

# **Testing novel combinations of amendments for stabilization of metals in heavily contaminated soils**

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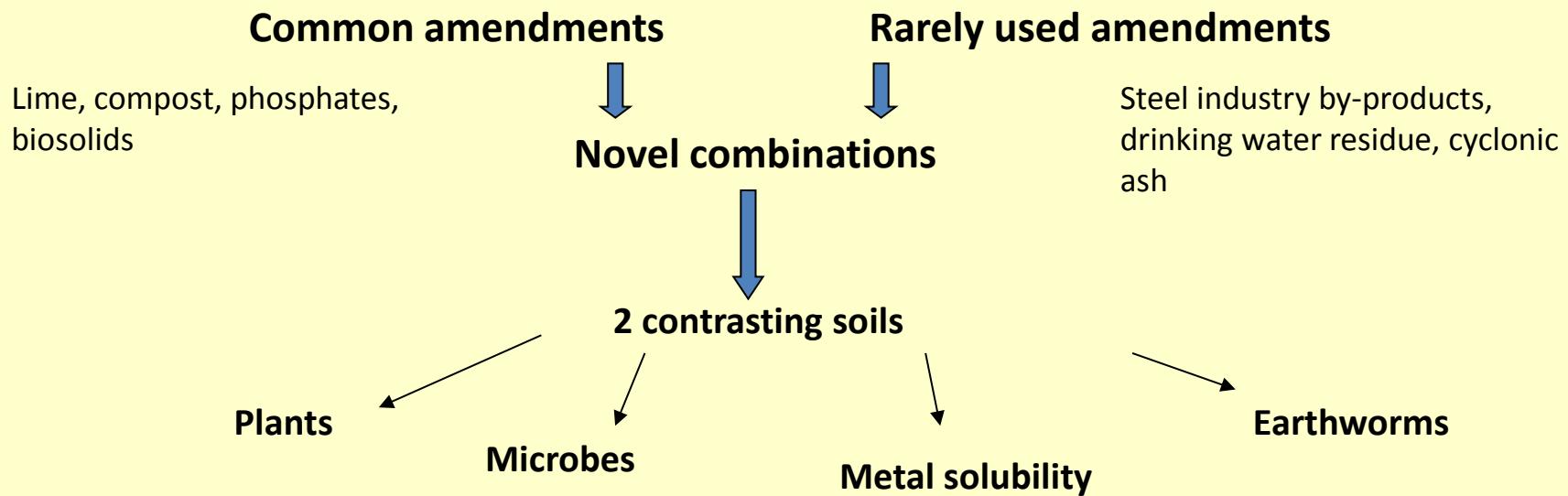


Institute of Soil Science  
and Plant Cultivation  
State Research Institute



*Cabernet 2014*

## 1. Combining amendments



## 2. Involving bacterial inoculation

## SOILS

- **soil A, less toxic agricultural soil contaminated through long-term Zn/Pb smelter emissions in Poland (pH 6.9, total Zn, Pb and Cd: 2670, 690 and 30 mg kg<sup>-1</sup>, respectively); PHYTOEXCLUSION**
- **soil B, toxic soil contaminated 20 years ago through smelter dust spill in Poland (pH 6.9, total Zn, Pb and Cd: 4070, 1770 and 27 mg kg<sup>-1</sup>, respectively, large pool of soluble Zn and Cd); PHYTOSTABILISATION**

Parameter		Soil A	Soil B
pH		6.9	6.9
Clay (%)		3	2
Soil texture		silt loam	sandy loam
Organic C (%)		0.56	0.56
Total metals (mg kg <sup>-1</sup> )	Zn	2670	4070
	Cd	30	27
	Pb	690	1770
1M NH <sub>4</sub> -nitrate extractable metals (mg kg <sup>-1</sup> )	Zn	8.6	485
	Cd	0.4	5.4
	Pb	0.2	13.5

## AMENDMENTS

**CaCO<sub>3</sub> – reagent grade**

**Drinking water residue**

pH 7.8, OM 3%, Fe 1.8%, Mn 7.2%, Al 0.63%, Ca 1.6%,

**Ca-phosphate – reagent grade CaHPO<sub>4</sub>**

**GWDA compost** – municipal green waste and sludge as feedstock

pH 6.1, OM 27%, Fe 1.9%, Mn 0.03%, Al 1.3%, Ca 2.6%,

**Thomas basic slag (TBS)**- steel manufacture by-product

pH 11.9, high Fe, Mn, Al, Ca, rich in P

**Linz-Donawitz slag (LD)** – steel industry by-product

pH 13.2, Fe 22.9%, Mn 3%, Al 1.5%, Ca 7.4%,

**Gravel sludge (GS)**

pH 8.1, Fe 5.2%, Mn 0.1%, Al 2.4%, Ca 4.2%,

**Siderite (SID)** – iron carbonate

pH 8.2, Fe 26%, Mn 1.2%, Al 0.29%, Ca 7.4%,

**Cyclonic ashes (CA)** are a modified aluminosilicate, originating from the fluidized bed burning of coal refuse. The CA used in this experiment originate from a Spanish coal burning plant.

pH 13.1, Fe 4.7%, Mn 0.03%, Al 8%, Ca 30%,

**Iron grit (IG)** - Steel shots are an industrial material intended for shaping metal surfaces prior to coating. They consist mainly of iron (Fe<sup>0</sup>) and contain native impurities such as Mn, Ni or Cr

pH 8.5, Fe, Mn, Al, Ca,

## Amendment characteristics

Amendment	pH	EC (mS/m)	OM (%)	Fe (%)	Mn (%)	Al (%)	Ca (%)
DWR	7.8	28	2.7	1.80	7.20	0.64	1.58
Compost GWDA	6.1	457	26.7	1.89	0.03	1.29	2.57
TBS	11.9	761	-	1.3	1.6	10	23.5
LD slag	13.2	598	-	22.9	3.01	1.49	30.7
Gravel sludge	8.1	14	1.4	5.25	0.11	2.40	4.19
Siderite	8.2	13	-	26.0	1.23	0.29	7.39
Cyclonic ash	13.1	968	-	4.73	0.03	7.97	7.40
Iron grit	8.5	4	-	97.3	0.77	0.06-0.1	-

