RECENT RESEARCH ON HERBICIDE PERSISTENCE IN COMPOSTS

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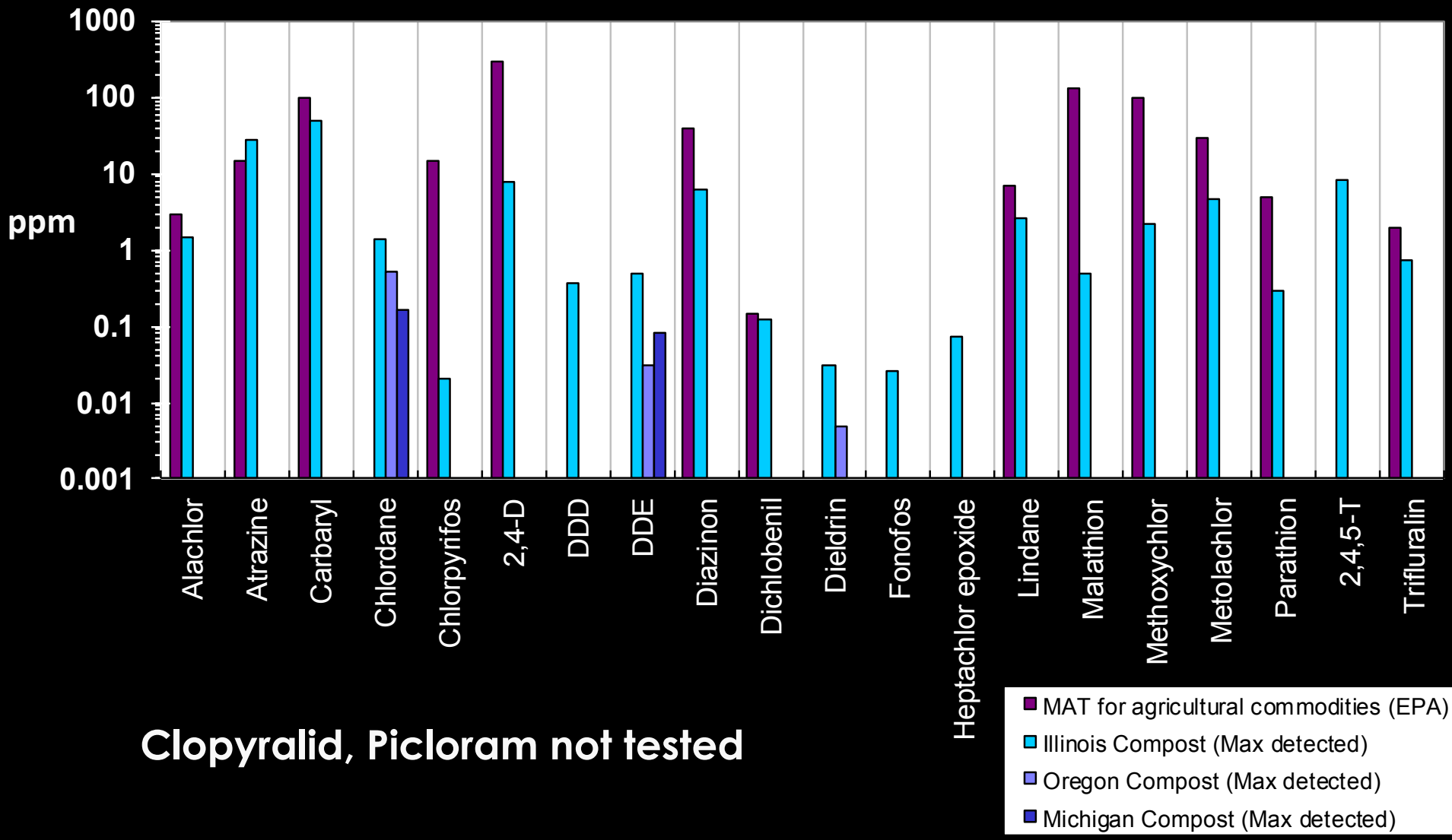
Introduction

- Recalcitrant herbicides and their potency
- Biodegradation during composting
- Plant bioassay development
- Analysis of Vermont composts
- Research Needs



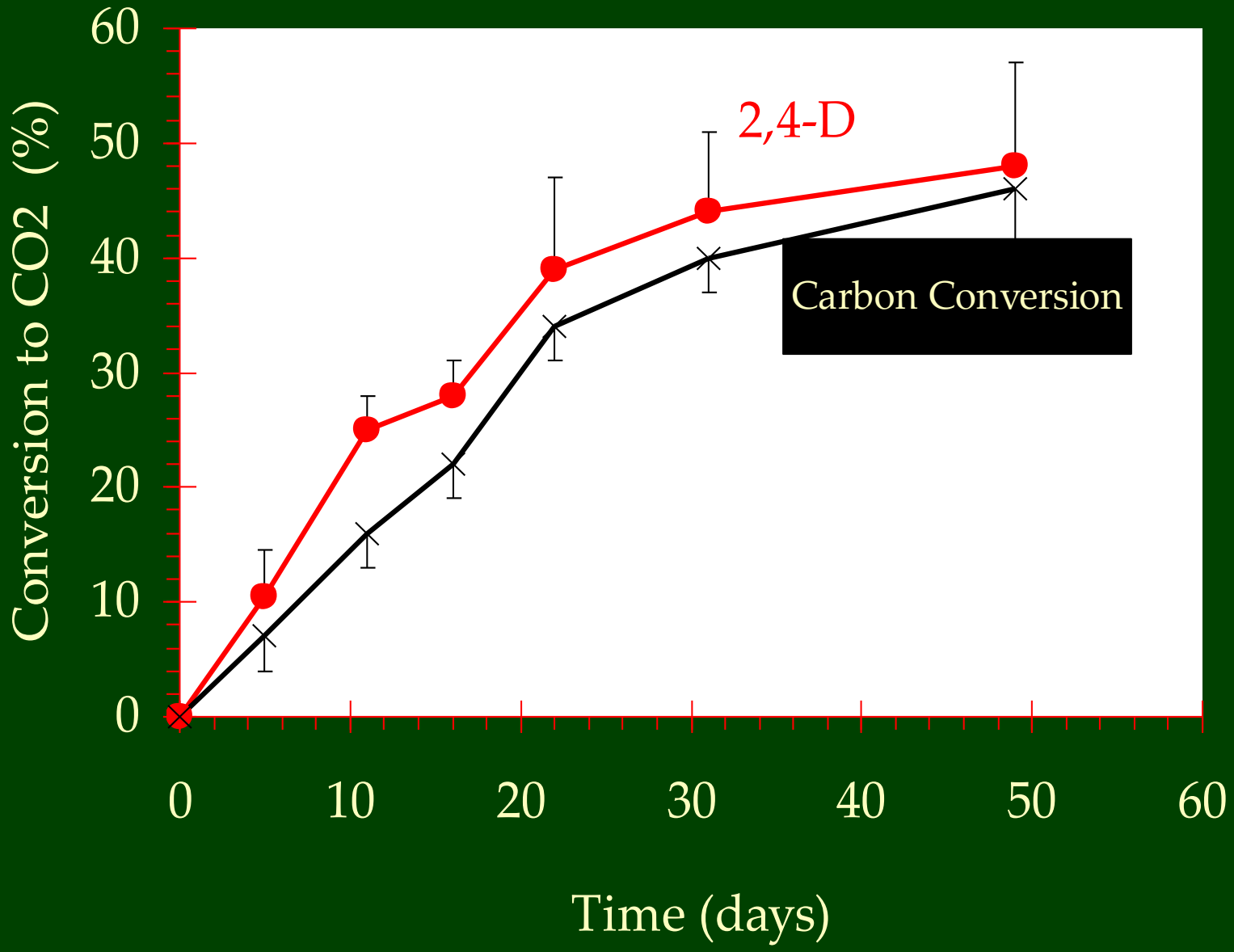

ORTHO

Maximum Concentrations of Pesticides Found in Composts in Illinois, Michigan and Oregon (1991)

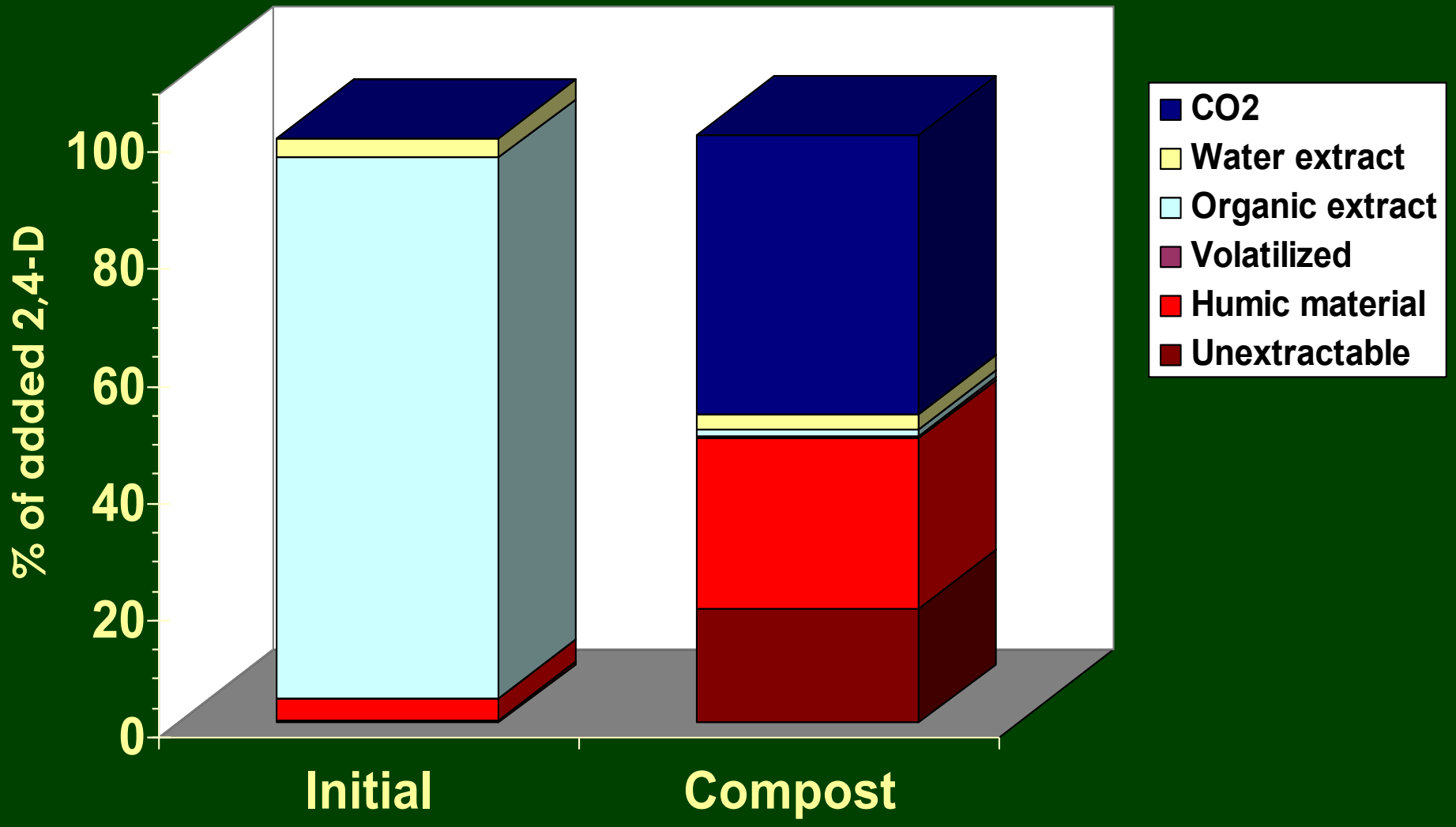


Clopyralid, Picloram not tested

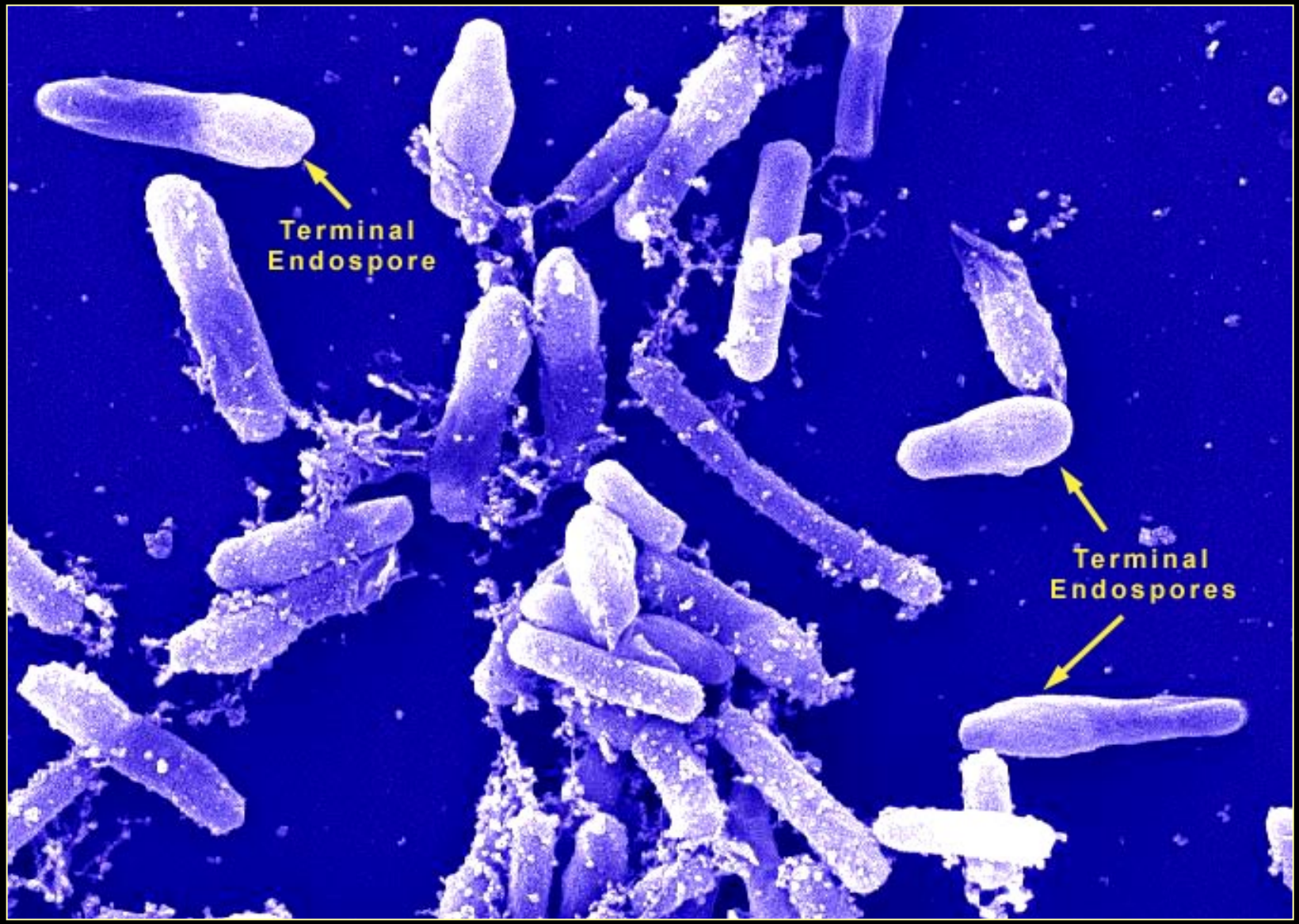
Pesticide mineralization during composting



