Overview of Chemical Research from Biosolids Land Application

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California Water Environment Association
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Focus of this Presentation:

- Pretreatment of industrial wastes and reduced use of Cd in products lowered Cd and other metals in biosolids.
- Enforcement of 503 regulations favor biosolids use.
  - Assume 1000 t/ha biosolids applied for each Pathway.
- Inorganic fraction of biosolids provides persistent increased metal/Cd adsorption by soil: “Corey Effect”.
- Biosolids are a remarkably valuable material for remediation of metal contaminated Superfund Areas
- Phosphate applied in biosolids has low solubility because of Fe and Al binding of P.
- New issues about As and Cr6 in biosolids due to changes in Drinking Water rules at EPA/CA.
- Changes needed in CWA-503: Mo, As?, Cr?, Fe?, Hg?
Pretreatment and Regulatory Controls
Reduced Cd in PA Biosolids (Stehouwer)

**Cadmium**
- Median
- $r^2 = .93$
- 90th Percentile
- Error bars range from 25th to 75th percentile

PSU data only
Madison Biosolids Zn, mg kg⁻¹ DW

Year


0 500 1000 1500 2000 2500 3000

503 APL Limit – Zn
Recommended Cd:Zn Limit

Madison Biosolids, Cd:Zn ratio

Year

## Results of the TNSSS for Cd, Zn and Cd:Zn Ratio

Calculated Mean, Geo. Mean, Range for the 84 samples ignoring the population representation aspect of the TNSSS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Statistical Measure</th>
<th></th>
<th></th>
<th></th>
<th>GOAL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>GM</td>
<td>Min</td>
<td>Max</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1030.</td>
<td>808.</td>
<td>216.</td>
<td>8550.</td>
<td>&lt;1500.</td>
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<tr>
<td>Cd</td>
<td>2.69</td>
<td>1.98</td>
<td>0.208</td>
<td>11.8</td>
<td>&lt;5-10.</td>
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<tr>
<td>Cd:Zn, %</td>
<td>0.282</td>
<td>0.245</td>
<td>0.064</td>
<td>1.06</td>
<td>&lt;1.5</td>
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<tr>
<td>Element</td>
<td>Min.</td>
<td>Max.</td>
<td>503</td>
<td>Goal</td>
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<tr>
<td>As, mg/kg</td>
<td>1.18</td>
<td>49.2</td>
<td>41.</td>
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<tr>
<td>Cd, mg/kg</td>
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<td>11.9</td>
<td>39.</td>
<td>&lt;5-10.</td>
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<tr>
<td>Cd/Zn, %</td>
<td>0.064</td>
<td>1.06</td>
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<td>&lt;1.5</td>
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<tr>
<td>Cr, mg/kg</td>
<td>6.74</td>
<td>1160</td>
<td></td>
<td>&lt;0.000002</td>
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<tr>
<td>Co, mg/kg</td>
<td>0.869</td>
<td>290</td>
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<td>&lt;25.</td>
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<td>Cu, mg/kg</td>
<td>115.</td>
<td>1720</td>
<td>1500</td>
<td>&lt;500.</td>
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<tr>
<td>Fe, %</td>
<td>0.158</td>
<td>19.5</td>
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<td>&lt;4.0</td>
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<td>Hg, mg/kg</td>
<td>0.19</td>
<td>7.5</td>
<td>17.</td>
<td>&lt;5.</td>
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<td>Mo, mg/kg</td>
<td>2.51</td>
<td>86.4</td>
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<td>&lt;40.</td>
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<td>Ni, mg/kg</td>
<td>7.60</td>
<td>526</td>
<td>290.</td>
<td>&lt;100.</td>
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<td>Se, mg/kg</td>
<td>1.1</td>
<td>24.2</td>
<td>28.</td>
<td>&lt;10.</td>
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<tr>
<td>Zn, mg/kg</td>
<td>216</td>
<td>8550</td>
<td>2800</td>
<td>&lt;1500.</td>
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</table>
Arsenic in US Soils
Naturally Exceed EPA SSL