## RATES

Untreated control

Drinking water residue (DWR) 5 %

Iron grit 0.5%+0.5%

Compost GWDA 5%

P as Ca-phosphate 2%

LD slag 0.5%

TBS 0.5%

Gravel sludge 2.5% + siderite 1%

DWR 5%+ GWDA 5%

Iron grit 0.5% 0.5%+ GWDA 5%

Iron grit 0.5% 0.5%+ LD slag

Iron grit 0.5% 0.5%+ LD slag + GWDA5%

TBS 0.5%+ GWDA 5%

GWDA 5%+ P as Ca-phosphate 2%+ DWR 5%

P as Ca-phosphate 2% + DWR 5%

Gravel sludge 2.5% + siderite 1%+ GWDA 5%

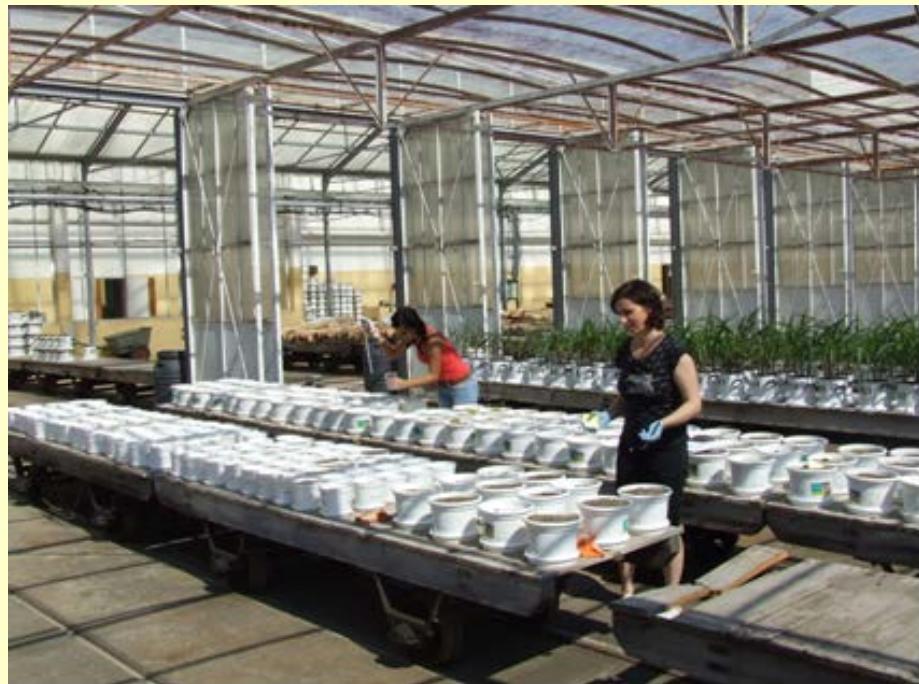
Cyclonic ash 1 or 1.5%

Iron grit 0.5% + 0.5%+ cyclonic ash 1 or 1.5%+

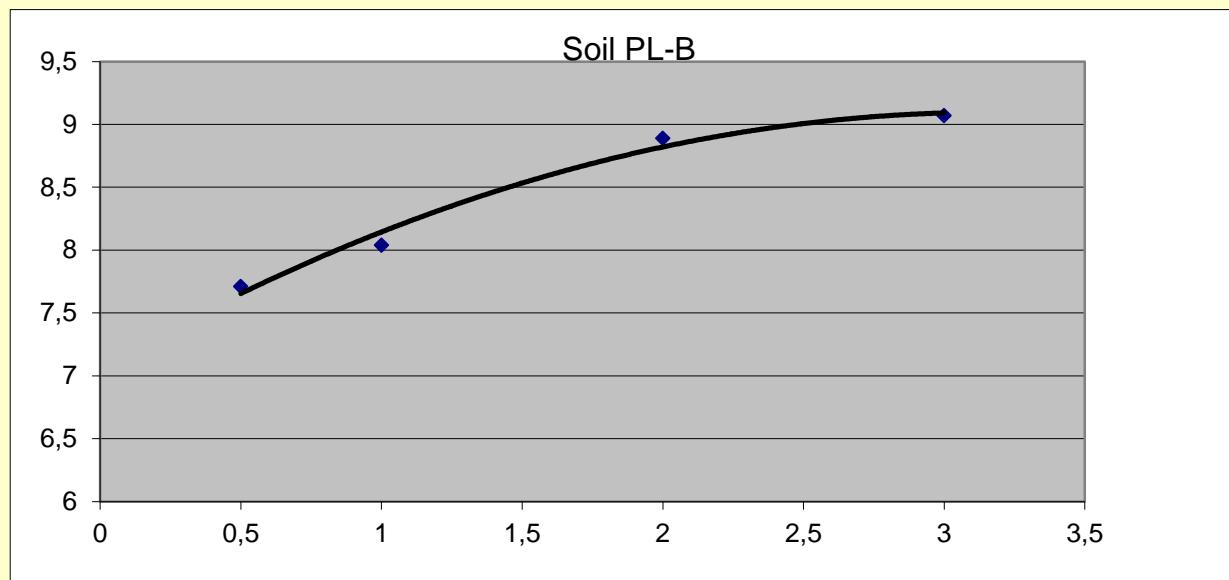
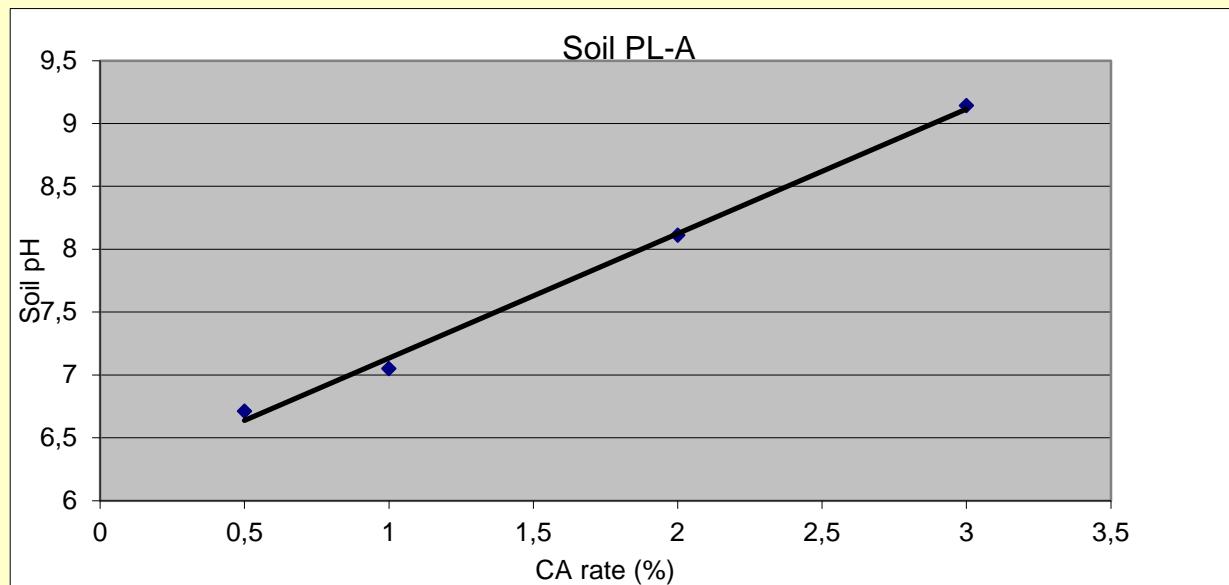
GWDA 5%