^{14}C 2,4-D


% of added 2,4-D
100
80
60
40
20
0
Initial
Compost
CO2
Water extract
Organic extract
Volatilized
Humic material
Unextractable

Thermophilic 2,4-D degrading Bacillus isolated from Compost



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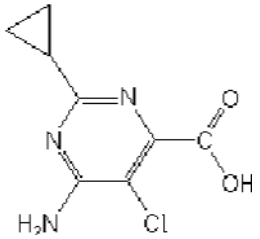
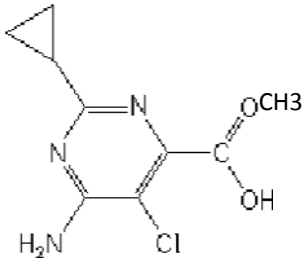
Pyrimidine/Pyridine Carboxylic Acid Herbicides

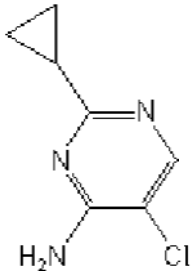
Aminocyclopyrachlor
(IMPRELIS)



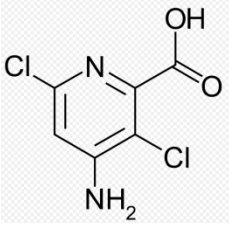
DPX -MAT28
Aminocyclopyrachlor
6-amino-5-chloro-2-Cyclopropyl pyrimidine 4-carboxylic acid



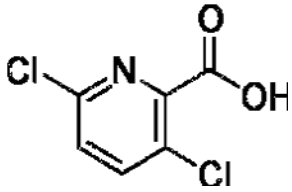
DPX -KJM44
Aminocyclopyrachlormethyl
6-amino-5-chloro-2-Cyclopropyl pyrimidine 4-carboxylic ac id methyl ester



IN -LXT69
Inactive Metabolite
6-amino-5-chloro-2-Cyclopropyl pyrimidine



Aminopyralid
1-amino 3,6-dichloro 2-Pyridine carboxylic acid

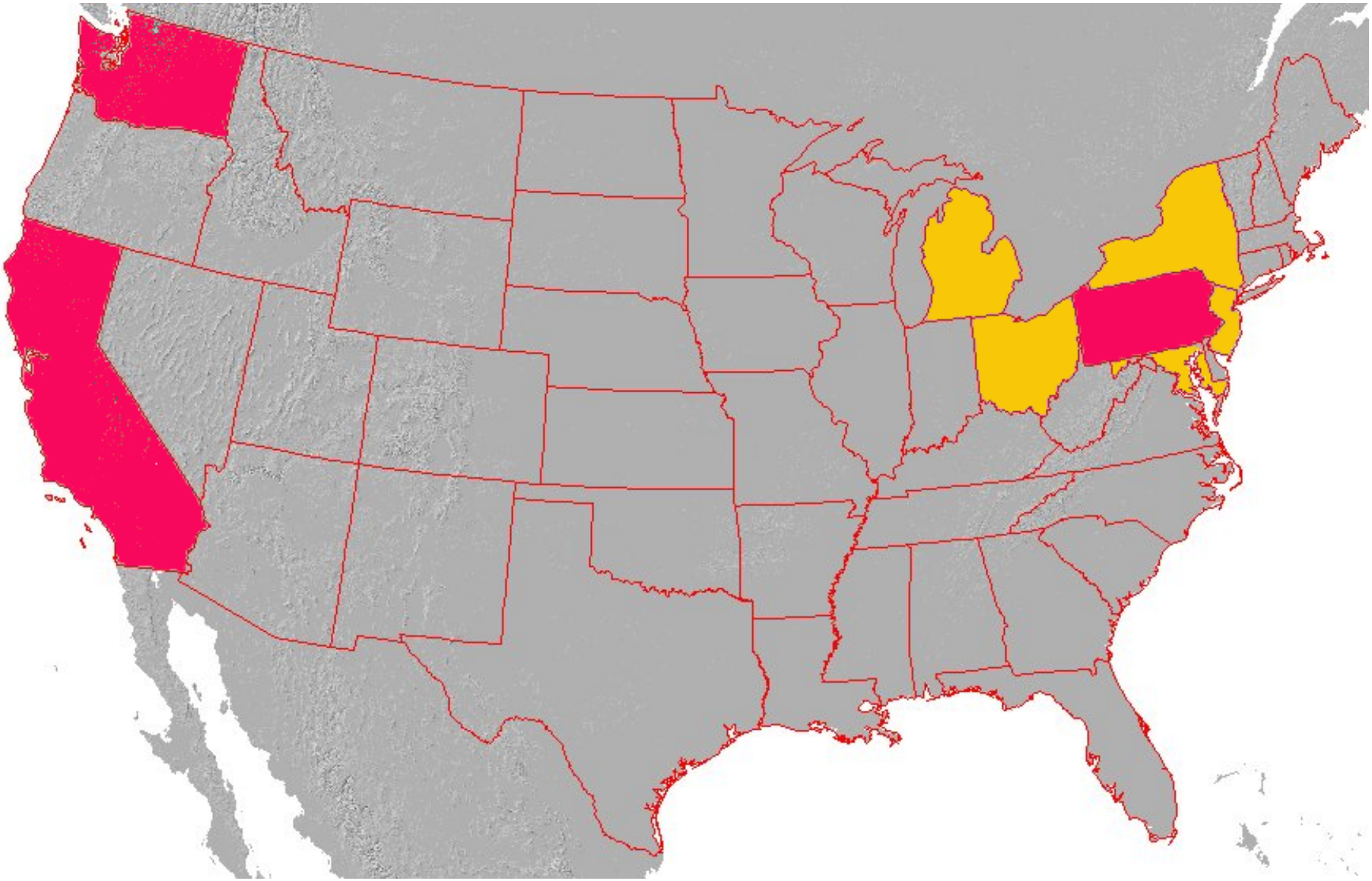


Clopyralid
3,6-dichloro-2-Pyridine carboxylic acid

Pyrimidine/Pyridine Carboxylic Acids

- Clopyralid, Aminopyralid, Aminocyclopyrachlor, Picloram
- Active ingredients in over 30 herbicides (Confront, Curtail and Stinger, Banish, Forefront, Halcyon, Pharaoh, Pro-Banish, Runway, Synero and Upfront, Imprelis).
- Highly effective at low dosages with very low human toxicity.
- Used to control annual and perennial weeds in crop production and turf as well as invasive weeds in natural areas and pasture.
- Effective against Creeping Thistle, Creeping Charlie and other noxious, difficult to control perennial broadleaf weeds.
- Persistence and potency means fewer applications.
- Compost feed stocks such as turf, manure, dead trees and hay may can contain residual amounts of these herbicides.

Clopyralid detections in Composts at phytotoxic levels (11/2002)



Clopyralid

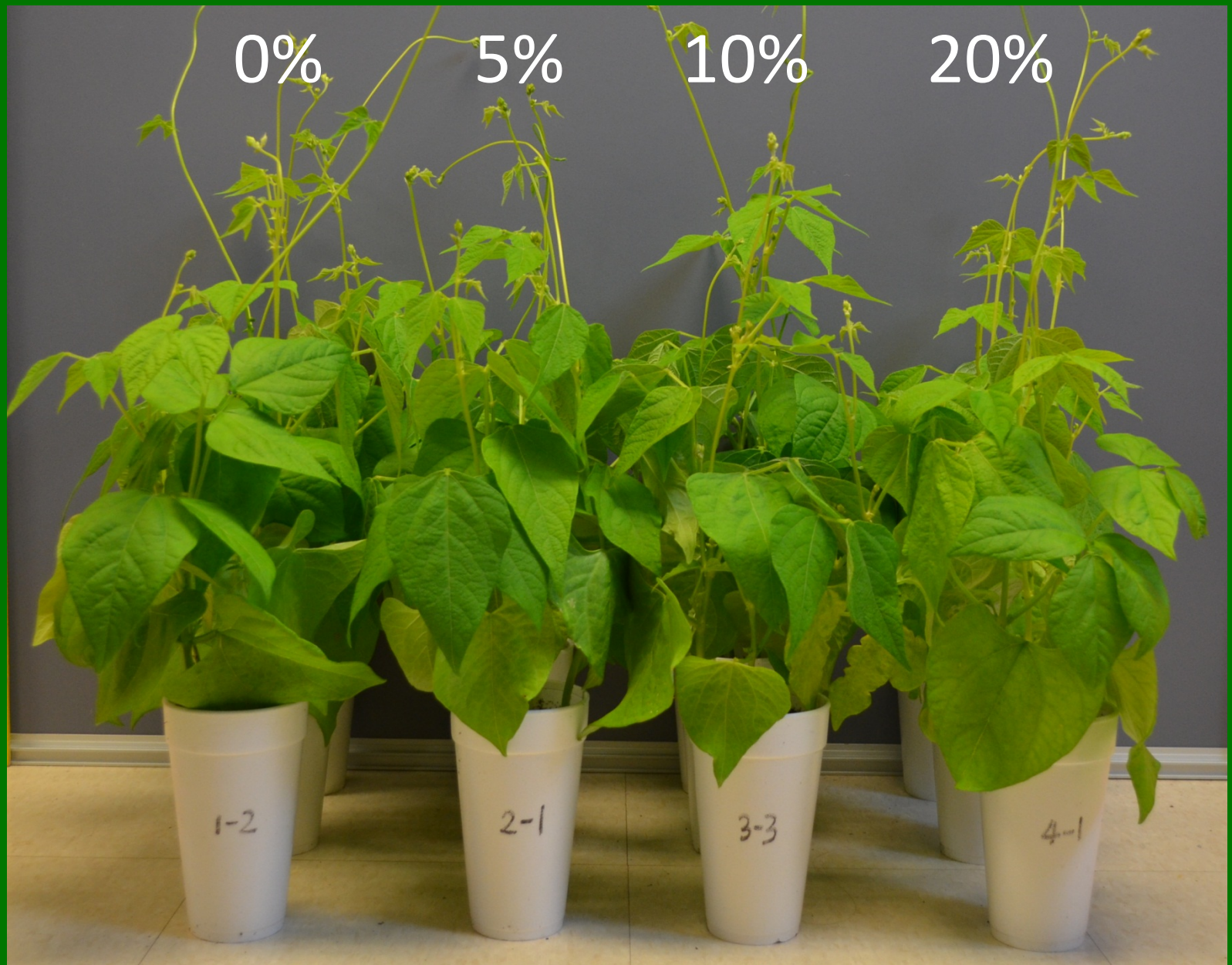
- Concentration in grass clippings the day of application is 54,000 ppb (sprayable formulation) to 16,000 ppb (granular formulation).
- Half life in soil up to 250 days.
- After 10 weeks, clopyralid averages 150 ppb in turf.
- Concentrations of $\leq$ 20 ppb can affect sensitive plants.
- Tomato, sunflower, potato, peas most susceptible
- Symptoms include leaf cupping, loss of apical dominance, prevention of fruit set.

Aminocyclopyrachlor (Imprelis) related damage to conifers in 2011

Herbicide Potency

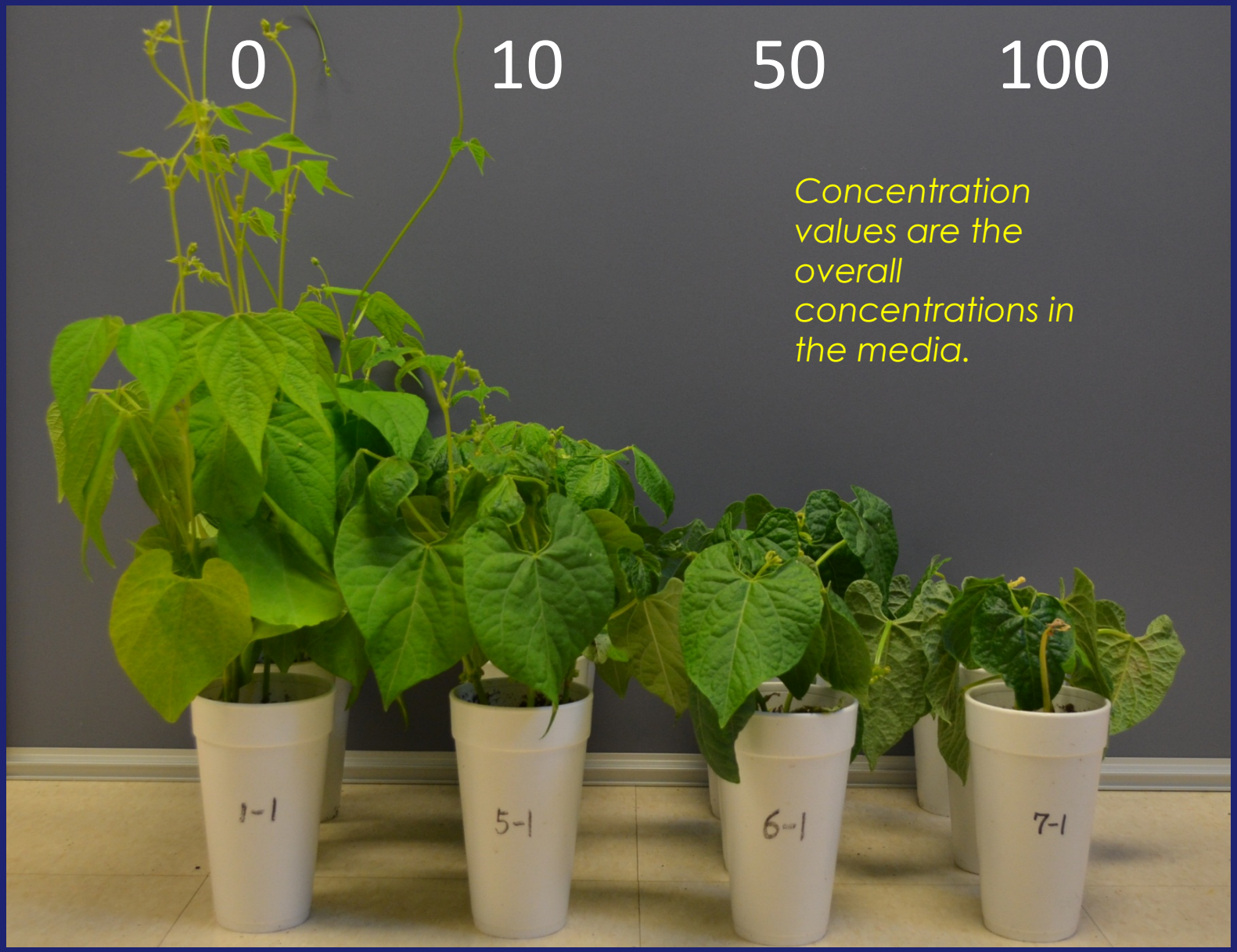
- Composts incorporated into potting media at 4 to 20%
  - Dairy manure compost, Yard trimmings compost
- Herbicides added to media **as liquid**
- Concentrations used (ug/kg in growth media dw basis)
  - Aminopyralid at 0, 10, 50, 100 ppb
  - Clopyralid at 0, 5, 25, 50 ppb
  - Trifluralin at 0, 100, 200, 1000 ppb
  - Imprelis at 0, 10, 50, 100 ppb
- Bean sown into media.
- Germination and plant growth assessed for 35 days.

