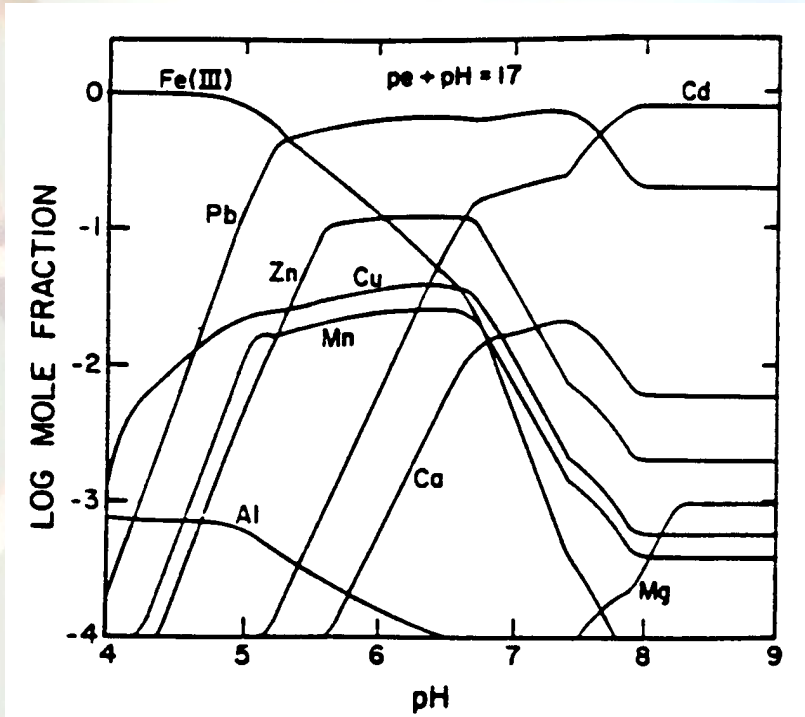
EDTA-Based Phytoextraction

- **Effective lead phytoextraction requires the use of chelating agents to make lead plant available.**
- **EDTA works best due to strong complexation with lead over typical soil pH ranges.**
- **EDTA is thought to be slowly biodegraded in soils.**
- **Potential mobility of Pb-EDTA complex, particularly in areas of sandy and/or endoaquic soils.**
- **USEPA. USACE, and HUD recently funded studies to test chelates known to biodegrade more rapidly than EDTA, called transient phytoextraction agents (TPAs), for effective lead phytoextraction.**



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TPA-Based Phytoextraction: The Next Generation

- **Proposed Definition of a TPA**
  - **Any agent that would exhibit effectiveness in triggering accumulation of the targeted metal in plants while minimizing the risk of migration of soluble metals through rapid degradation or inactivation of the soluble complex.**

- **Expected Behavior of the Pb-TPA Complex**
  - **Following degradation or dissociation of the metal-agent complex, the metal is expected to quickly precipitate from solution or resorb onto soil particles, thereby reverting to a low-solubility state.**

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Objective of Study

- **Test effectiveness of several possible TPAs for lead extraction and uptake from contaminated soils in comparison to EDTA.**
  - **Assess lead extraction in batch studies**
  - **Assess uptake in growth chamber studies using Indian mustard, sunflower, and turf grass.**

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Potential TPAs

- **Baypure**
  - **active ingredient is tetrasodium iminodisuccinate, $C_8H_{11}NO_8Na_4$**
  - **won USEPA's Green Chemistry award based on its rapid biodegradability and considered "ecotoxicologically benign"**
- **Citric Acid and Other Organic Acids**
  - **$C_6H_8O_7$**
  - **called "environmentally benign" by DOD**
- **NTA**
  - **nitrilotriacetic acid, $C_6H_9NO_6$**
  - **degradation rate similar to that of citrate and glucose**
- **GLDA**
  - **dicarboxymethyl glutamic acid tetrasodium salt, $C_9H_9NO_8Na_4$**
  - **biodegradable chelating agent used in Japan**
- **EDDS**
  - **ethylenediamine disuccinic acid, $C_{10}H_{13}N_2O_8Na_3$**
  - **behavior meets internationally accepted criteria for biodegradable chemicals**

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Metal Formation Constants for TPAs Compared to EDTA

Metal Ion	$EDTA^{4-}$	$EDDS^{4-}$	$Citrate^{3-}$	Baypure	NTA
Ca^{2+}	10.7	4.58	4.3	4.3	6.3
Zn^{2+}	16.68	13.4	5.6	9.88	10.45
Pb^{2+}	18.3	12.7	5.2	9.75	11.34
Cu^{2+}	18.86	18.45	6.7	12.7	12.7
Fe^{3+}	26.5	22.0	12.3	15.2	15.9

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Effectiveness of TPAs for Lead Extraction