- As SSL (10E-6) is 0.43 mg/kg
- Normal range in US soils is 2-12 mg/kg
  - 5\textsuperscript{th} to 95\textsuperscript{th} percentile levels.
- Re-estimation of cancer slope factor at EPA (IRIS) is 17-fold higher; this yields SSL of 0.025 mg/kg.
- How can EPA set SSL below background soils?
  - Prohibit rice, seaweed, many fish and shellfish.
  - All based on refuted Taiwan database.
- After SAB hearing in 2010, EPA is reconsidering.
- All rules connected with As are on hold.
- CA has large area of gold mine tailings rich in As.
Chromate (Cr6) Issues

• Cr removed from 503 by lawsuit from leather industry
  — Cr in biosolids is Cr3; no plant uptake or toxicity shown
• CA OEHHA has proposed low Cr 6 limits in DW
  — 9/2010 – 0.06 μg/L
  — 12/2010 – 0.02 μg/L
• EWG measured Cr6 in many DW, found nearly all exceeded the 0.06 μg/L limit.
• But this limit is based on Nat. Toxicol. Prog. Feeding study at Maximum Tolerated Dose.
• But Cr6 is reduced to Cr3 in stomach until dose reaches the massive levels used by NTP.
• Logically, biosolids Cr remains insignificant issue.
• CA has over 500,000 A of Cr-rich soils >1000 mg/kg!
• Expect craziness regarding Cr6, especially in CA
503 Is A Defensible Rule

Pathways for Risk Assessment of Elements in Soils, and Highly Exposed Individuals

Highly Exposed Individuals

Practical Worst Case Loadings: 1000 t/ha.

SOIL-PLANT BARRIER

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

PHYTOTOTOXICITY

Possible at very low soil pH, but sorbents in biosolids limit potential phytotoxicity—Zn Cu Ni
Potential Environmental Problems From Inadequately Regulated Use of Biosolids on Cropland and Gardens

• **Phytotoxicity from Zn (possibly Cu, Ni):**
  - Involved sensitive vegetable crops.
  - High cumulative applications and low soil pH, <<5.5
  - Highly contaminated biosolids.

• **Excessive Cd in crops:**
  - Highly contaminated biosolids (before regulations).
  - Low soil pH. High Cd/Zn ratio allow food-chain transfer.

• **Excessive PCB transfer to livestock:**
  - Highly contaminated biosolids before regulation.
  - Surface application on pastures = highest transfer.
  - Cessation of PCB use limits PCBs in biosolids.
Potential Environmental Problems From Inadequately Regulated Use of Biosolids on Cropland and Gardens

• Excess Mo or Se in forages; alkaline soils.

• Lime-induced Mn deficiency:
  − Leached soils low in total Mn.
  − Calcareous soils from limed sludge or limestone applied to correct Zn phytotoxicity.

• Excess mineralizable N application
  − Nitrate leaching or lodging of small grains.
  − Prevented by regulations/mineralization data.

• Infections of livestock by parasites.
PCB models Apply to PPCPs

- Lipophilic compounds can be accumulated in biosolids at measurable concentration.
- Other hydrophilic compounds in effluent.
- Detergents retained in anaerobic digesters are rapidly biodegraded in soils or aerobic systems.
- Apply 503 risk assessment methods shows that direct ingestion of biosolids is most sensitive pathway for risk.
- Plant uptake is minor to irrelevant.
- Lipophilic compounds bound to biosolids humics.
- Aged PPCPs bound to OM lower uptake.
- No evidence of risk as levels in crops/worst case.
Before Regulations, Bad Practices Occurred.


Bioslids applied 1967-1975; approx. 20 t/ha
Biosolids contained 700 mg Cd/kg, Cd:Zn=10%
Field soil contained 8.2 mg Cd/kg, Cd:Zn = 15%.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Trt</td>
<td>pH</td>
<td>Chard</td>
<td>Lettuce</td>
<td>Soybean</td>
<td>Oat</td>
<td>Soybean</td>
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<tr>
<td>Biosolids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>5.7</td>
<td>70.4</td>
<td>49.9</td>
<td>2.64</td>
<td>3.38</td>
<td>2.05</td>
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<tr>
<td>Limed</td>
<td>6.4</td>
<td>17.7</td>
<td>9.9</td>
<td>0.65</td>
<td>0.54</td>
<td>0.46</td>
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<tr>
<td>Control</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nil</td>
<td>5.2</td>
<td>0.9</td>
<td>1.5</td>
<td>0.16</td>
<td>0.11</td>
<td>0.11</td>
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<tr>
<td>Limed</td>
<td>6.2</td>
<td>0.5</td>
<td>0.6</td>
<td>0.13</td>
<td>0.07</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Cd Examples From Old Reports