Yard Trimmings Compost

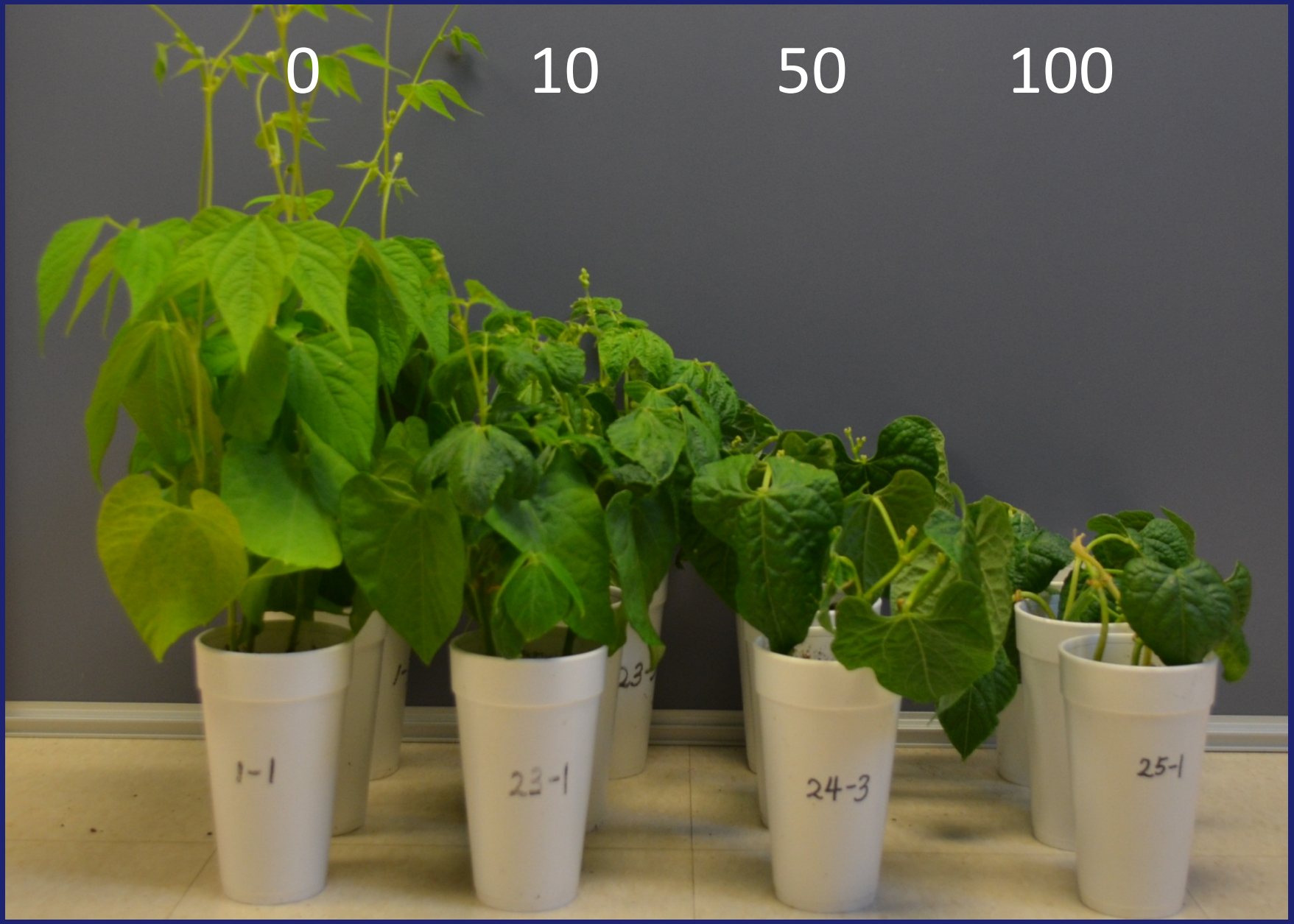


Dairy Manure Compost

Aminopyralid in YT (ppb db)



Aminopyralid in DM (ppb db)

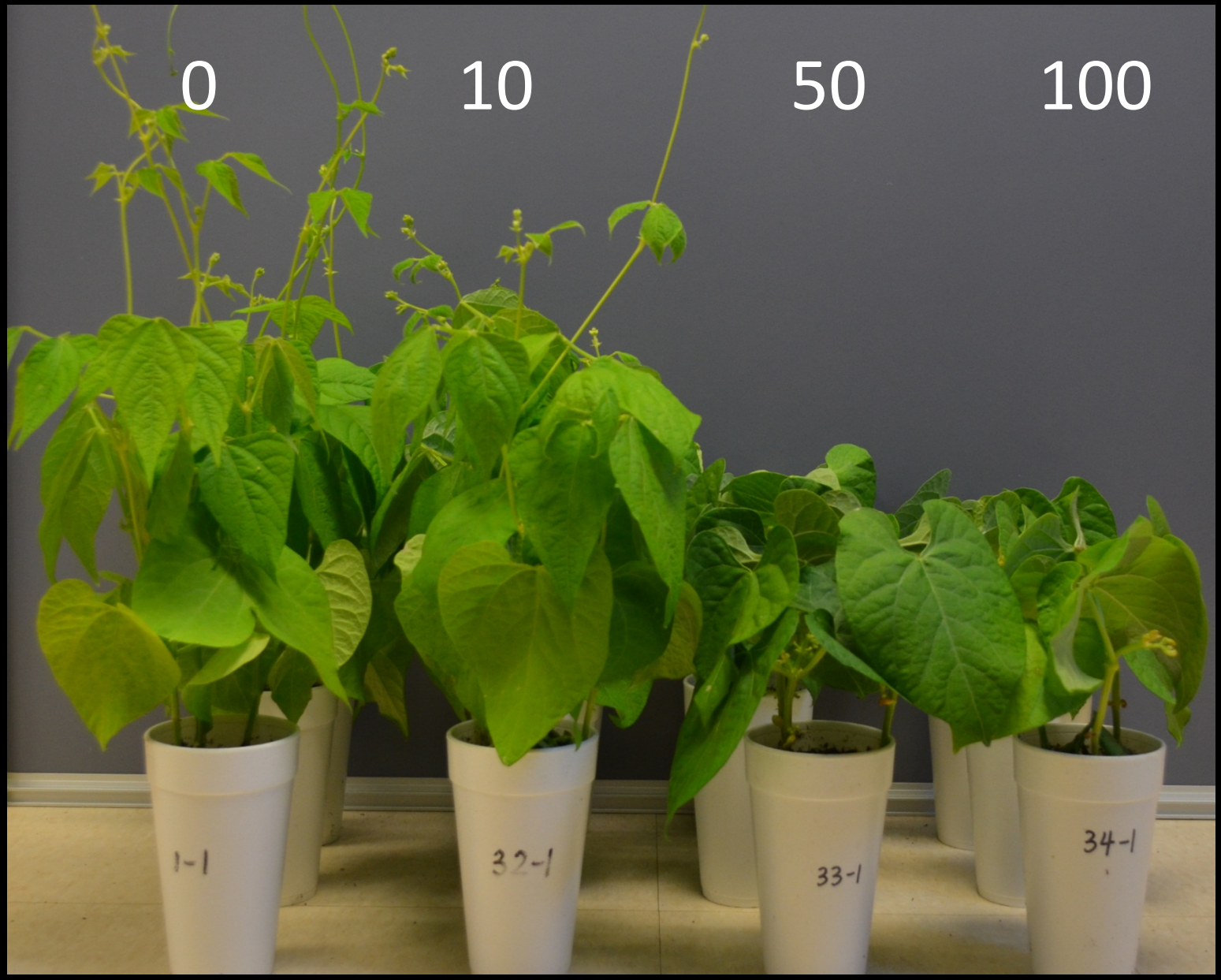


Clopyralid in YT (ppb dw)

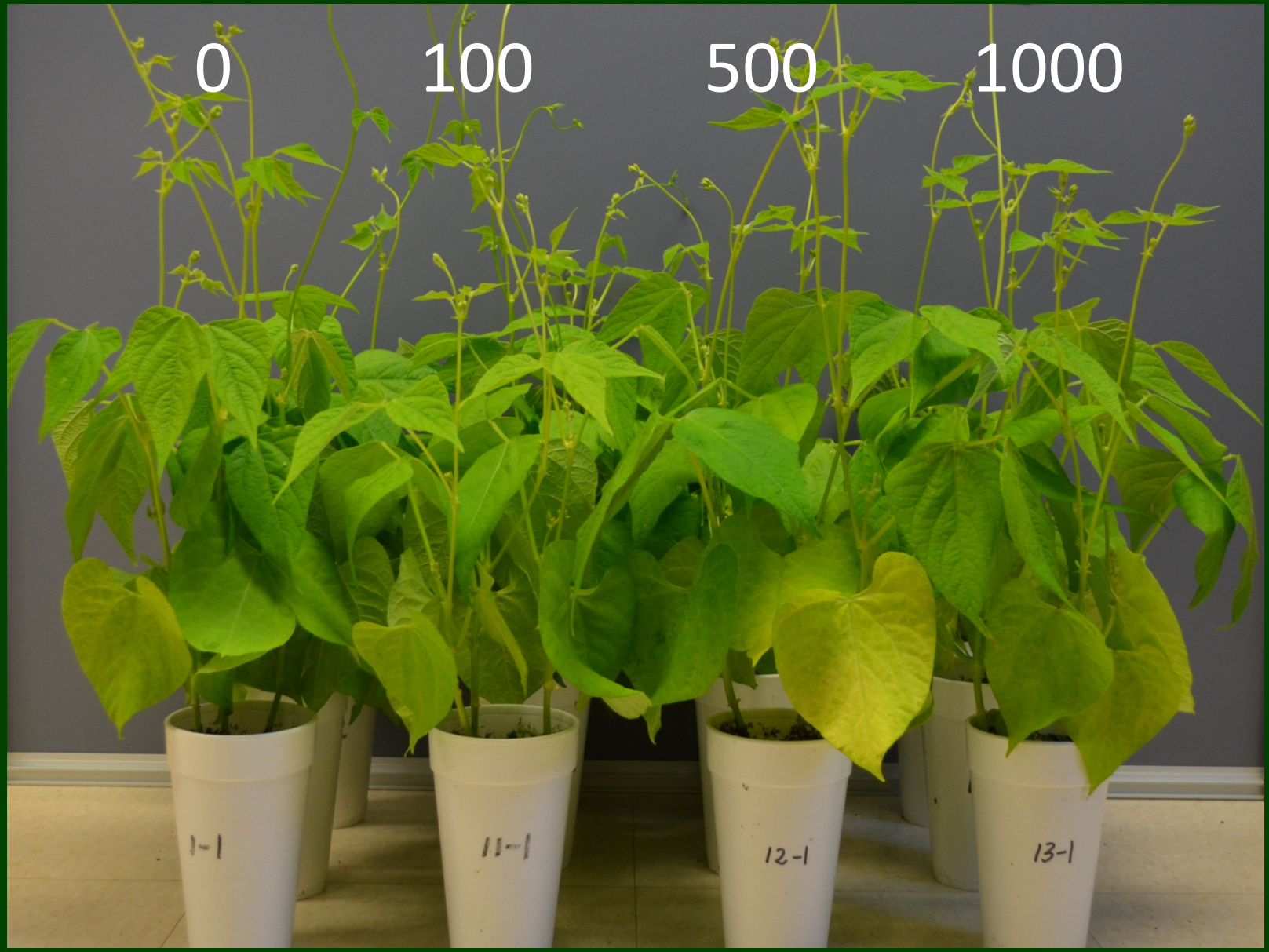
Clopyralid in DM (ppb dw)

Imprelis in YT (ppb dw)

Imprelis in DM (ppb dw)



Trifluralin in YT (ppb)



Trifluralin in DM (ppb)

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Methods

- Grass field plots established that received one of four treatments:
  - Untreated (UT)
  - Granular mixture of free acid and methyl ester of aminocyclopyrachlor (GH)
  - Liquid application of aminocyclopyrachlor mixture (LH)
  - Liquid application of Clopyralid (CH).

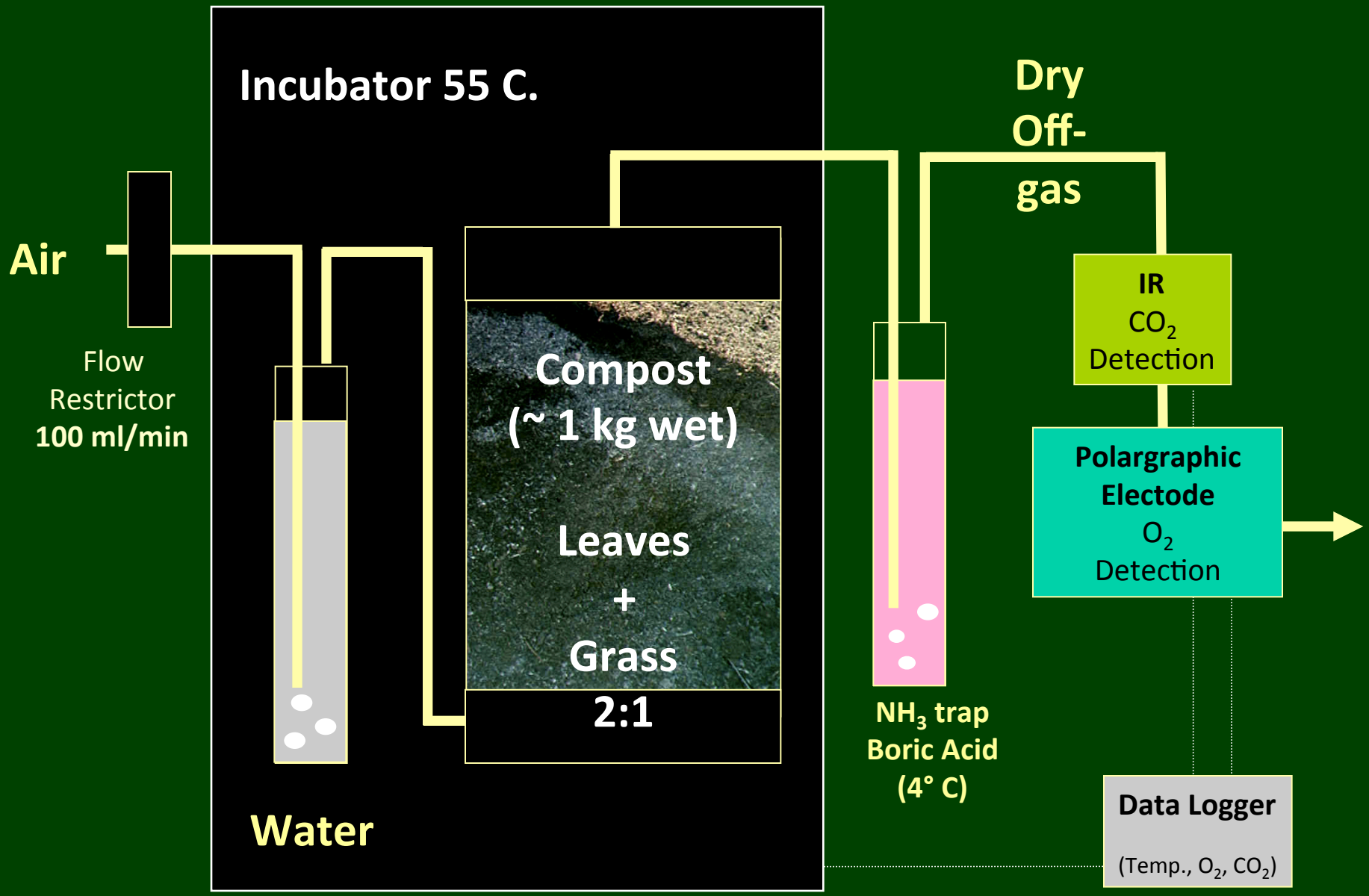
- Herbicides applied as directed
  - Granular aminocyclopyrachlor: 84 g AI/hectare irrigated into the turfgrass within 24 hours.
  - Liquid aminocyclopyrachlor: 84 g AI g per hectare
  - Clopyralid: 209 g AI/ha.