- 2.5 grams of soil placed in 50 mL centrifuge tube
- Extracted with 25 mL of either
  - 5 mM EDTA, NTA, GLDA, EDDS, Baypure, Succinic acid
  - 20 mM Acetic acid, Ascorbic acid, Citric acid, Malic acid, Oxalic acid, Succinic acid
- All tubes placed on shaker for two hours after chelate addition
- Each tube centrifuged for 10 minutes at 4300 rpm
- Supernatant filtered through syringe filters (0.45 µm)
- Filtrate analyzed by ICP spectroscopy for lead

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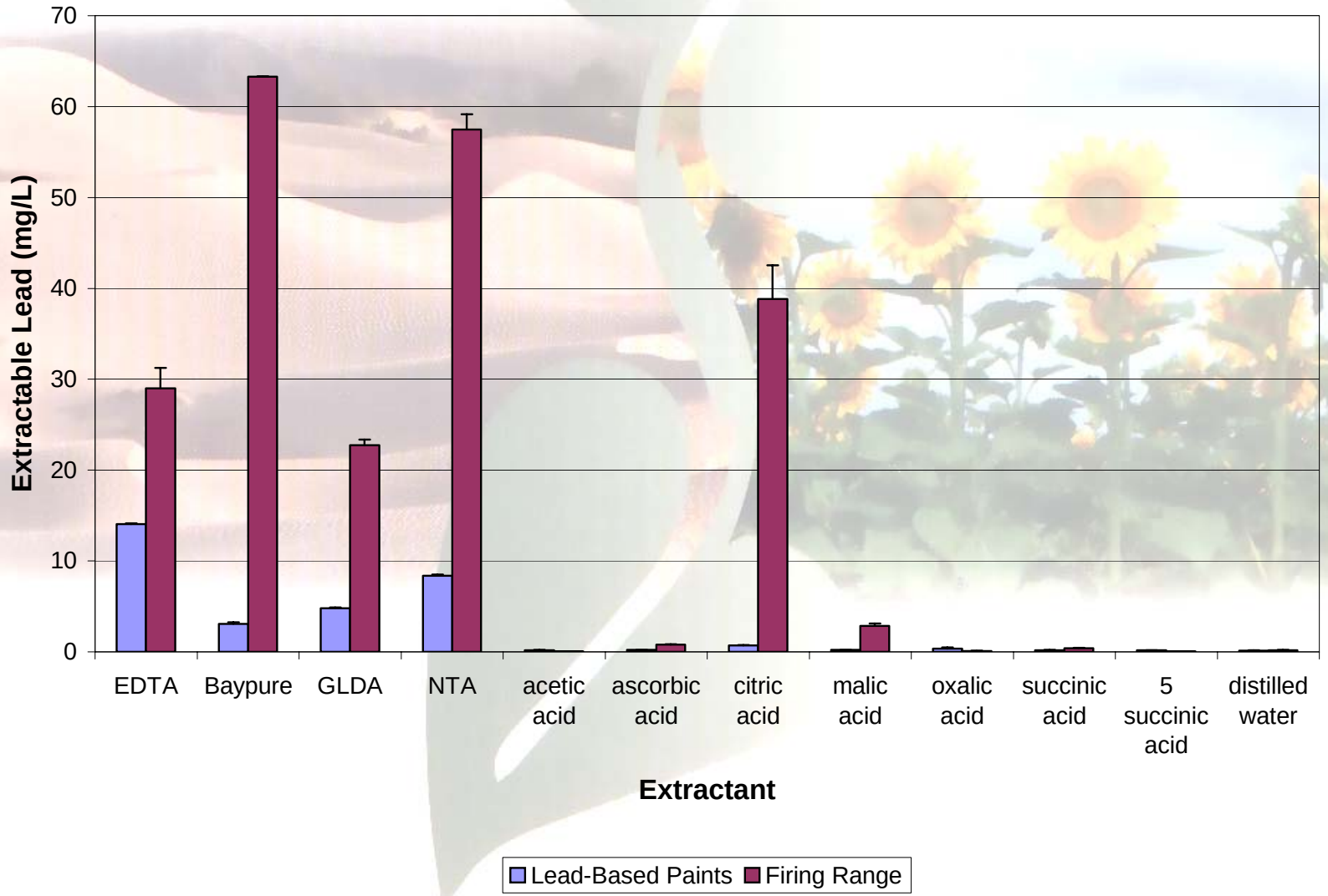
TPA Extraction of Lead Compared to EDTA



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Plant Uptake Experiment

- **Firing range soil seeded with Indian mustard, sunflower, and turf grass; placed in growth chamber with four replicates per treatment.**
- **At the appropriate growth stage for each plant species, the appropriate pots were treated**
  - **EDTA, Baypure, EDDS, or NTA applied at 5 mmol/kg rate**
  - **Citric acid applied at 20 mmol/kg rate**
- **All plant species harvested one week later, above ground biomass placed in paper bag, oven-dried, weighed, and ground prior to analysis.**
- **Analyzed by ICP spectroscopy for lead.**