- **Long term sludge utilization farms in NE:**
  - City 9 Elizabethtown, PA  169 Cd  0.033 Cd:Zn
  - City 13 Pottstown, PA  700 Cd  0.150 Cd:Zn
  - City 25 St. Marys, PA  970 Cd  0.780 Cd:Zn
  - City 1 York, PA  150 Cd  0.028 Cd:Zn
  - City 2 Harrisburg, PA  160 Cd  0.049 Cd:Zn

- **Purdue study of high metal sludges:**
  - Frankfort, IN.  284 Cd  0.042 Cd:Zn
  - Anderson, IN.  247 Cd  0.048 Cd:Zn
  - Merion, IN.  1210 Cd  0.637 Cd:Zn

- **Literature reports:**
  - Fort Collins, CO.  98 Cd  0.056 Cd:Zn
  - Chicago, IL  210 Cd  0.051 Cd:Zn
What should be done with contaminated biosolids application sites from before regulations?

- Before 1979, there were no Federal biosolids regulations; a few states started permitting biosolids based on metals and PCB levels.
- A few severely contaminated sites were identified and remediated using local funds and state rules.
- What about all the other sites with high soil Pb, Hg, As, Cd, etc., that are known to exist?
- I asked EPA about my recollection that the 1979 Rule required POTWs/States to investigate previous sites to look for problems? They say “Not in rules.”
- States need to do something about known sites with excessive metal accumulation from biosolids.
Heat-Treated Biosolids applied at Hayden Farm Plots, 1976.

Linear Regression slope used for 503 Rule

Plateau regression and extrapolation.

Actual Means

Low pH

Biosolids and Cadmium Application Rates

Lettuce Cd, µg/g DW

1000 Mg/ha

13.4 kg/ha

0 250 500 750 1000

0 1 2 3 4 5

13.4 kg/ha
Claims of Biosolids Metals as Environmental Time-Bombs

• In the early 1970s, many scientists discussed the possibility that organic matter biodegradation after biosolids application may increase metal uptake.
  ‒ Leeper, Page, Chaney, Giordano, and many others.
  ‒ Beckett et al. (1979) wrote “Time-Bomb” Hypothesis.
  ‒ They got funding and did tests to evaluate hypothesis; concluded no evidence that Time-Bomb occurred.

• McBride Raised Time-Bomb in 1995 Paper
  ‒ Raised arguments to support the Time-Bomb hypothesis.
  ‒ Reported different interpretation of Mahler and Ryan papers on crop uptake of Cd from long-term biosolids amended soils.

• Ryan et al. illustrated effects of biosolids inorganic matter on Cd adsorption by long-term biosolids-amended soils.
  ‒ Removed OM from control and amended soils using Chlorox.
  ‒ Measured Cd adsorption at relevant concentrations \([0.01 \text{ Ca(NO}_3\text{)}_2]\)
Hettiarchichi, Ryan et al. 2002. Effect of Long-Term Biosolids Application On Cd adsorption at pH 5.5; composted limed biosolids vs. control soil.
Effect of Long-Term Applied Biosolids on Phytoavailability of Cumulative Soil Cd?

• Biosolids applied to controlled field plots 16-25 years before sampling both control and biosolids-amended soils.
• All soils amended with 0, 2.5, 5.0, 7.5, and 10.0 mg Cd/kg using soluble $^{111}$Cd nitrate.
• All soils adjusted to pH 6.5 [in 0.01 M Ca(NO$_3$)$_2$]
• Appropriate fertilizers for pot test applied.
• Grew Romaine Lettuce to maturity.
• Analyzed with good quality control in analysis.
Romaine Lettuce grown on Hayden Farm Control and Long-Term Biosolids Compost-amended (672 t/ha) soils with 0-10 mg Cd/kg, at pH 6.5 in Ca(NO₃)₂. Reduced uptake/toxicity of Cd by lettuce (control vs. biosolids-amended).
Phytoavailability of Cd added to Long-Term Biosolids-Amended Soils