- Clippings collected to allow for maximum absorption into the grass
  - after 7 days for the granular application
  - after 1 day for the liquid applications

- Grass amended with leaves at a 2:1 mix ratio and composted 180 days in lab scale system.

- Compost samples removed and extracted with three solvents, purified and analyzed by high-performance liquid chromatography tandem mass spectrometry (HPLC/MS/MS). Limit of quantitation = 10 ng/g (parts per billion).

Composting Reactor System



Bioreactor vessels for composting simulation

Bioreactor System

Bioreactor Vessels

Bioreactor incubator

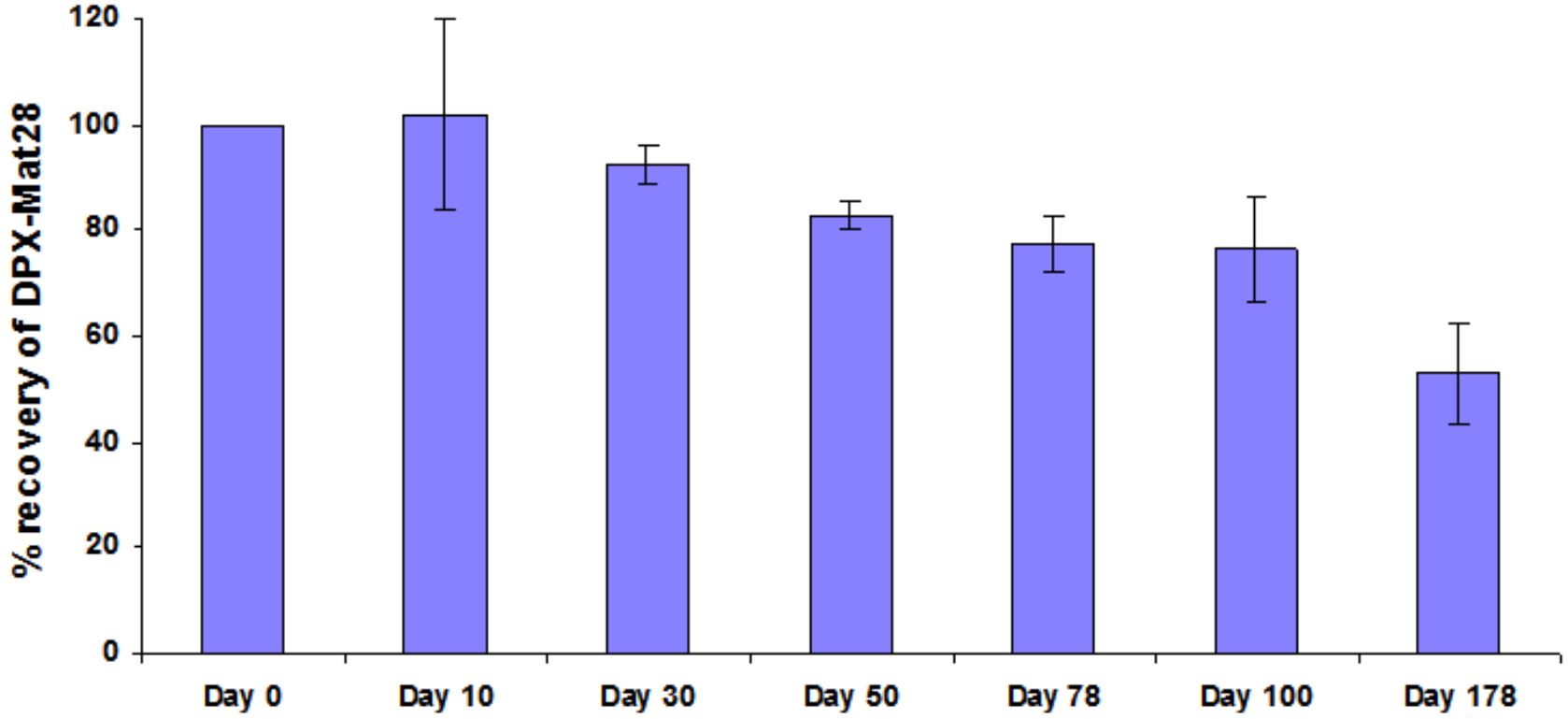
CO_2, O_2 and temperature measurement, calibration and data acquisition.

Flow restrictor system
(air 100 ±3 ml/min)

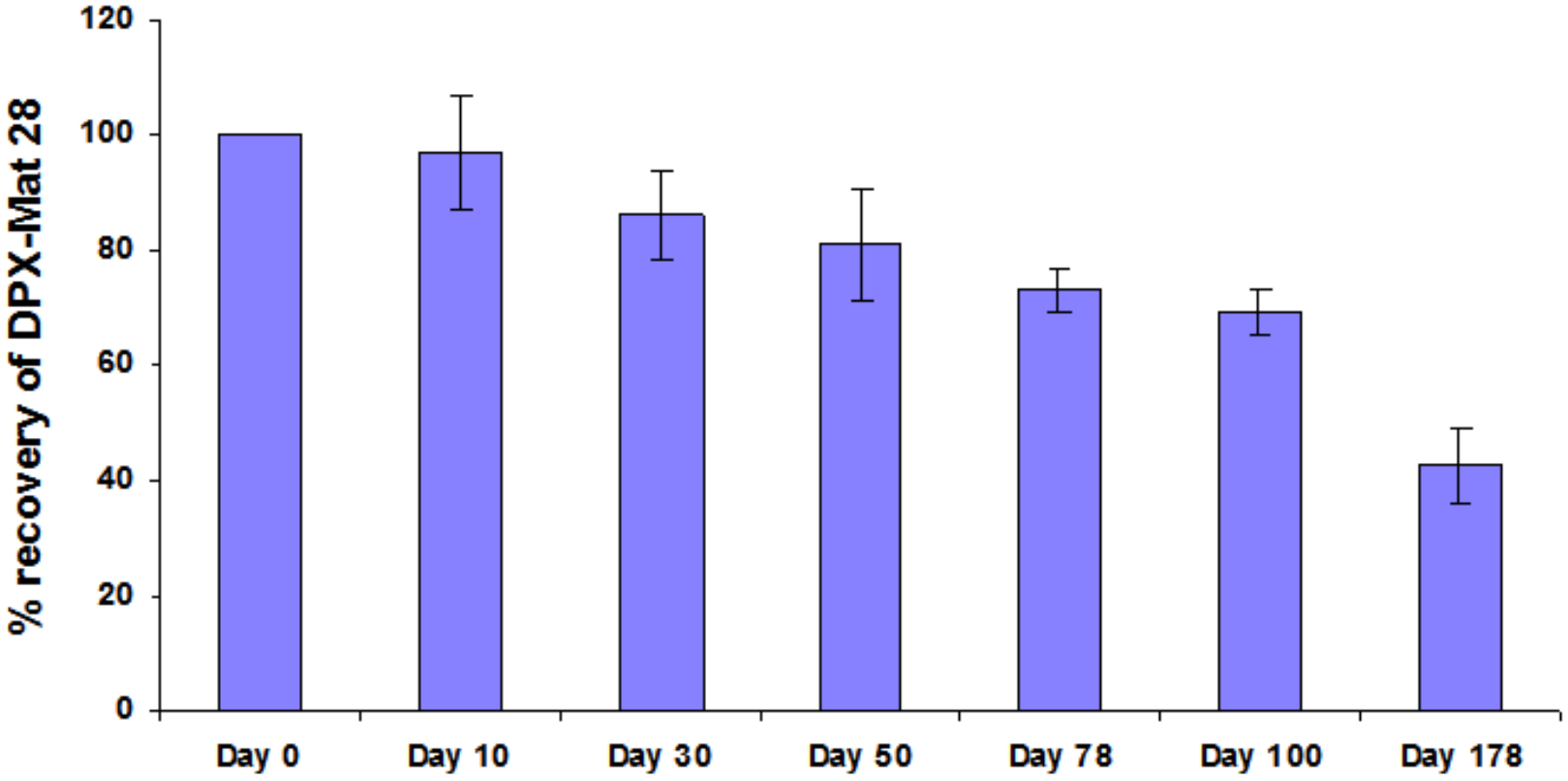
Water condensor and
ammonia trap (9° C.)

Data collection computer

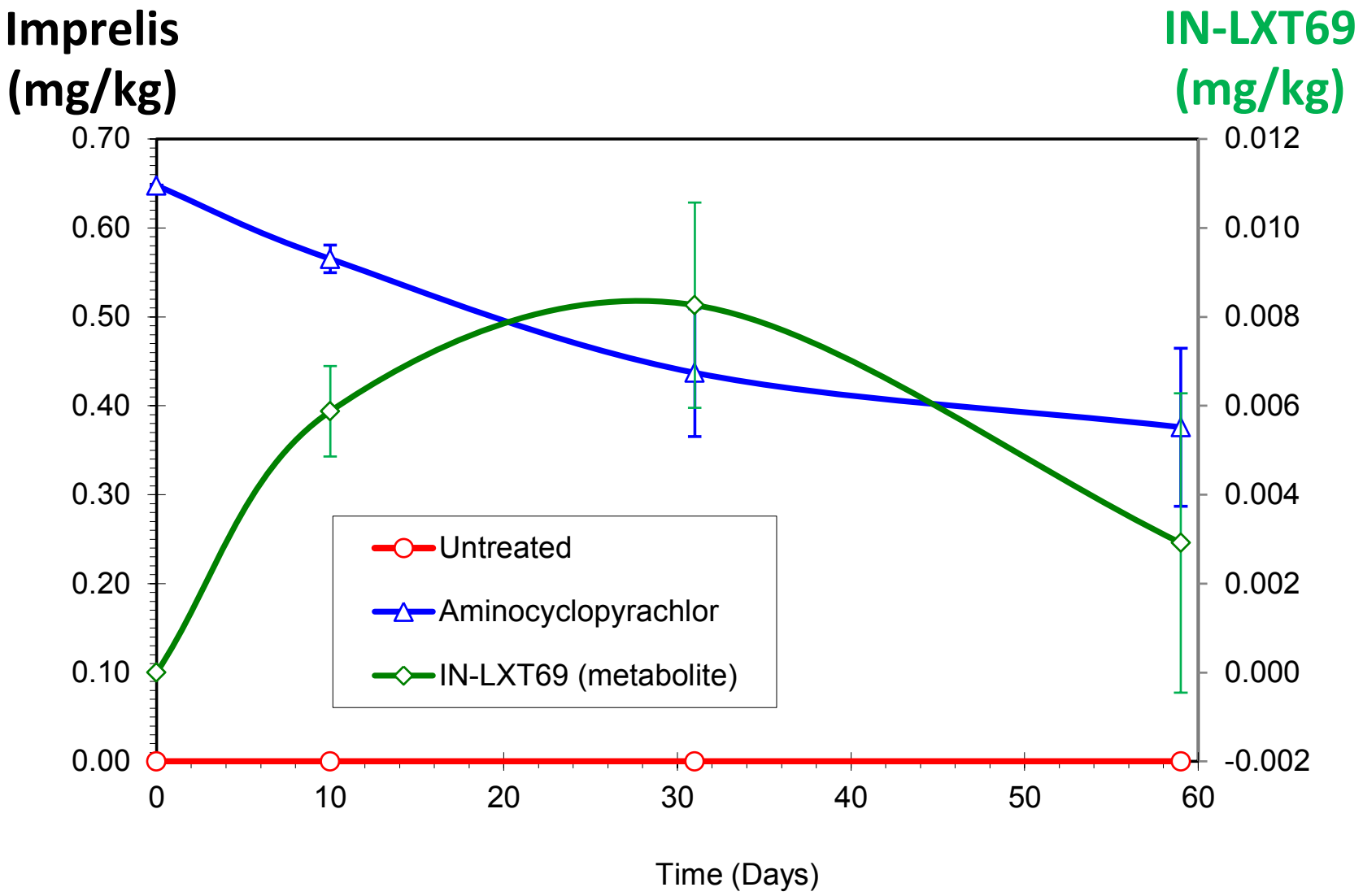
Recovery of Aminocyclopyrachlor during composting (Granular formulation DPX-MAT 28)



Recovery of Aminocyclopyrachlor during composting (Liquid formulation DPX-MAT 28)