CaCO<sub>3</sub> 5%

Cyclonic ash 1.5% or 1%



## pH batch test – Cyclonic ash



## Application scheme

Control				
DWR 5%	<b>DWR</b>	<b>CaCO<sub>3</sub></b>		
Iron grit 0,5%+0,5%	<b>1/2 Iron grit</b>	<b>1/2 Iron grit</b>	<b>CaCO<sub>3</sub></b>	
GWDA 5%	<b>GWDA</b>	<b>CaCO<sub>3</sub></b>		
CaHPO <sub>4</sub> 2%	<b>CaHPO<sub>4</sub></b>	<b>CaCO<sub>3</sub></b>		
LD slag	<b>LD slag</b>			
TBS 0,5%	<b>TBS</b>			
Gravel sludge 2,5% + siderite 1%	<b>Gravel sludge</b>	<b>Siderite</b>	<b>CaCO<sub>3</sub></b>	
DWR 5%+ GWDA 5%	<b>DWR</b>	<b>GWDA</b>	<b>CaCO<sub>3</sub></b>	
Iron grit 0,5% 0,5%+ GWDA 5%	<b>1/2 Iron grit</b>	<b>1/2 Iron grit</b>	<b>GWDA</b>	<b>CaCO<sub>3</sub></b>
Iron grit 0,5% 0,5%+ LD slag	<b>1/2 Iron grit</b>	<b>1/2 Iron grit</b>	<b>LD slag</b>	
Iron grit 0,5% 0,5%+ LD slag + GWDA5%	<b>1/2 Iron grit</b>	<b>1/2 Iron grit</b>	<b>GWDA</b>	<b>LD slag</b>
TBS 0,5%+ GWDA 5%	<b>GWDA</b>	<b>TBS</b>		
GWDA 5%+ CaHPO <sub>4</sub> 2%+ DWR 5%	<b>CaHPO<sub>4</sub></b>	<b>DWR</b>	<b>GWDA</b>	<b>CaCO<sub>3</sub></b>
CaHPO <sub>4</sub> 2% + DWR 5%	<b>CaHPO<sub>4</sub></b>	<b>DWR</b>	<b>CaCO<sub>3</sub></b>	
Gravel sludge 2,5% + siderite 1%+ GWDA 5%	<b>Gravel sludge</b>	<b>Siderite</b>	<b>GWDA</b>	<b>CaCO<sub>3</sub></b>
Iron grit 0,5% 0,5%+ cyclonic ash + GWDA 5%	<b>1/2 Iron grit</b>	<b>1/2 Iron grit</b>	<b>GWDA</b>	<b>Cyclonic ash</b>
CaCO <sub>3</sub> 5%	<b>CaCO<sub>3</sub></b>			
Cyclonic ash 1,5% or 1%	<b>Cyclonic ash</b>			

## METHODOLOGY DESCRIPTION

Reagent grade CaCO<sub>3</sub> was added to soils if needed in order to establish soil pH at comparable level in all treatments.

The more toxic soils (B and C) were planted with **grasses** (tall fescue) whereas soil A was seeded with **lettuce**.

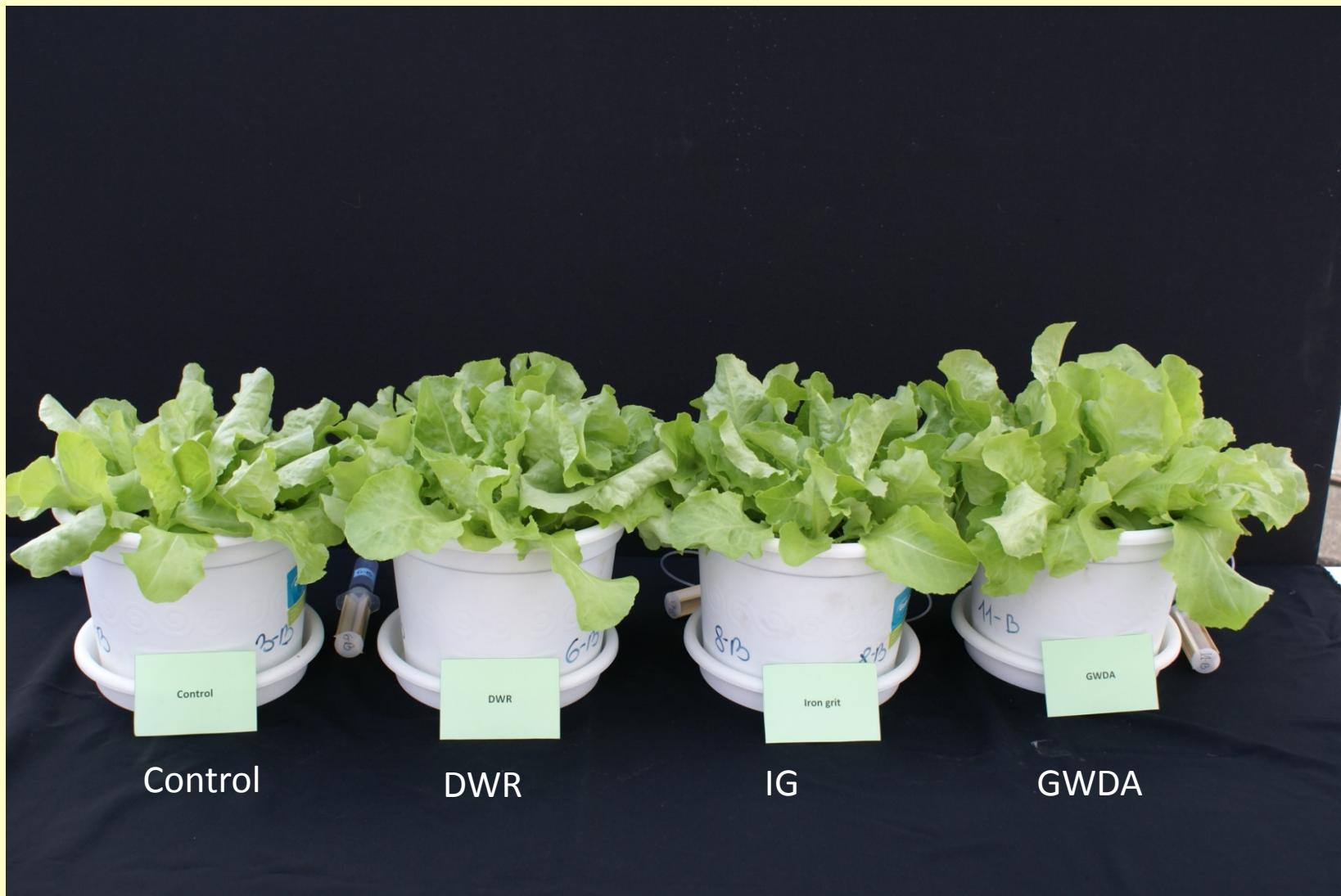
The experiment was run for 1-year, and plants were periodically harvested, the **yields** recorded and samples analyzed for metal content.

Soil samples were collected for analysis of **metal extractability, soil pH, electric conductivity and enzymatic activity**.