Hayden Farm Plots
Biosolids Experiment
Beltsville, MD

Soil Total Cd, mg/kg DW

Romaine Lettuce Cd, mg/kg DW

pH=6.5

672 t/ha Compost
7.2 ppm Cd

224 t/ha Heat-Treated
13.4 ppm Cd

672 t/ha Compost
7.2 ppm Cd

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

- Biosolids Cd remains in labile pool for indefinite period, as does most soil Cd.
- Persistent biosolids sorption reduces Cd uptake compared to untreated soils.
- Phytotoxicity of added Zn is very effective limit to excessive bioavailable Cd in crops.
- With high quality biosolids, bioavailable crop Cd is not increased even when Cd is increased.
- Only subsistence rice farmers suffered Cd disease from soil contamination; all “home grown” rice for lifetime; high bioavailability.

—Polished rice is deficient in Fe, Zn and Ca for humans
Additional Protection Factors for Biosolids Cadmium Limits in the USA.

- **Acidic Garden Scenario:**
  - 50 years exposure at maximum soil Cd.
  - Always strongly acidic, about pH 5.5.
  - 50-65% of Garden Vegetables.

- Uses linear uptake slopes from field studies.
- Uses 70 µg Cd/day limit; includes safety factors.
  - Data shows full protection at 200 µg/day.
- Ignores bioavailability of crop Cd.
- Ignores natural limitation on maximum crop Cd
  - From Zn phytotoxicity at low crop Cd if Cd:Zn < 0.015.
- Evidence that malnutrition due to subsistence rice diets was major factor in Cd disease in Japan.
Bioavailability of Cadmium in Biosolids-Fertilized Swiss Chard Fed at 28% of Diet to Guinea Pigs for 80 Days (Chaney et al., 1978)

<table>
<thead>
<tr>
<th>Treatment Rate</th>
<th>Soil Cd t/ha</th>
<th>Soil pH</th>
<th>Chard Cd mg/kg dry</th>
<th>Chard Zn mg/kg dry</th>
<th>Kidney Cd ---mg/kg dry---</th>
<th>Liver Cd ---mg/kg dry---</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0.04</td>
<td>6.0</td>
<td>0.5</td>
<td>70</td>
<td>14.9 a†</td>
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<tr>
<td>Biosolids-1</td>
<td>56</td>
<td>0.32</td>
<td>5.7</td>
<td>1.5</td>
<td>950</td>
<td>14.5 a</td>
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<tr>
<td>Biosolids-2</td>
<td>112</td>
<td>0.94</td>
<td>5.5</td>
<td>2.7</td>
<td>580</td>
<td>14.5 a</td>
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<td>Biosolids-3</td>
<td>224</td>
<td>0.89</td>
<td>6.6</td>
<td>1.4</td>
<td>257</td>
<td>15.8 a</td>
</tr>
</tbody>
</table>

†Means in a column followed by the same letter are not significantly different, P<0.05.
New Feeding Tests To Measure Bioavailability of Grain Cd

- Food sunflower kernels were roasted, ground, and mixed with complete diets at 20% DW; intrinsic Cd = 0.8 µg/g.
- Polished rice was cooked, freeze-dried, and mixed with complete diets at 40% DW; intrinsic Cd = 0.1 µg/g.
- $^{109}$Cd was incorporated during cooking SFK; Cd and $^{109}$Cd during cooking of rice. Diets about 0.4 µg Cd/g DW.
- Diets contained marginal or adequate Fe, Zn, and Ca for growing rats in factorial combinations; normal weight gain for rats on marginal diets confirm mild deficiencies.
- Female rats fed 8 varied diets for 35 days; then fasted and fed 1 g of $^{109}$Cd-labeled diets; then returned to varied diets for 16 more days to follow $^{109}$Cd excretion and absorption.
- Kidney and Liver $^{109}$Cd best measure of Bioavailable Cd.
Effect of Marginal vs. Adequate Zn, Fe, or Ca on Cd absorption to L+K (P.G. Reeves et al.).
History of Plots with Limed Biosolids Which Induced Mn Deficiency