Aminocyclopyrachlor Metabolite formation during Composting



Recovery of Clopyralid during composting

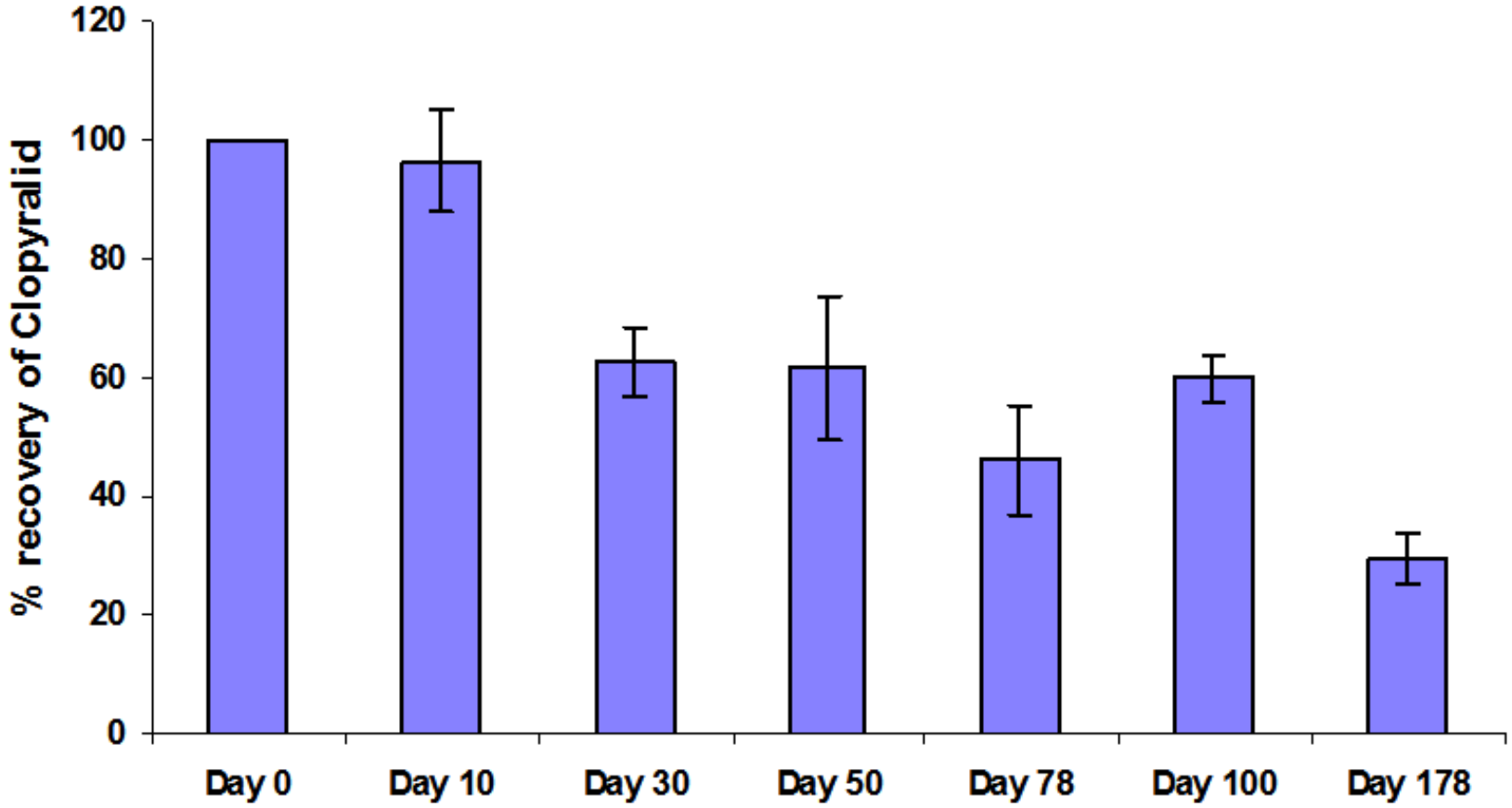
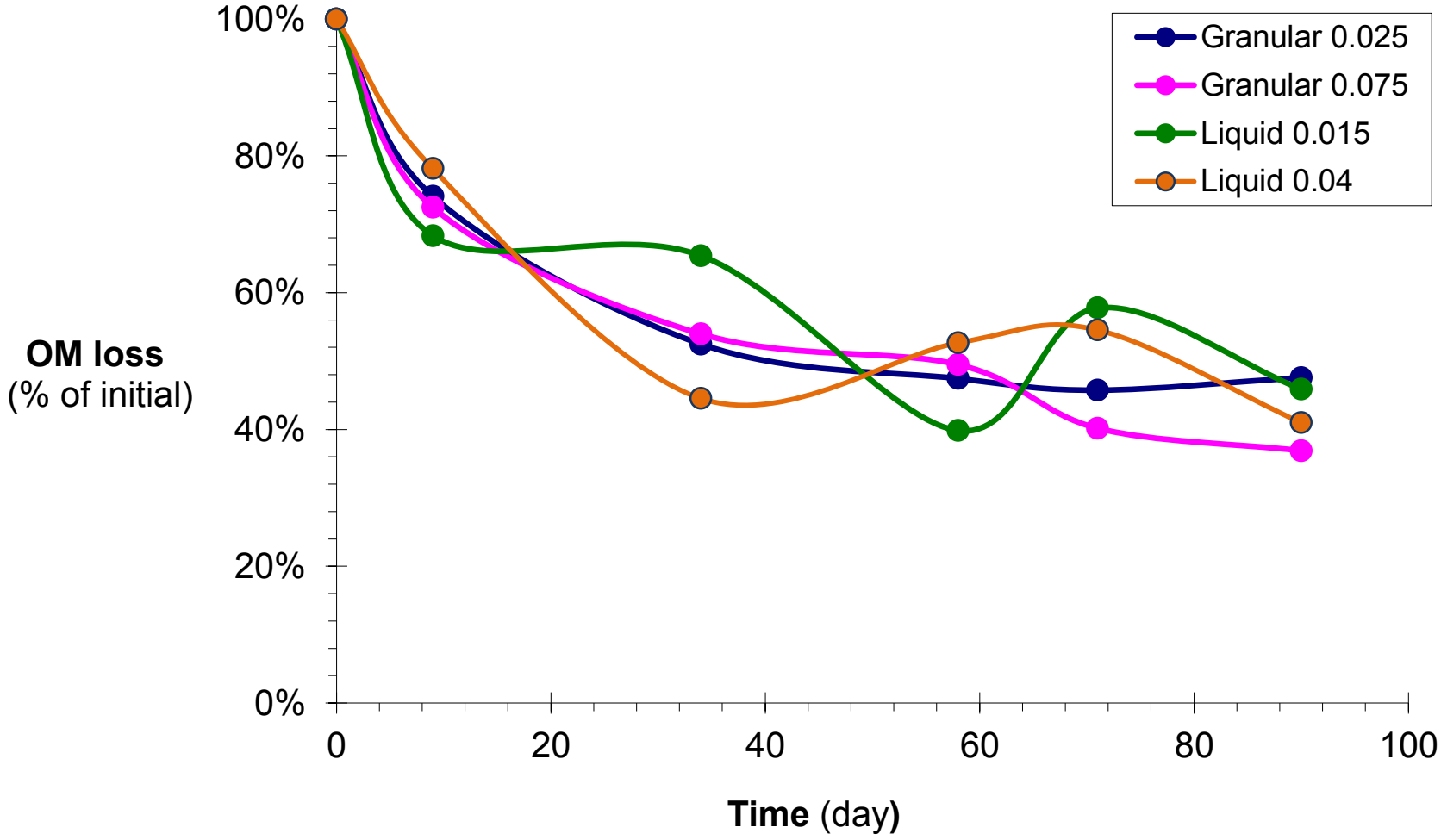


Table 3. Concentrations of aminocyclopyrachlor (DPX-MAT 28) and clopyralid in compost mixes on wet, dry and ash basis.

	Treatments (Values are mg/kg)									
Sample day	Untreated	Granular Herbicide			Liquid Herbicide			Clopyralid		
	wet	wet	dry	ash	wet	dry	ash	wet	dry	ash
Day 0	NT	1.5±0.3	5.2±1.0	37.5 ±8.1	3.8±0.4	13.4±1.2	85.2 ±15.1	34±4	112±14	661 ±54
Day 1 0	NT	2.0±0.4	6.9±1.5	37.8 ±7.7	4.7±0.9	17.1±2.5	82.9 ±19.0	44±5	142±20	637 ±60
Day 30	NT	2.9±0.5	6.9±1.6	34.6 ±8.0	6.5±1.4	16.7±2.2	73.8 ±17.8	47±1	99±2	413 ±13
Day 50	NT	3.0±0.5	6.5±1.6	31.2 ±7.8	6.7±1.4	17.2±2.9	69.7 ±18.5	53±4	104±12	403 ±51
Day 78	<0.01	3.5±0.5	6.3±1.5	28.9 ±6.2	6.6±1.6	16.1±2.0	62.8 ±14.3	49±4	81±16	305 ±56
Day 100	<0.01	2.8±0.5	6.5±1.6	28.7 ±7.5	6.6±1.2	15.3±2.1	59.4 ±13.8	50±4	109±15	395 ±34
Day 178	NT	2.5±0.7	4.8±1.6	20.0 ±6.2	6.9±1.2	10.7±2.2	37.0 ±12.1	31±2	57±3	194 ±16
% Loss		+67%	-8%	-47%	+82%	-20%	-57%	-9%	-49%	-71%

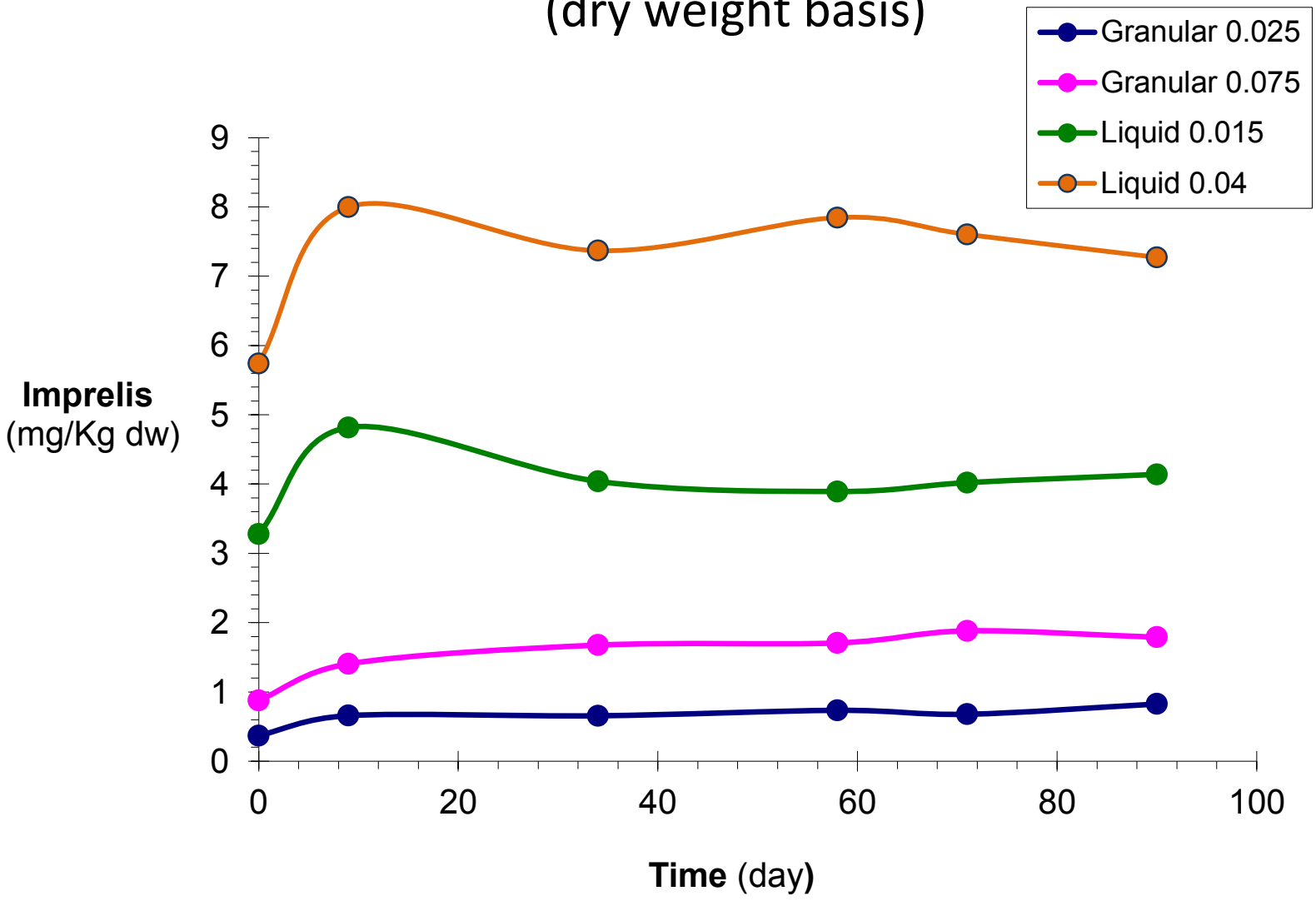
Values are averages of triplicate reactors ± standard deviation. NT = Not tested

Organic Matter Loss



Aminocyclopyrachlor Concentration during composting

(dry weight basis)



Are the composts made from herbicide treated grass phytotoxic?

Methods

- Composts made from herbicide treated grass incorporated into potting media at 4, 10 and 20%
- Cucumber, Tomato and Bean sown into media.
- Plant growth assessed for 35 days.