Soil **pore waters** were collected periodically to determine trace element and nutrient concentrations

Planted and unplanted

## PHYTOEXCLUSION – soil A, 1st lettuce



## Single vs combined amendments – Soil A (phytoexclusion) 2nd lettuce



## Iron grit combinations



## Compost combinations



## DWR combinations



## LD slag combinations



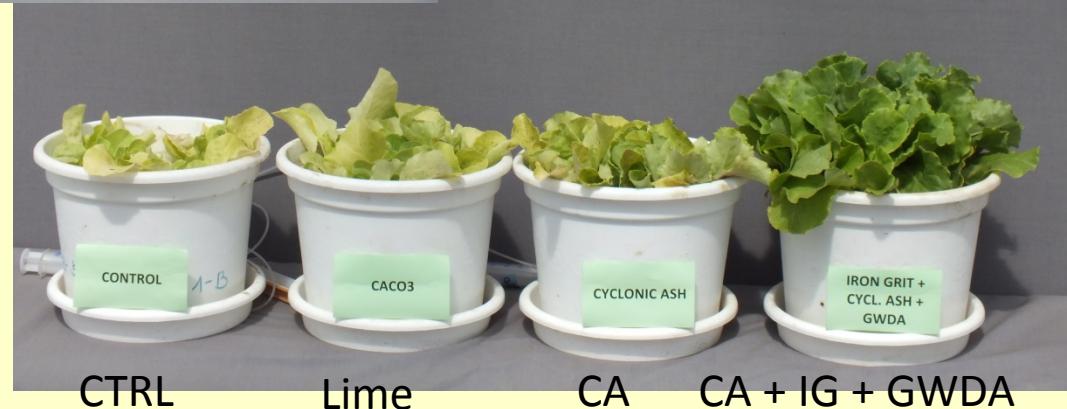


CTRL

Lime

TBS

TBS + GWDA



CTRL

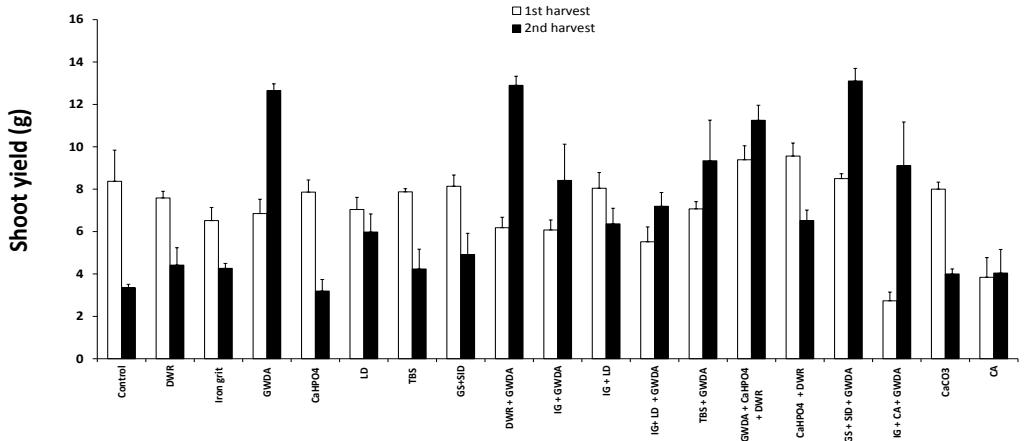
Lime

CA

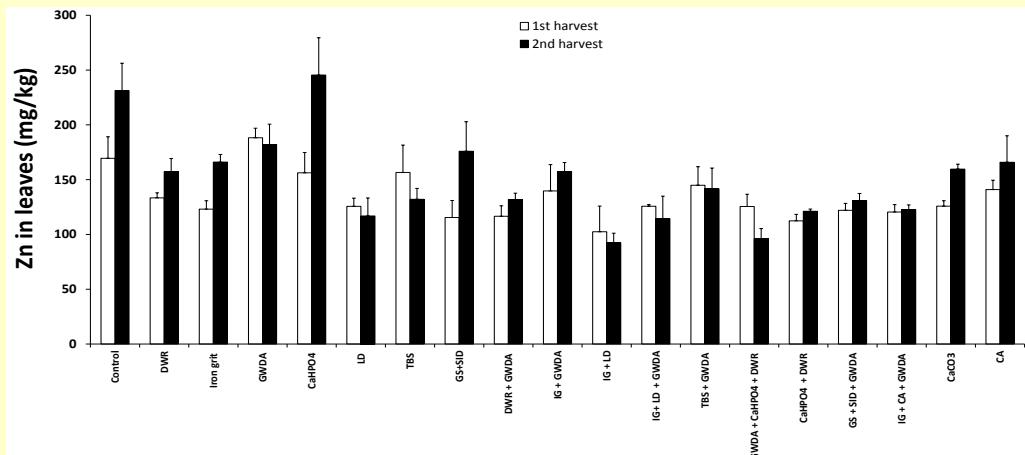
CA + IG + GWDA

Effect of treatments on:

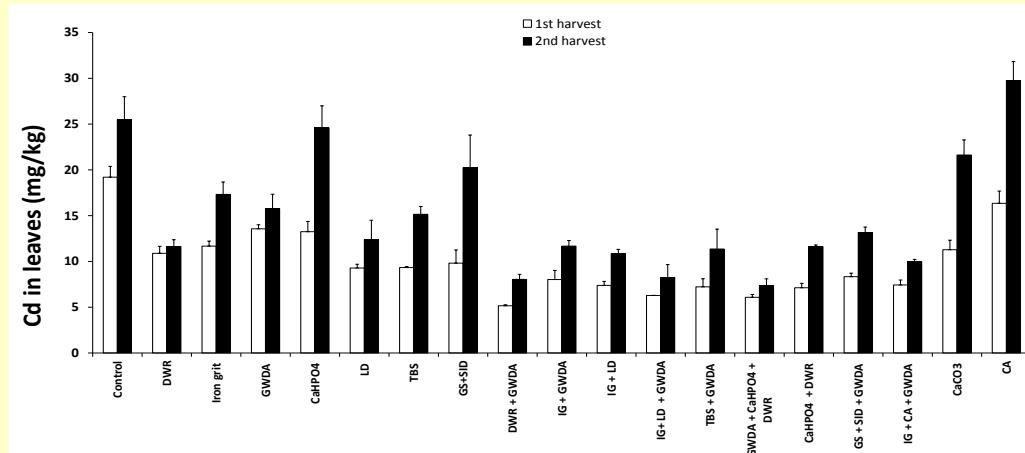
## Lettuce yield



## Zn in leaves



## Cd in leaves





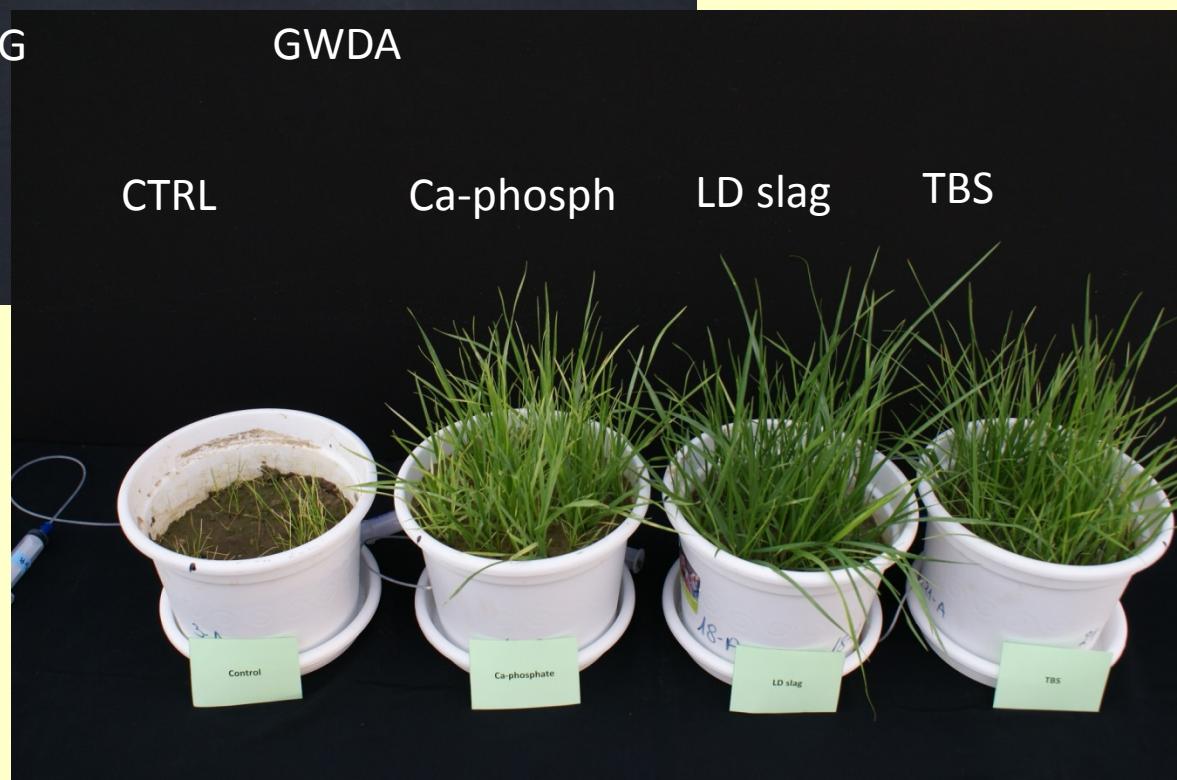
CTRL

DWR

IG

GWDA

Single amendments- Soil  
PL-B  
1st harvest