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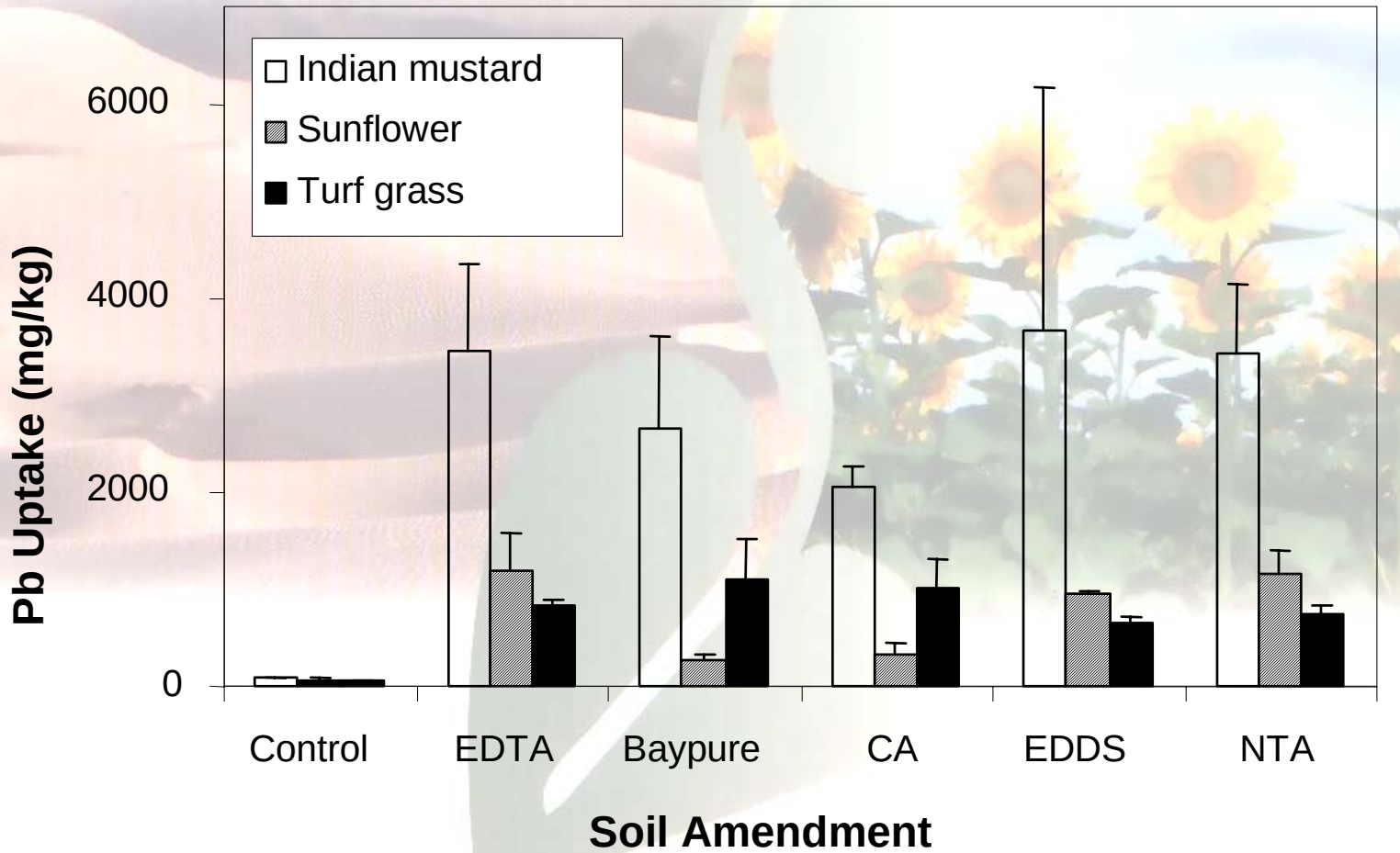
TPAs Similar to EDTA for Lead Uptake



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Conclusions

- **Lead-contaminated soils remain a persistent environmental problem, requiring remediation.**
- **Current remedial technologies flawed based on cost-effectiveness, impracticality for large areas, non-removal of lead, and potential leaching issues.**
- **Performance of TPA-based phytoextraction similar to that of EDTA-based phytoextraction in terms of lead extraction and uptake.**
- **By minimizing the potential of leaching using biodegradable chelating agents, TPA-based phytoextraction is capable of safely and effectively remediating these problem soils.**

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Future Work

- **Characterization of biodegradation of the Pb-TPA complex is currently underway to define TPA behavior.**
- **Possible quantifiable parameters for defining TPA behavior**
  - **Plant Uptake**
    - $[Pb]_{TPA}/[Pb]_{CTRL} \geq 10$
  - **Migration Control 1**
    - $[Pb]_{t=14d}/[Pb]_{t=0d} \leq 0.1$
  - **Migration Control 2**
    - $[Pb]_{t=14d}/[Pb]_{WE} \leq 1$
- **Field demonstration of TPA-based phytoextraction will be conducted this summer at ten homes in Baltimore, Maryland as part of a HUD–funded study examining the use of turf grass to remove paint-derived lead from residential soils.**

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Acknowledgements

- **Funding for this research was made possible from grants from the U.S. EPA, U.S. Army, and HUD.**