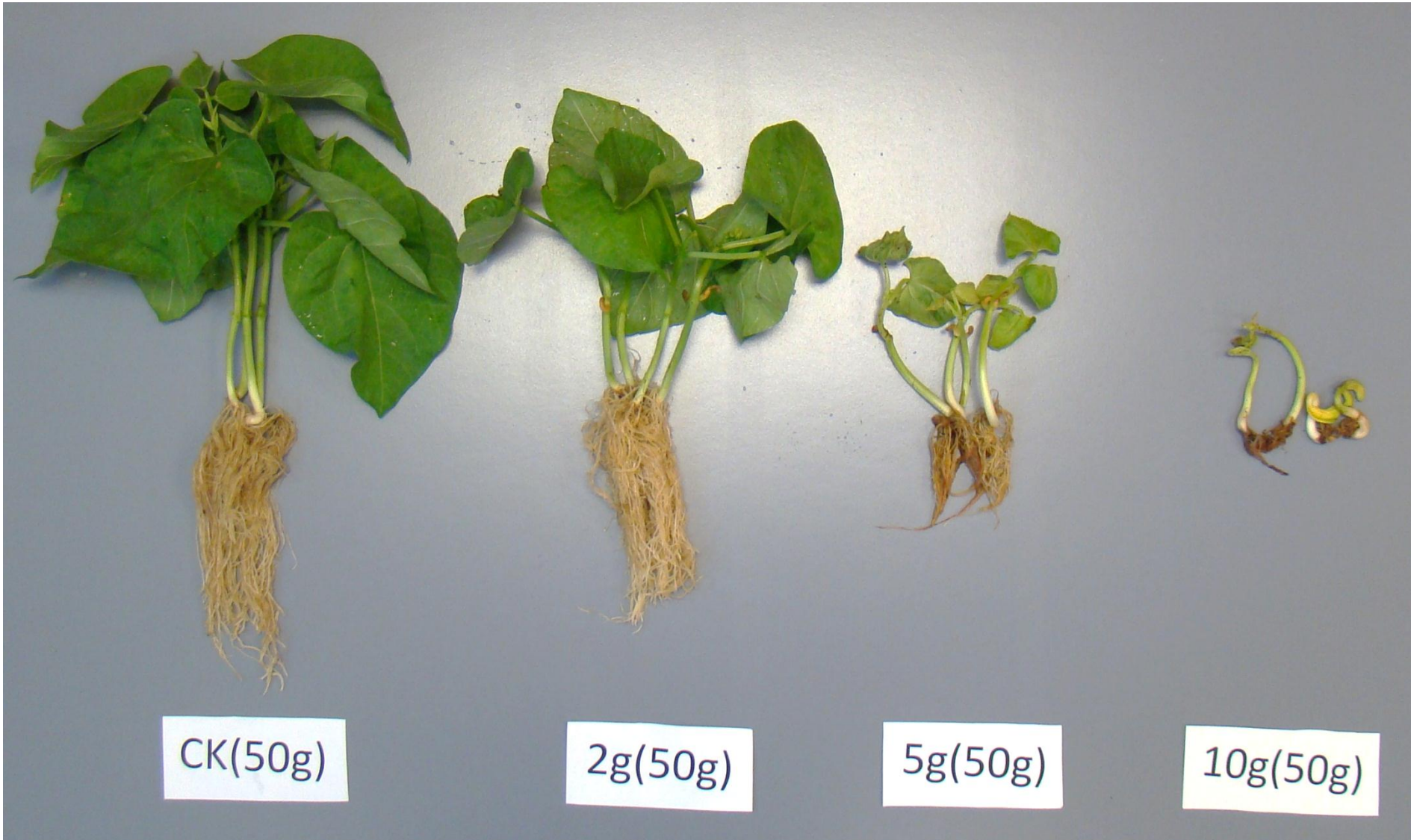


Triplicate pots

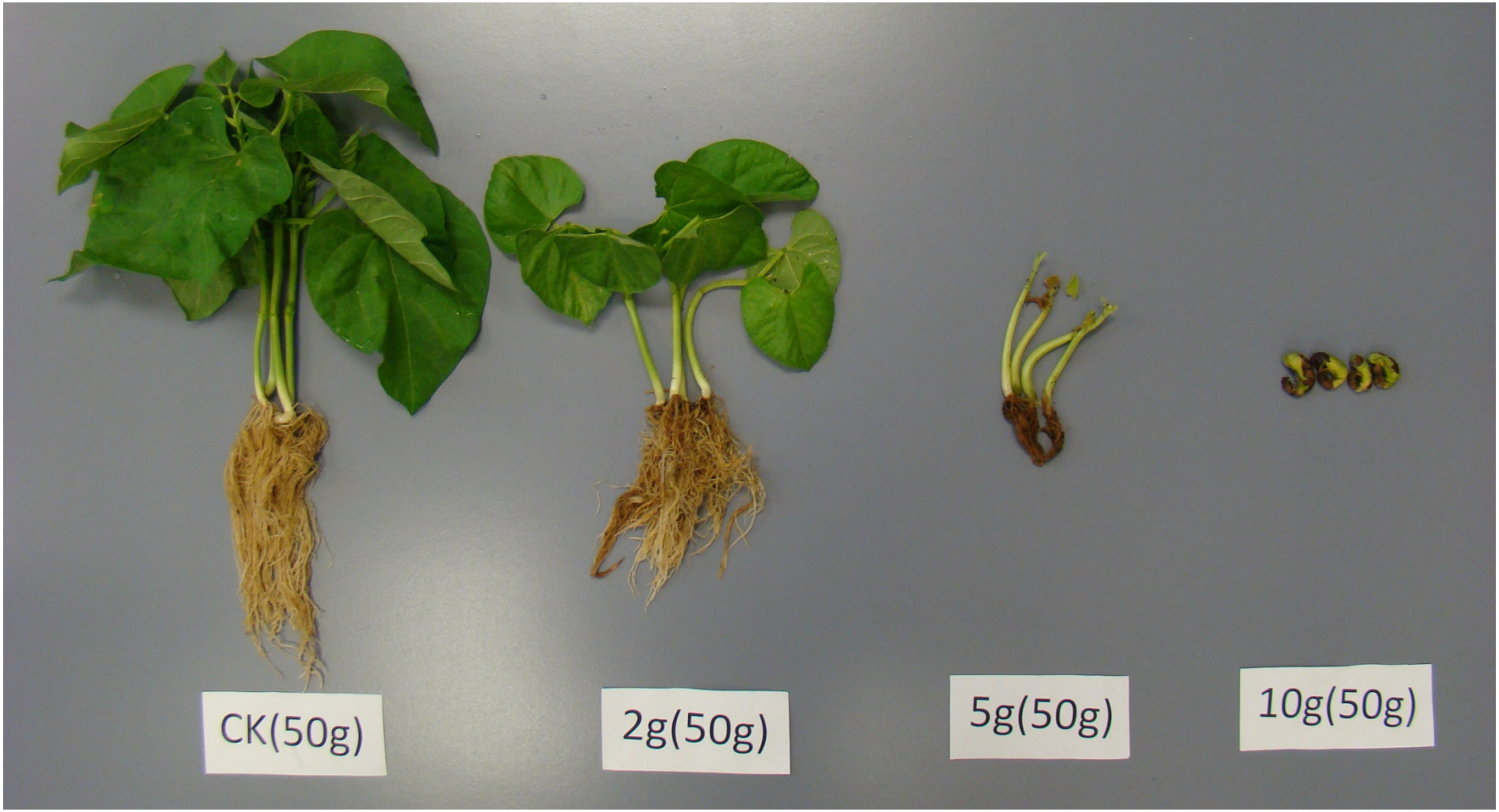
Day 35 Bean Plant

Untreated Compost

Beans planted in growth media containing compost made from grass treated with Aminocyclopyrachlor



Day 35 Bean Plant



Liquid Aminocyclopyrachlor Compost

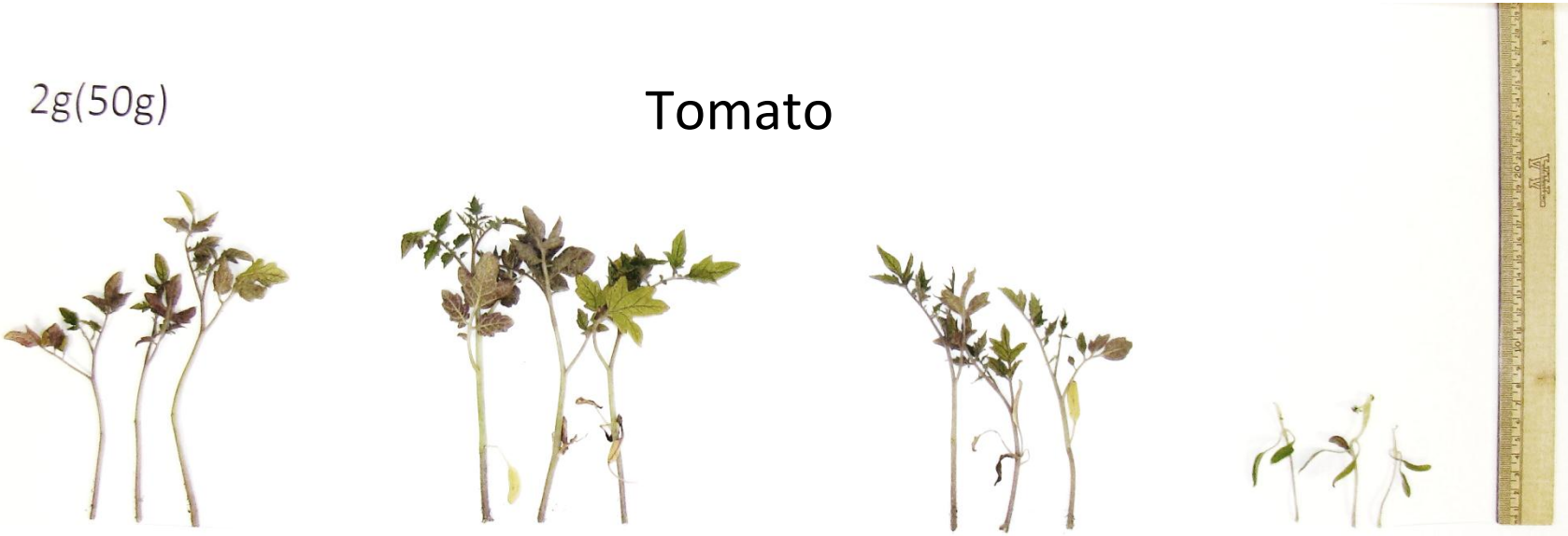
Day 35 Bean Plant

Clopyralid Compost

Day 35 (4% potting mix)

2g(50g)

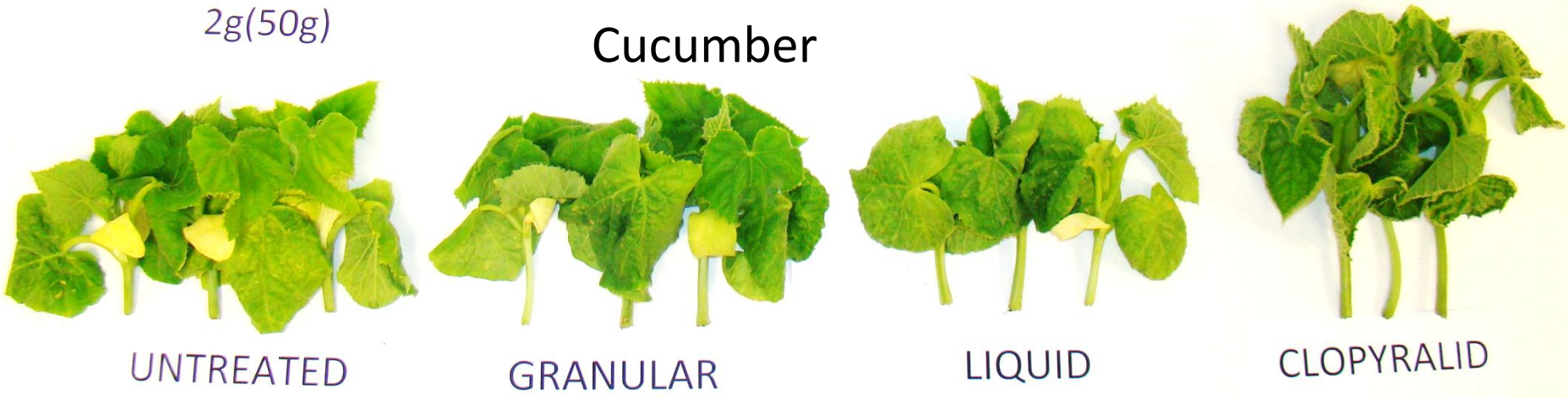
Tomato



UNTREATED GRANULAR LIQUID CLOPYRALID

2g(50g)

Cucumber

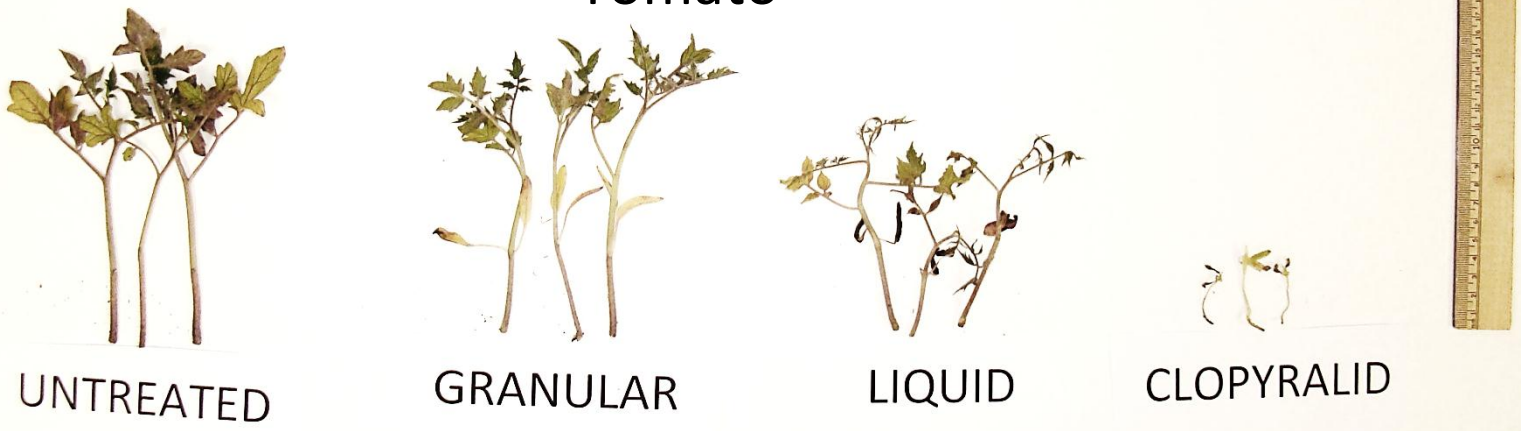


UNTREATED GRANULAR LIQUID CLOPYRALID

Day 35 (10% potting mix)

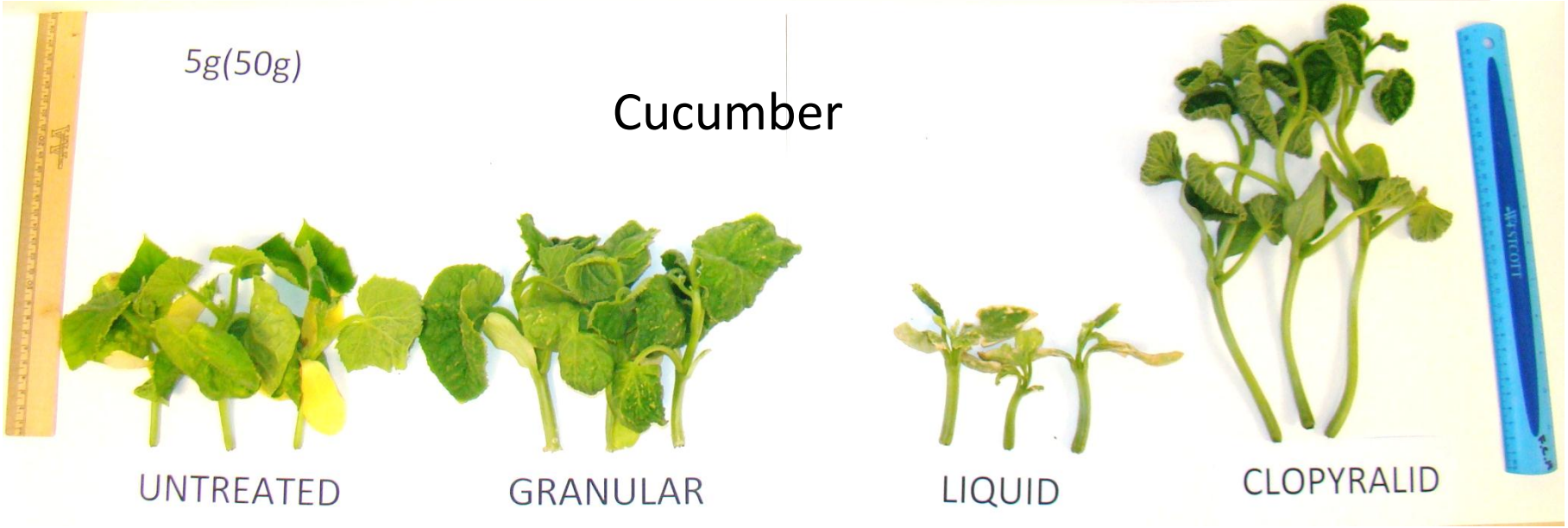
5g(50g)