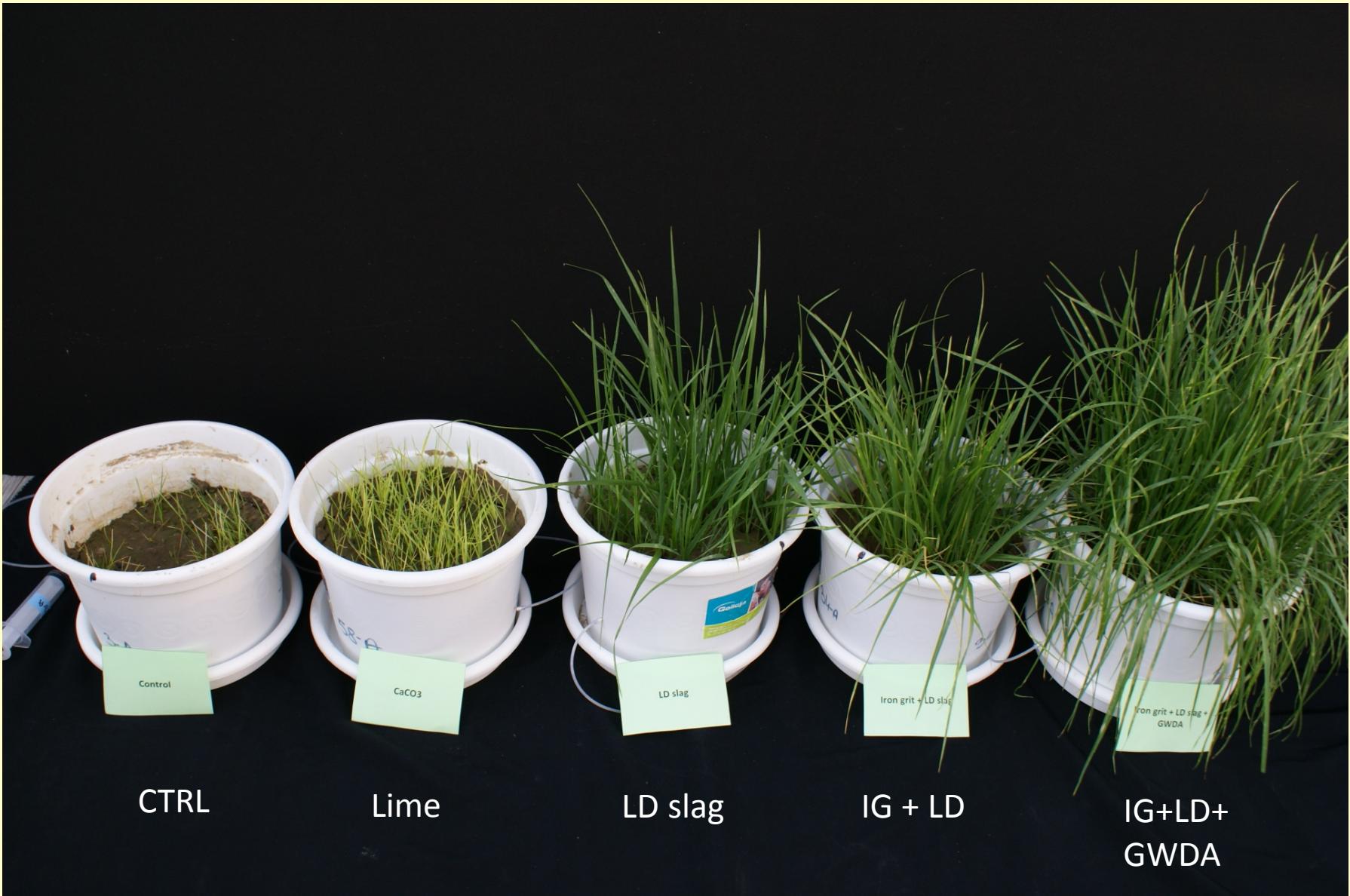


Control

Ca-phosphate

LD slag

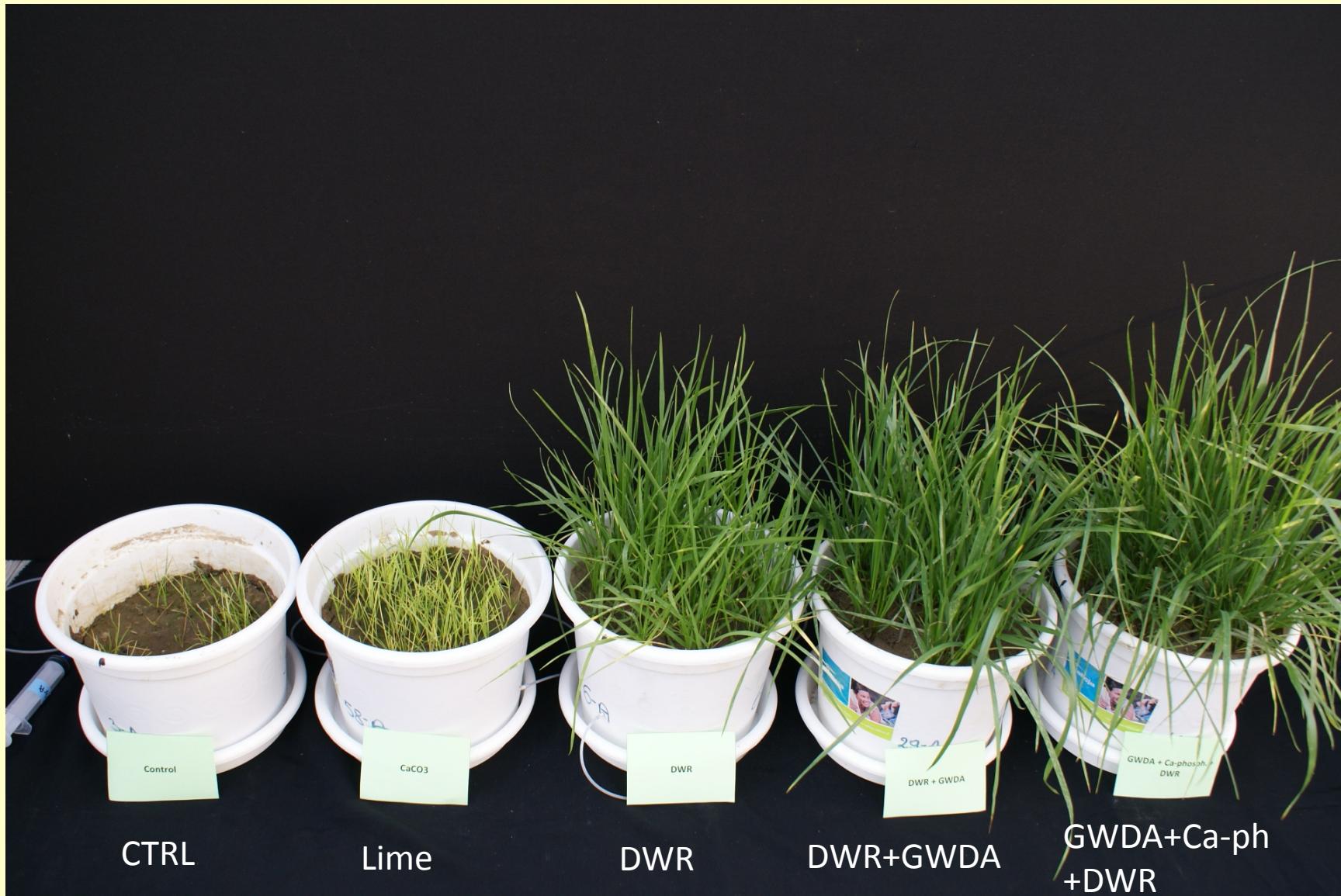
TBS



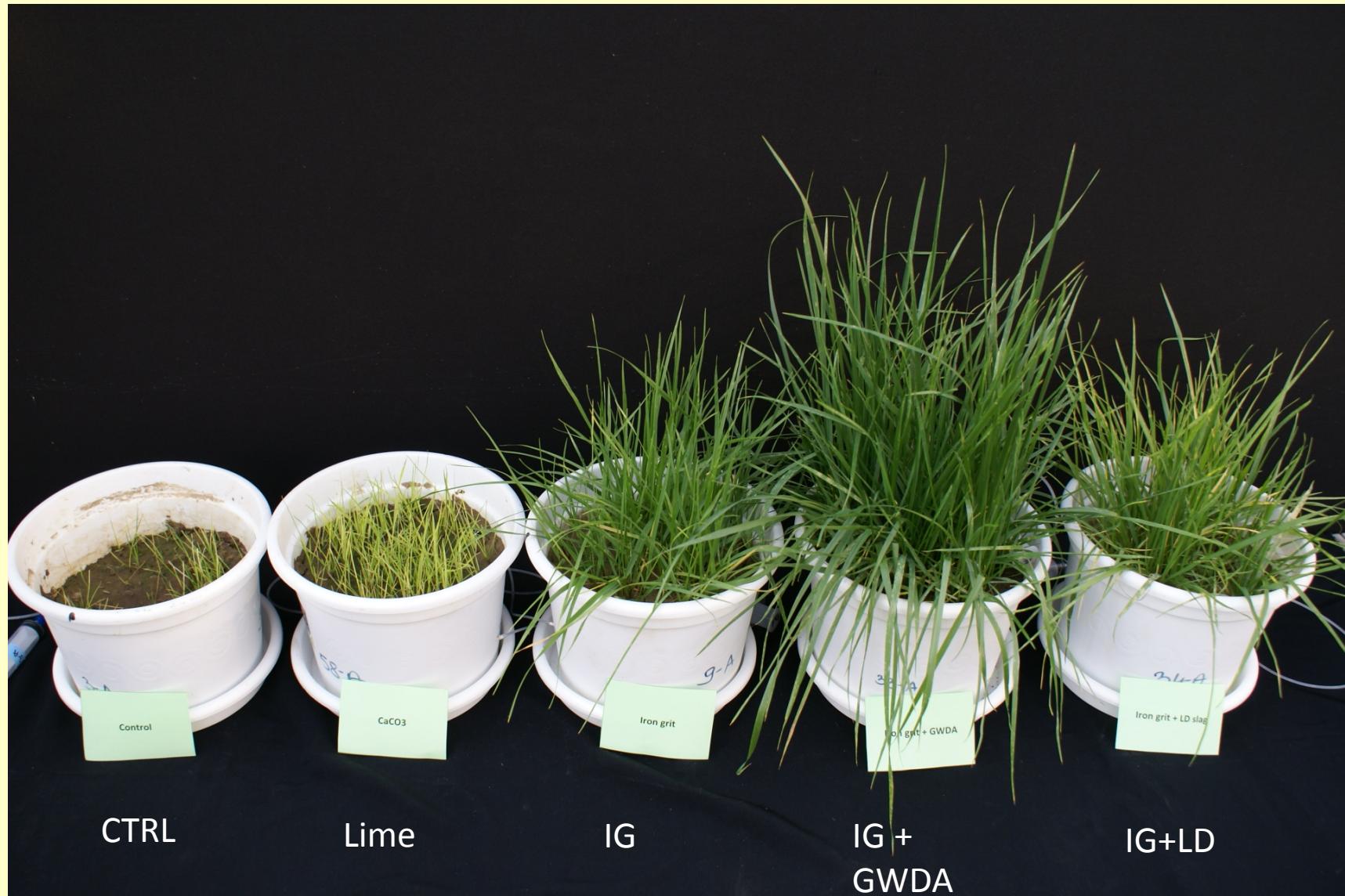
LD slag single vs. in combination (Soil PL-B)