- Limed digested dewatered biosolids from Piscataway, MD, was applied to plots of Galestown sand in 1976; 0, 224, and 448 t/ha applied and corn grown to assess potential nitrate leaching and crop response.
- Corn, soybean wheat rotation post experiment.
- By the late 1980s, symptoms of Mn deficiency were noted by field staff.
- By the early 1990s, severe Mn deficiency in wheat was observed and pot boundaries marked.
- Mn soil and spray treatments were established to characterize how to prevent Mn deficiency problems on such soils amended with low Mn biosolids.
Manganese Deficiency in wheat growing on Evesboro loamy sand amended 17 years earlier with 225 t/ha of limed digested sludge.
Spray application of fluid biosolids on tall fescue pastures at Beltsville, MD, 1976, in cooperation with WSSC, UMD and USDA; Decker et al. (1980).
Rotation paddocks and Angus cattle grazing control or surface applied fluid biosolids treatments; Beltsville, MD 1977; Decker et al. (1980)
Surface organic layer (thatch) on orchardgrass pasture which received fluid Biosolids applications for 28 years without tillage; Hagerstown, MD, 1975.
Corrected Limits for Biosolids-Applied PCBs if PCBs had been included in the Final 503 Rule:

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Limit</th>
<th>Units</th>
</tr>
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<tbody>
<tr>
<td>2 Garden Foods</td>
<td>17.</td>
<td>mg/kg soil maximum</td>
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<tr>
<td></td>
<td>2.3</td>
<td>kg/ha•yr</td>
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<tr>
<td>3 Soil Ingestion</td>
<td>14.</td>
<td>mg/kg Biosolids</td>
</tr>
<tr>
<td>4 Livestock Feed</td>
<td>18.</td>
<td>mg/kg soil maximum</td>
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<tr>
<td></td>
<td>2.4</td>
<td>kg/ha•yr</td>
</tr>
<tr>
<td>5 Grazing Livestock</td>
<td>2.1</td>
<td>mg/kg Biosolids (surface)</td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>kg/ha•yr (annual incorp)</td>
</tr>
<tr>
<td>10 Predator Wildlife</td>
<td>4.0</td>
<td>mg/kg soil maximum</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
<td>kg/ha•yr</td>
</tr>
</tbody>
</table>
PCB Risk Models Apply to PPCPs

- Lipophilic compounds can be accumulated in biosolids at measurable concentrations.
- Other hydrophilic compounds in effluent.
- Detergents retained in anaerobic digesters are rapidly biodegraded in soils or aerobic systems.
- Apply 503 risk assessment methods show that direct ingestion of biosolids is the most sensitive pathway for risk.
- Plant uptake is minor to irrelevant.
- Lipophilic compounds bound to biosolids humics.
- Aged PPCPs bound to OM lower uptake.
- No evidence of risk as levels in crops/worst case.
THE SAFE SLUDGE MATRIX

Guidelines for the Application of Sewage Sludge to Agricultural Land
Summary

- Industrial Pretreatment improved biosolids.
- 503 Regulation protects humans and environment from contaminants in biosolids.
- Sorbents in biosolids (Fe, Mn, Al oxides) persistently increase metal and P binding by soil.
- Natural Soil-Plant Barrier protects consumers.
- Biosolids provide valuable fertilizers and soil conditioning of amended soils.
- Biosolids remarkably valuable for remediation of mine sites, etc., and Pb in urban soils.
- Injection/Incorporation is best practice.
- Need to correct problems from before 503.
• PPCP causing alarm in some environmentalists
  — But levels in biosolids low.
  — Either strongly adsorbed by biosolids or in effluent.
  — Uptake to edible crop tissues miniscule.
• EPA’s focus on As gives soil As limits lower than background levels in US soils!
  — Seeking 17-fold lower MCLG for DW.
  — But DW gets practical MCLs.
  — Old soil limit was 0.43 mg/kg; new = 0.025 mg/kg.
  — Normal levels in US soils: 5th to 95th = 2-12 mg/kg.
• CA focus on chromate cancer risk is extreme.
  — Chromate is reduced in stomach to chromic.
  — NTP uses “Maximum Tolerated Dose in testing