Tomato

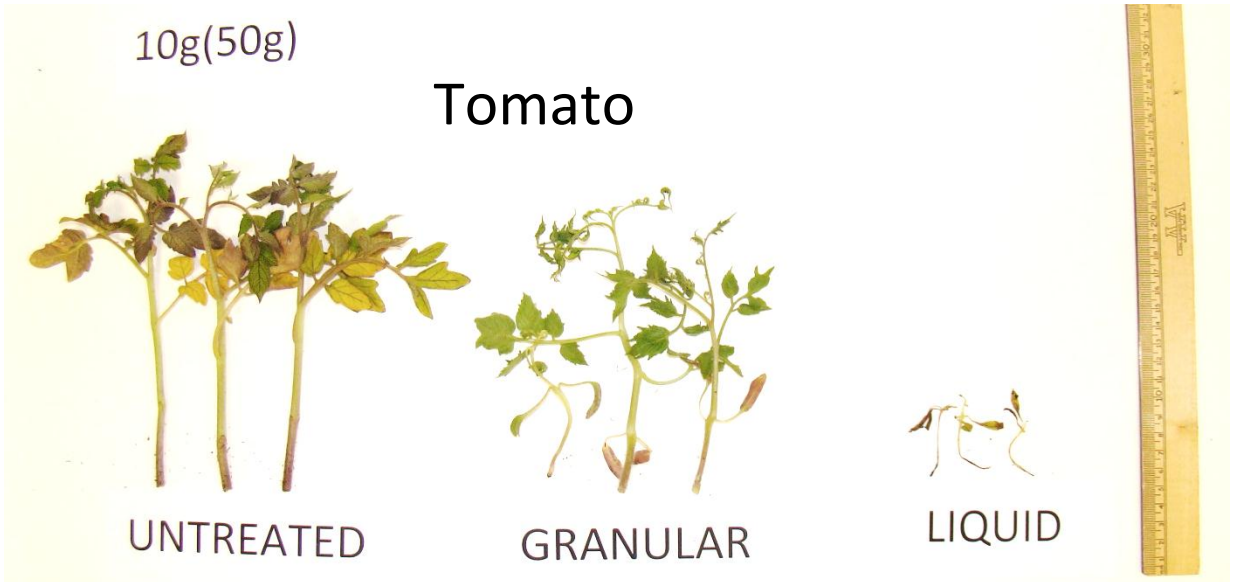


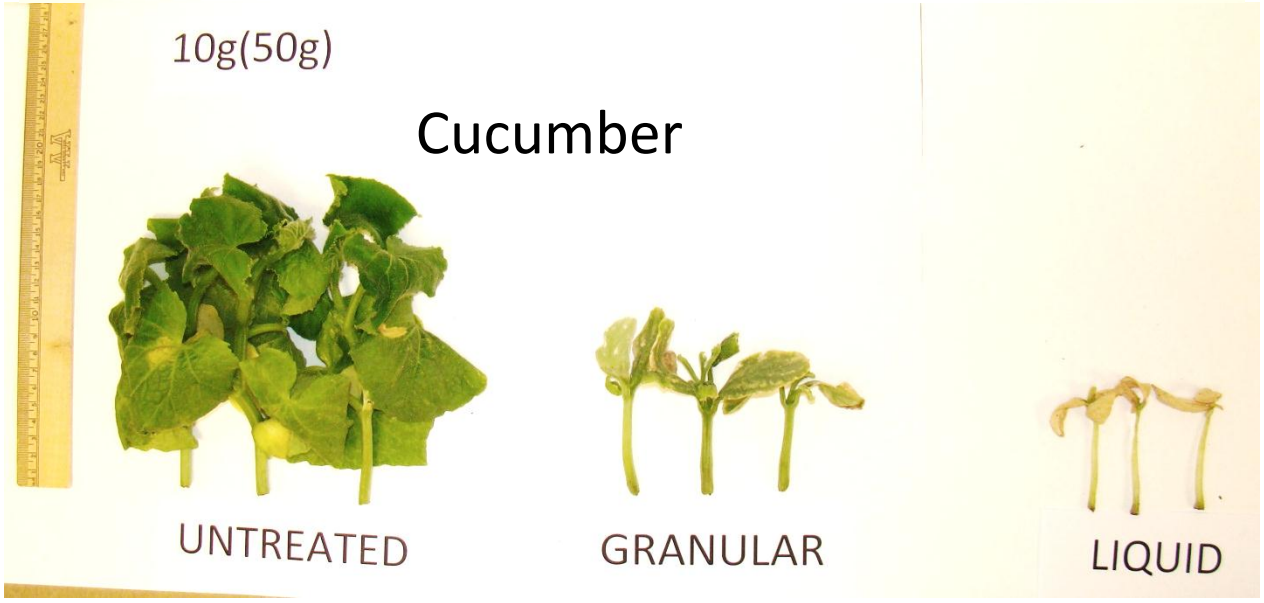
5g(50g)

Cucumber



Day 35 (20% potting mix)





Results

- Mass balance analysis showed that 53% of the granular aminocyclopyrachlor, 42% of the liquid aminocyclopyrachlor and 30% of the clopyralid remain after 178 days of composting
- The final concentrations of all of the herbicides (4.8, 10.7 and 57 ppm dry wt, respectively), were well above levels of <0.1 ppm likely to affect sensitive plants.
- Dilution of treated composts would need to be on the order of 50:1 to prevent phytotoxic effects in sensitive plants.
- Plants had different sensitivities to herbicide residues. Tomatoes most sensitive to clopyralid, beans to aminocyclopyrachlor.

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Factors that affect compost bioassays

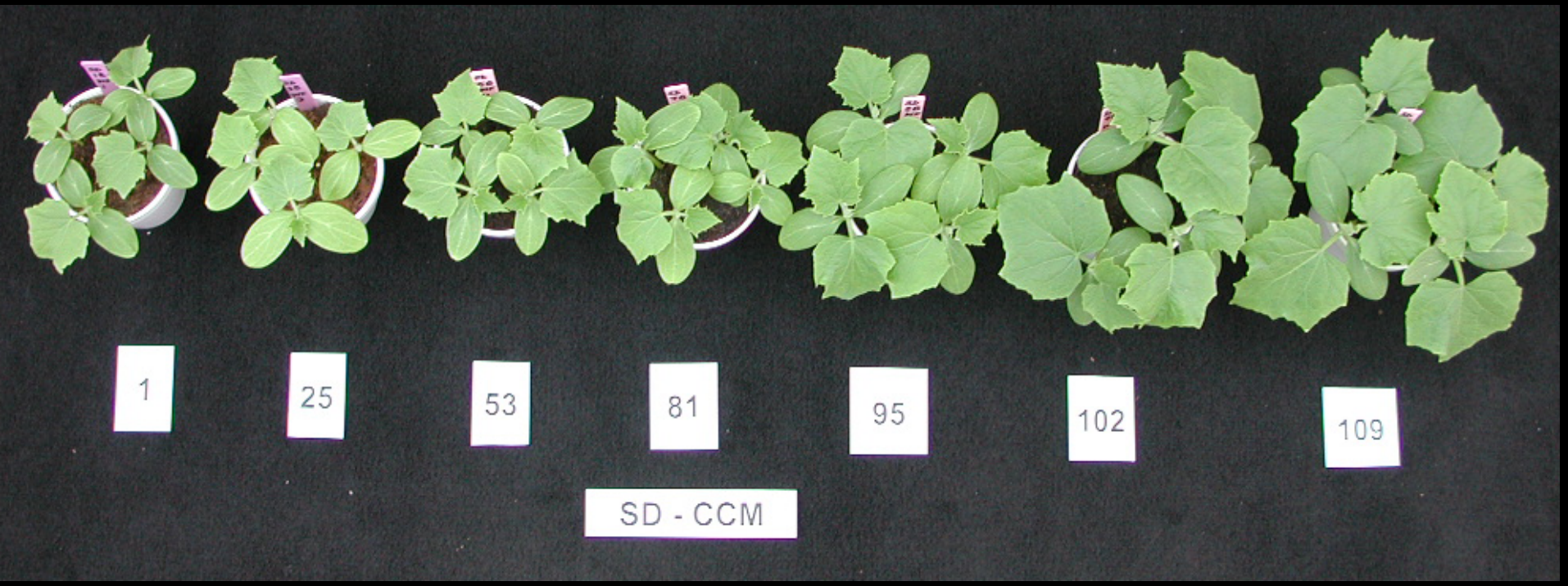
- Compost stability and maturity
- Soluble salts in compost
- Media fertility
- Amount of compost in growth media



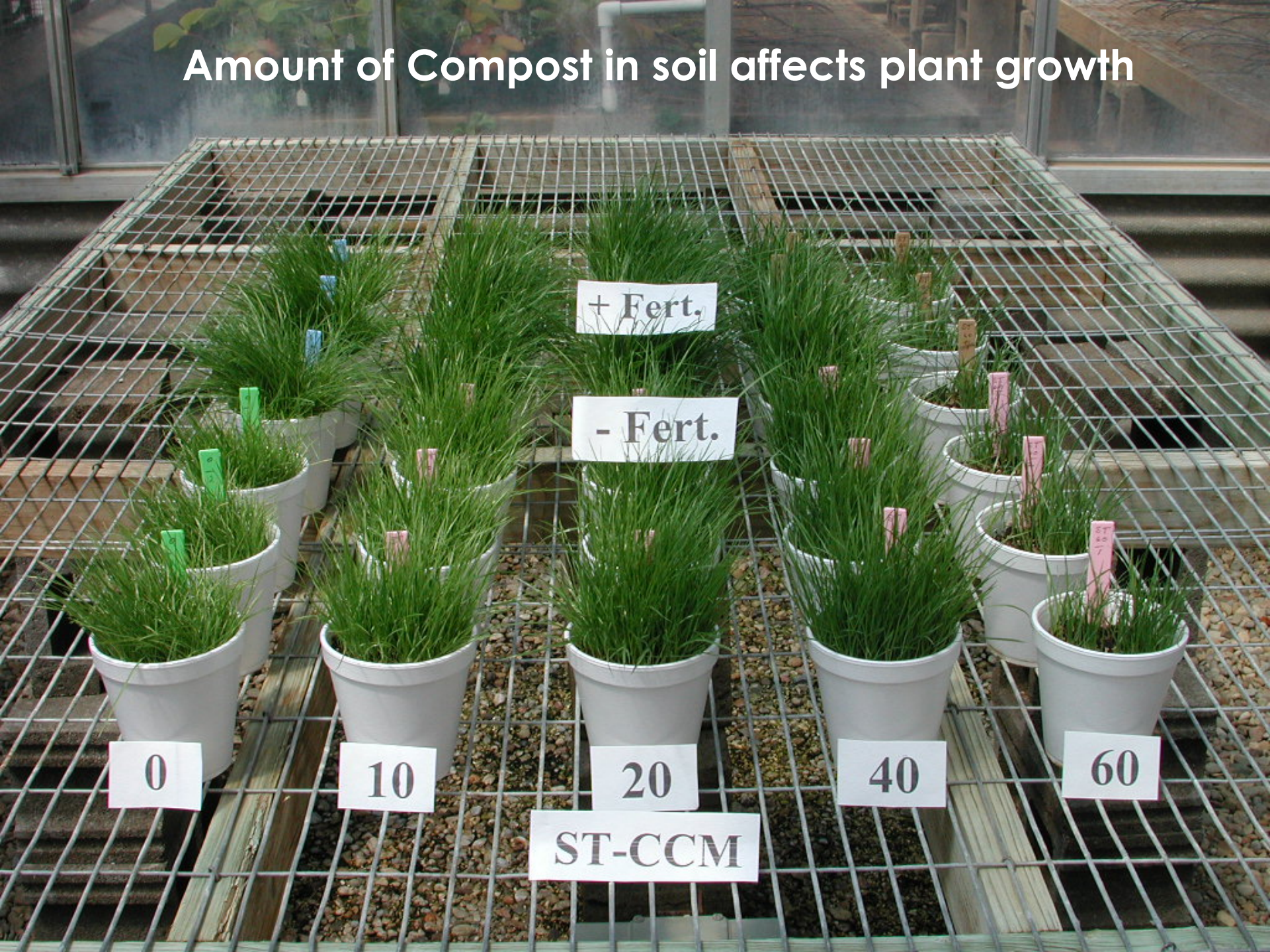
Soil Soluble Salts (mMhos/cm)

	Saturated Media Extract	2 : 1 Dilution
Satisfactory if soil is high in organic matter, but too low if soil is low in organic matter.	Below 2	0.15 to 0.50
Satisfactory range for established plants, but upper range may be too high for some seedlings.	3 to 4	0.50 to 1.80
Slightly higher than desirable.	4 to 8	1.80 to 2.25

90 to 110 days of composting required for maturity



Amount of Compost in soil affects plant growth



Fertility Effects on Plant Growth Response

Introduction

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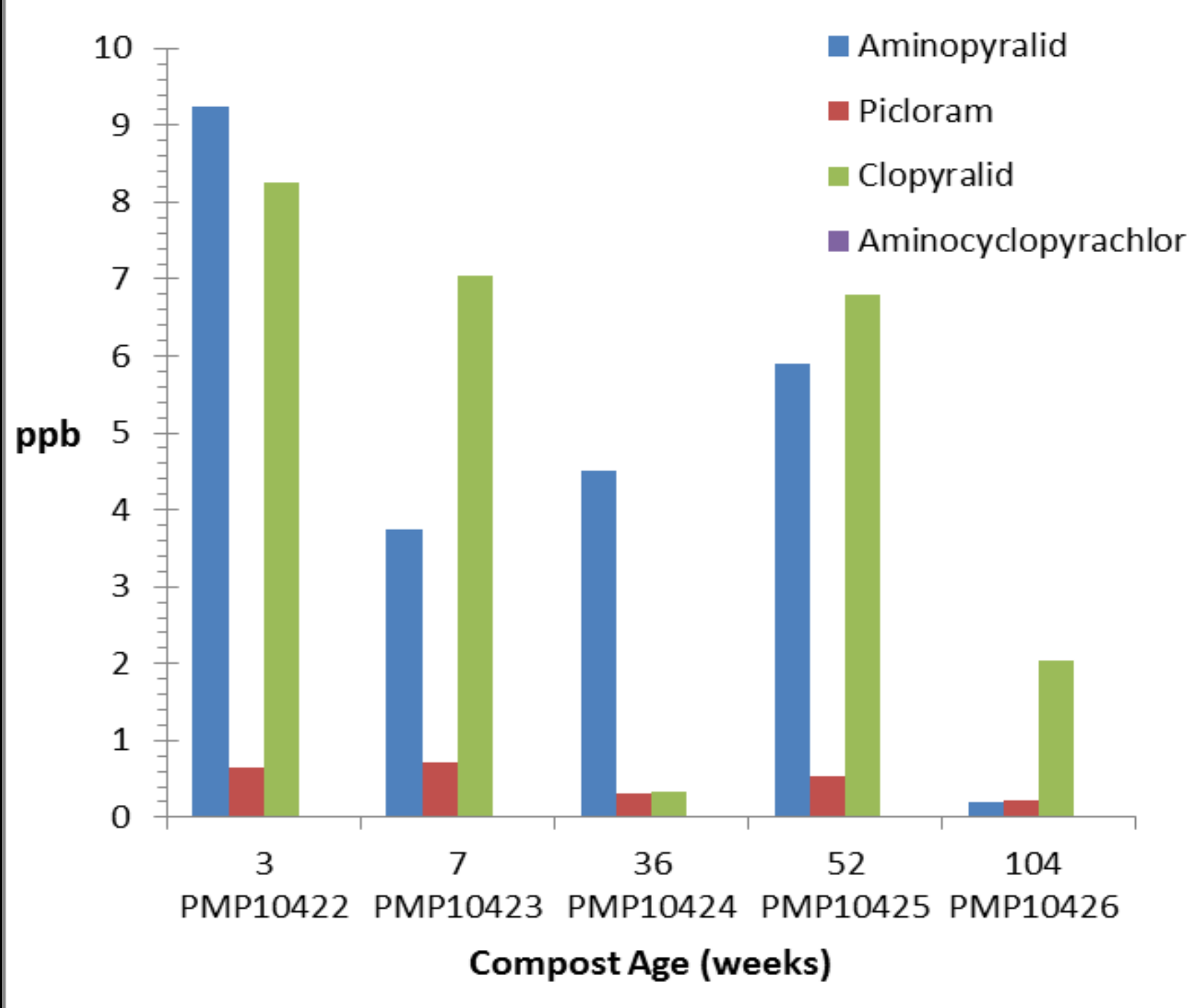
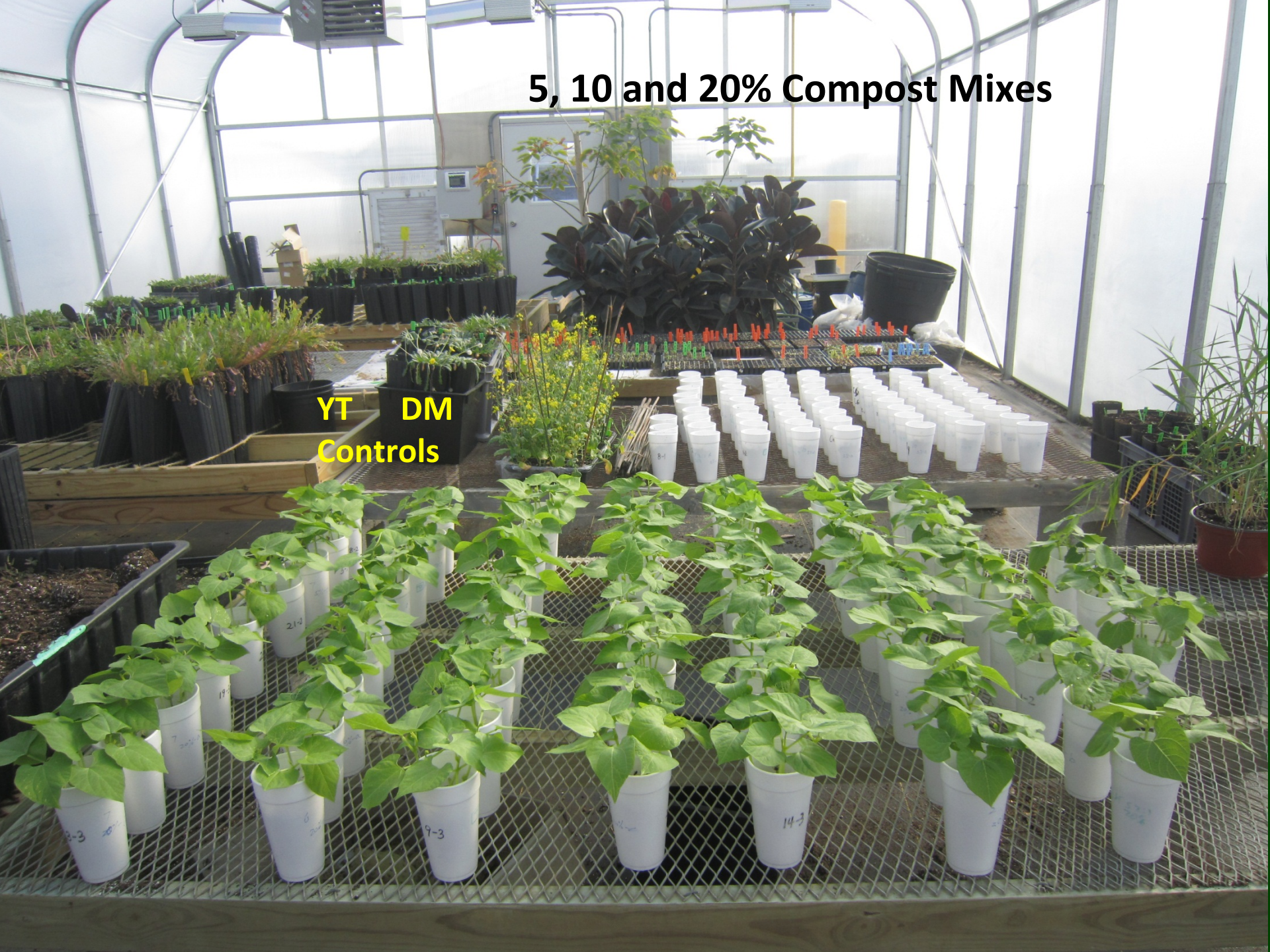