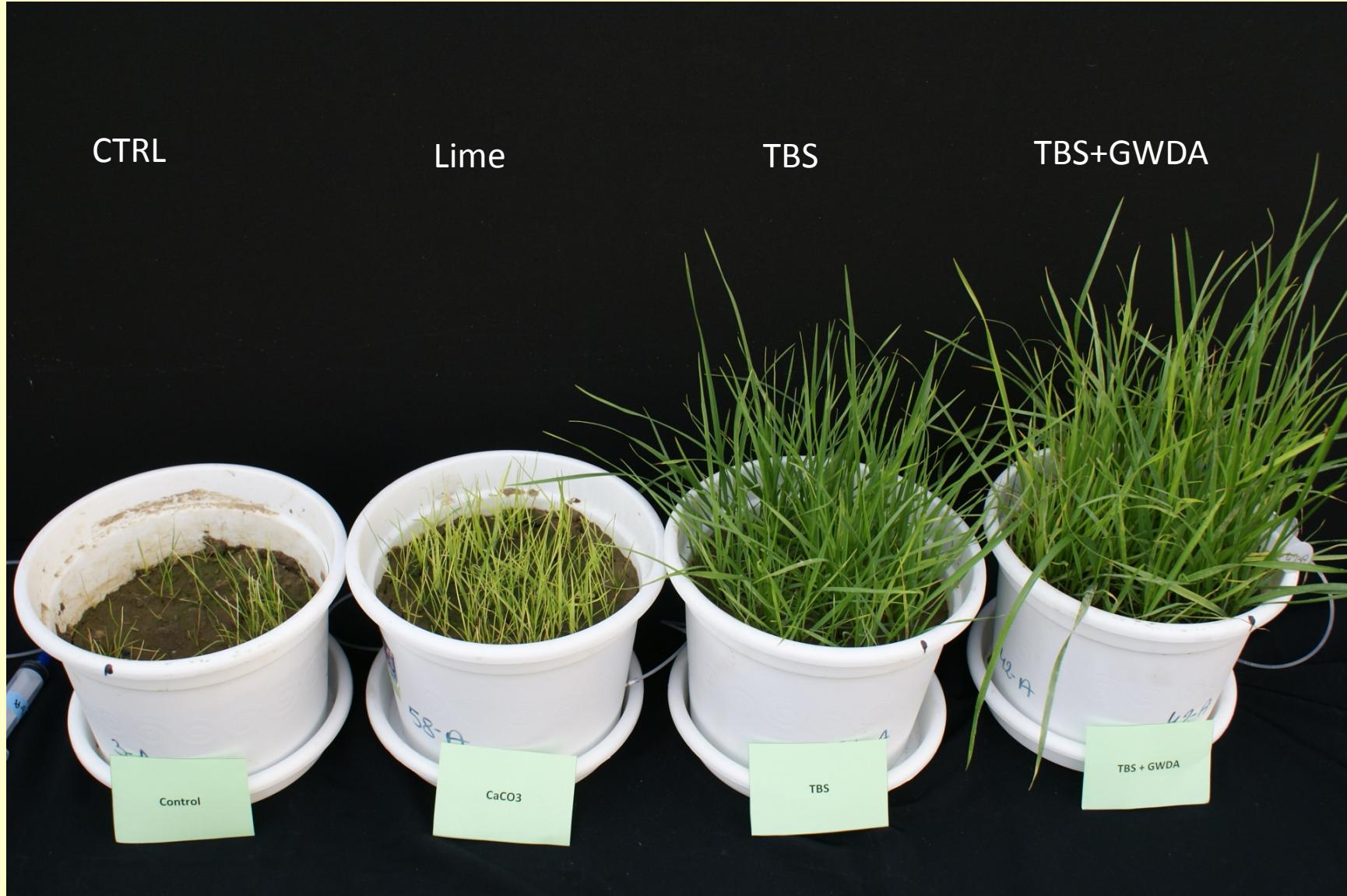
Compost as single amendment vs. Combined with other materials (Soil PL-B)



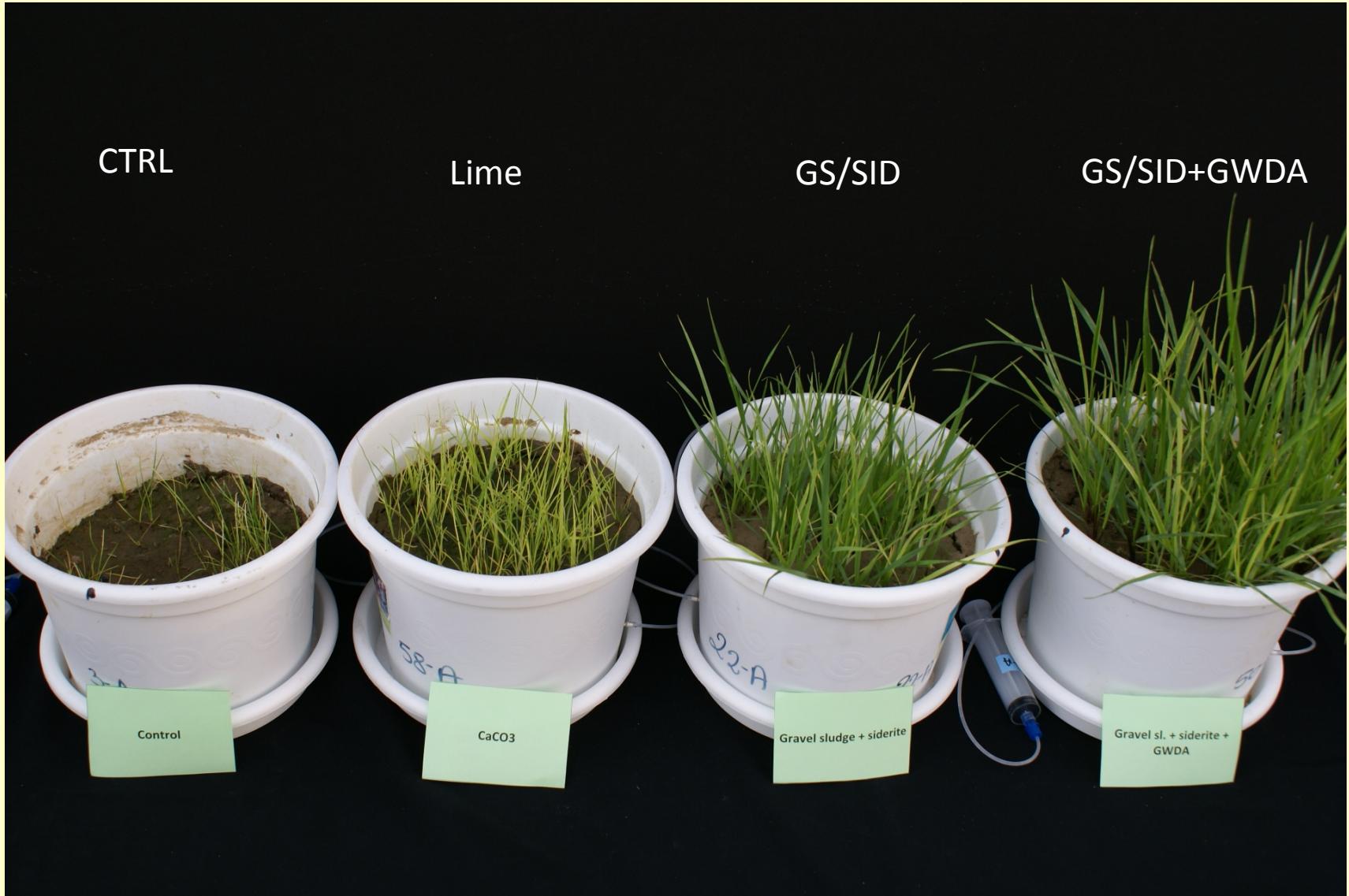
DWR as single amendment vs. Combined with other materials (Soil PL-B)



Iron grit as single amendment vs. Combined with other materials (Soil PL-B)