Aminopyralid
Picloram
Clopyralid
Aminocyclopyrachlor
ppb
10
9
8
7
6
5
4
3
2
1
0
3
PMP10422
7
PMP10423
36
PMP10424
52
PMP10425
104
PMP10426
Compost Age (weeks)


5, 10 and 20% Compost Mixes
YT DM
Controls

Dairy Manure Compost Control
50% Compost

Yard Trimmings Compost Control
50% Compost

ProMix Control
50% Compost

PMP10422

50% Compost

9 ppb aminopyralid, 8 ppb clopyralid

PMP10423

50% Compost

4 ppb aminopyralid, 8 ppb clopyralid

PMP10424

50% Compost

5 ppb aminopyralid

PMP10425

50% Compost

6 ppb aminopyralid, 7 ppb clopyralid

Oldest ICP

50% Compost

2 ppb clopyralid

Research Needs

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3. Validation and publication of chemical test methods for the measurement of herbicides in composts at ppb detection limits.

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4. Determination of the fate and persistence of recalcitrant herbicides during composting and whether their rate of degradation in composts differs from that in soil.

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3. Validation and publication of chemical test methods for the measurement of herbicides in composts at ppb detection limits.
4. Determination of the fate and persistence of recalcitrant herbicides during composting and whether their rate of degradation in composts differs from that in soil.
5. Compost based inoculants that contain consortia of microorganisms able to rapidly degrade recalcitrant herbicides in contaminated composts.

Questions?

RESEARCH ON HERBICIDE PERSISTENCE IN COMPOSTS

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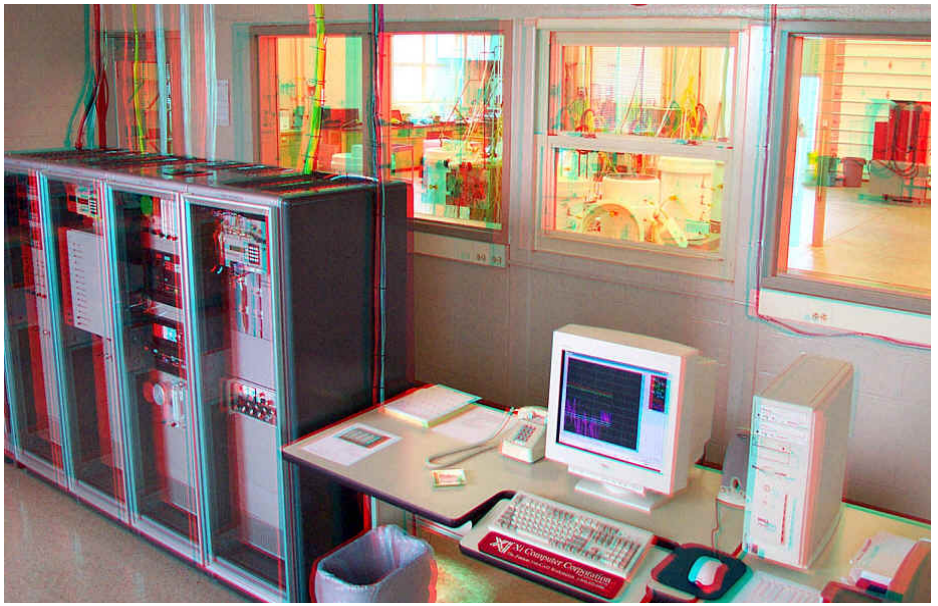
Research Questions

- At what concentrations are these herbicides phytotoxic in composts ?
- Do these compounds biodegrade during composting?
- Is there a danger of generating phytotoxic composts when these compounds are used as directed?

Experiment 1

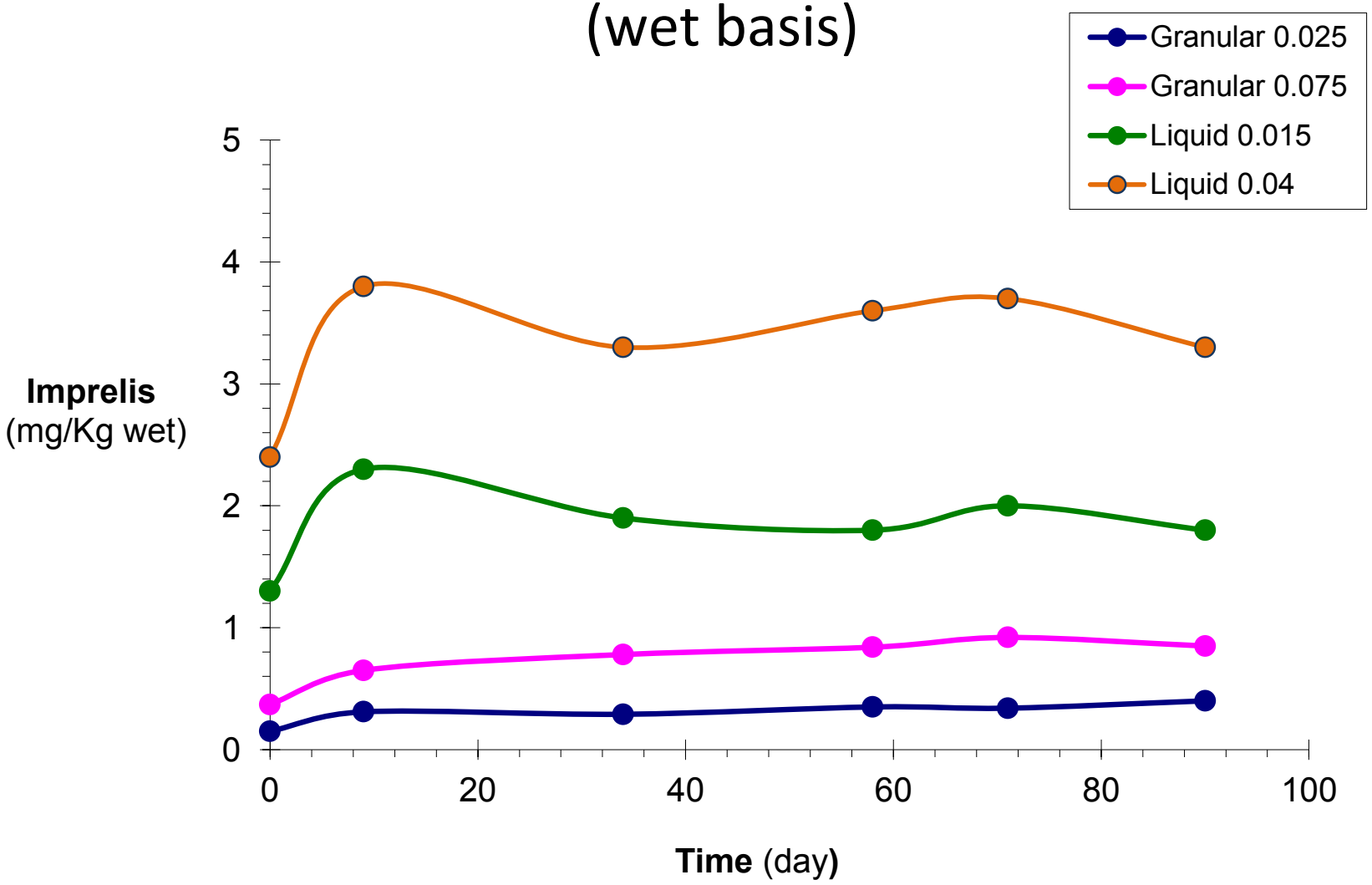
- Compost in a large scale adiabatic system (no heat input or loss)
- Reactor volume 200 liters
- Compost for 90 days
- Treatments
    - 1 - granular application at 0.025 lb AI/acre
    - 2 - granular application at 0.075 lb AI/acre
    - 3 - liquid application at 0.015 lb AI/acre
    - 4 - liquid application at 0.04 lb AI/acre

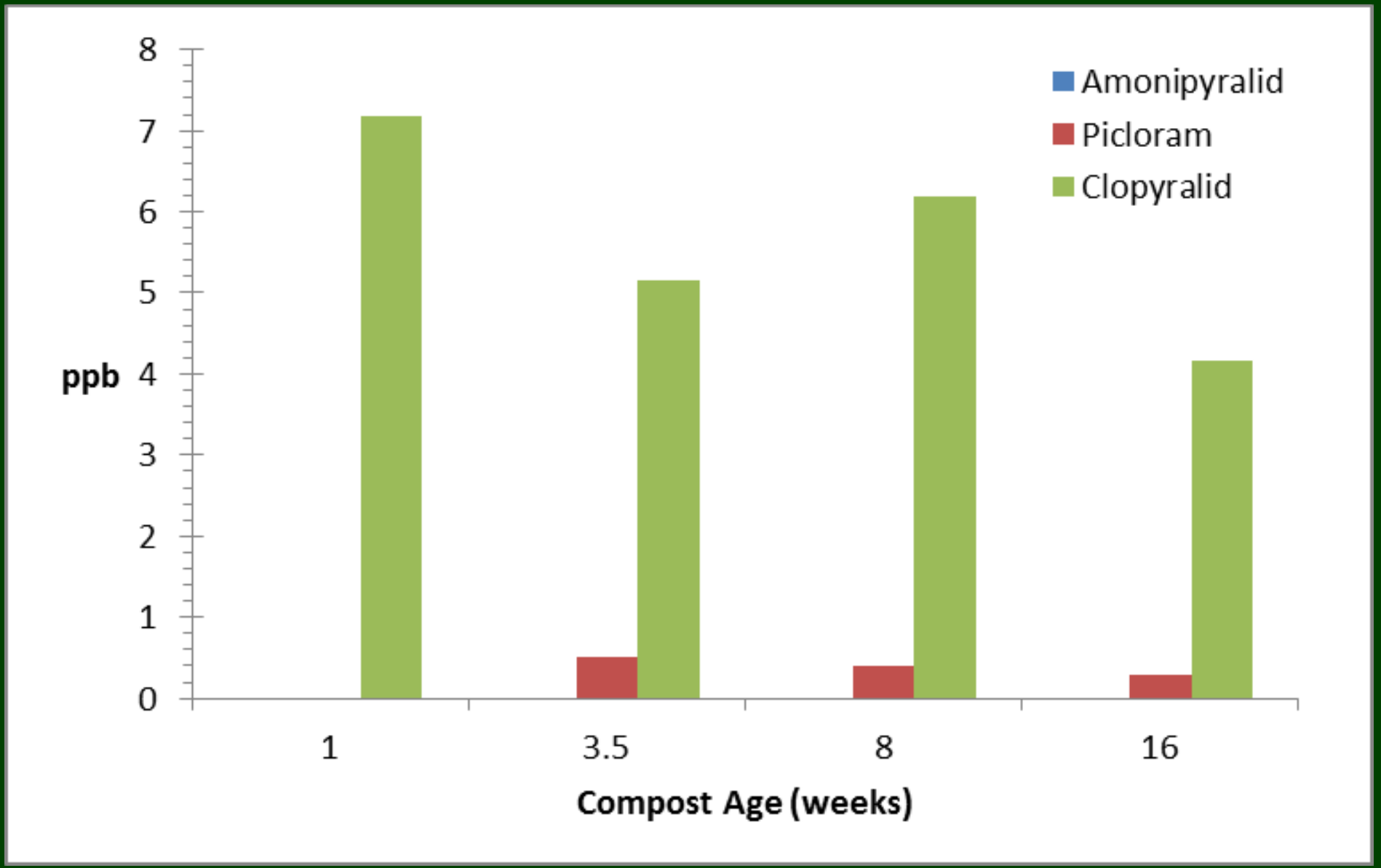


Day 0

Day 90

Aminocyclopyrachlor loss (wet basis)




8
7
6
5
4
3
2
1
0
ppb
Amonipyralid
Picloram
Clopyralid
1
3.5
8
16
Compost Age (weeks)

Are the composts phytotoxic? Methods

- Incorporate composts made from herbicide treated grass into potting media at 4, 10 and 20%
- Sow Cucumber, Tomato and Bean into media.
- Assess plant growth for 35 days.
- Concentrations in the media overall were the following for the 3 different mix levels:

ppb in compost (dw basis)

	Imprelis		
	Granular	Liquid	Clopyralid
4%	192	428	2280
10%	480	1070	5700
20%	960	2140	11400

Aminocyclopyrachlor loss
(ash basis)