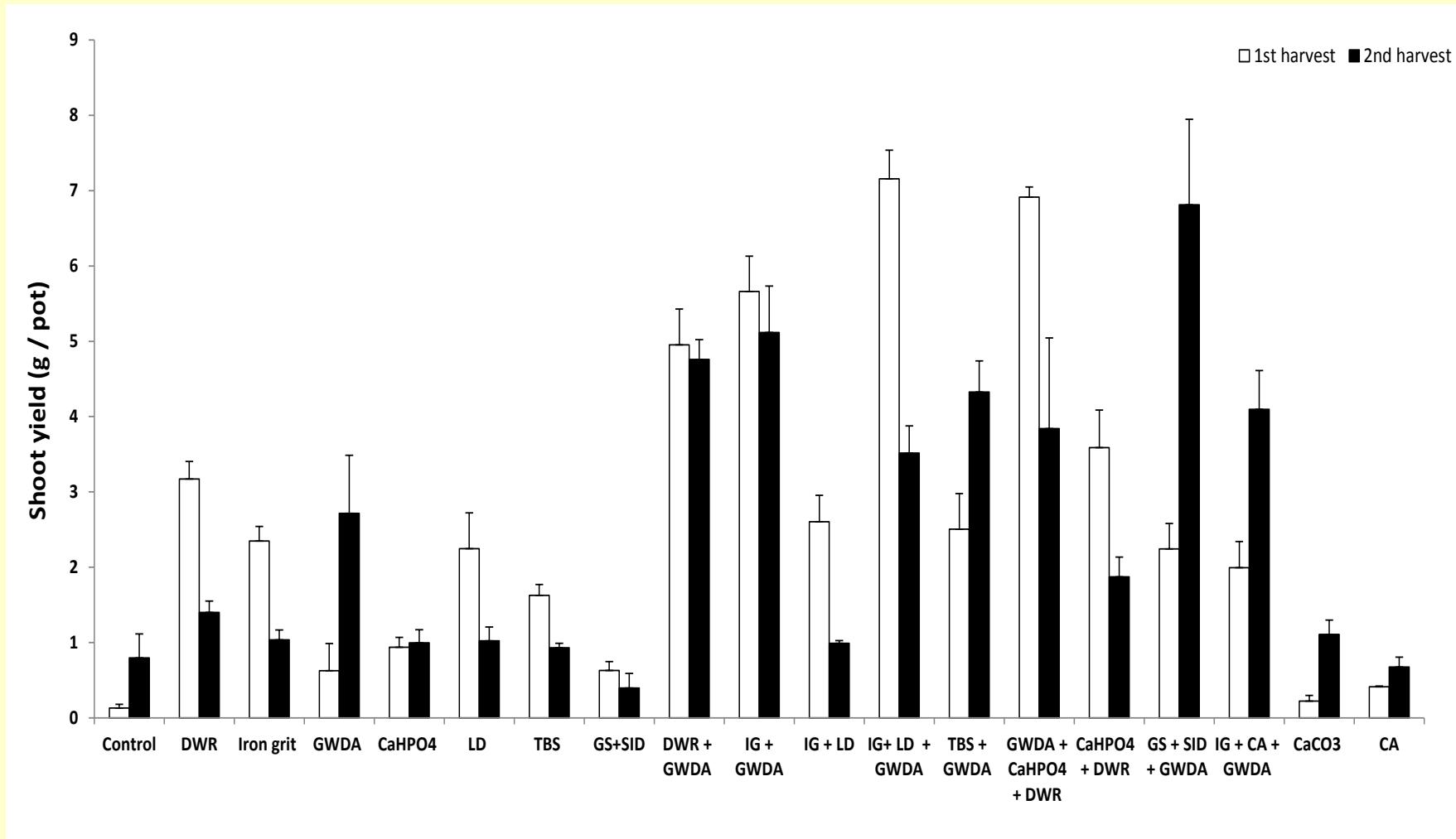


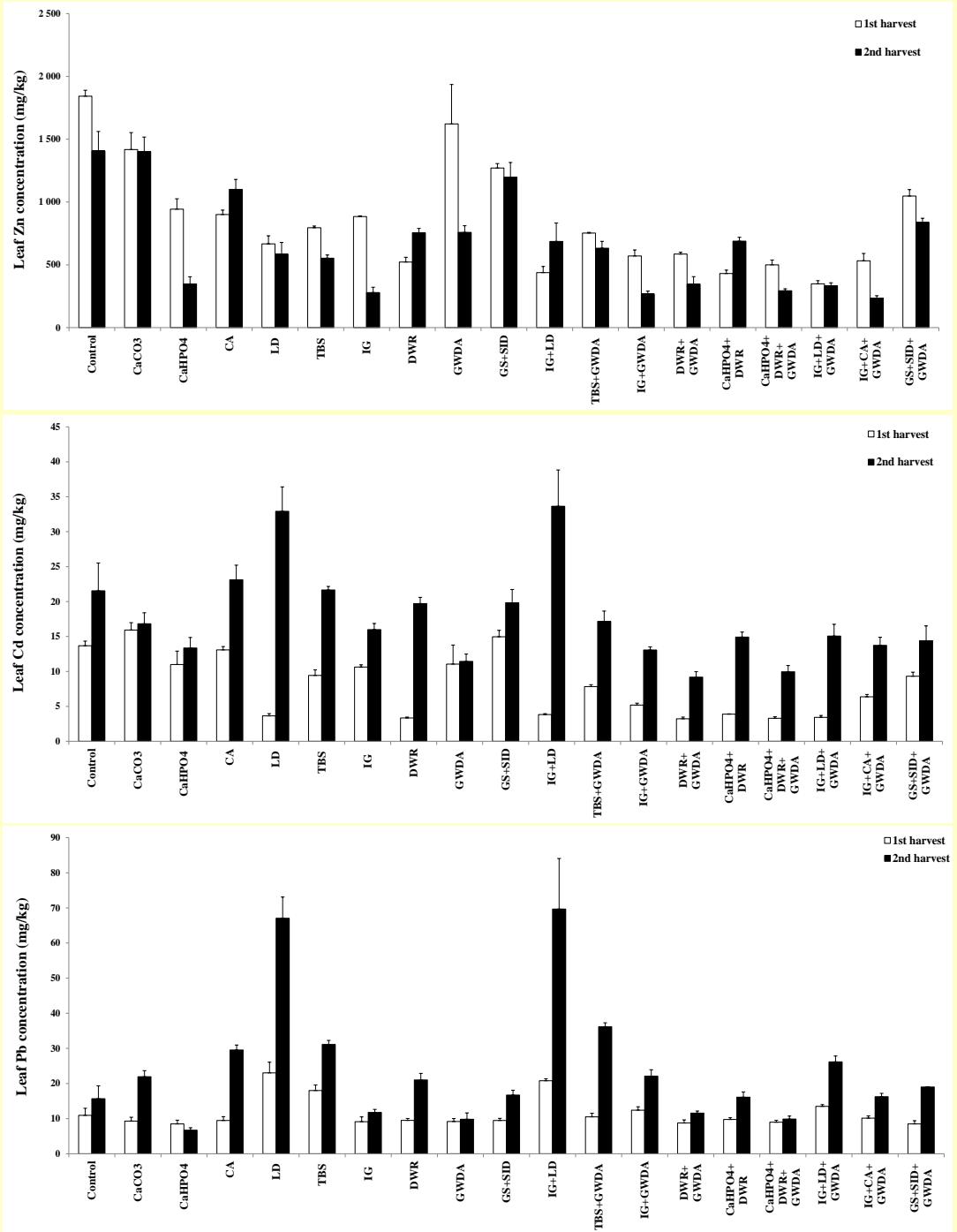
TBS as single amendment vs. Combined with other materials (Soil PL-B)



GS/SID as single amendment vs. Combined with other materials (Soil PL-B)

## Effect of treatments on grass yield



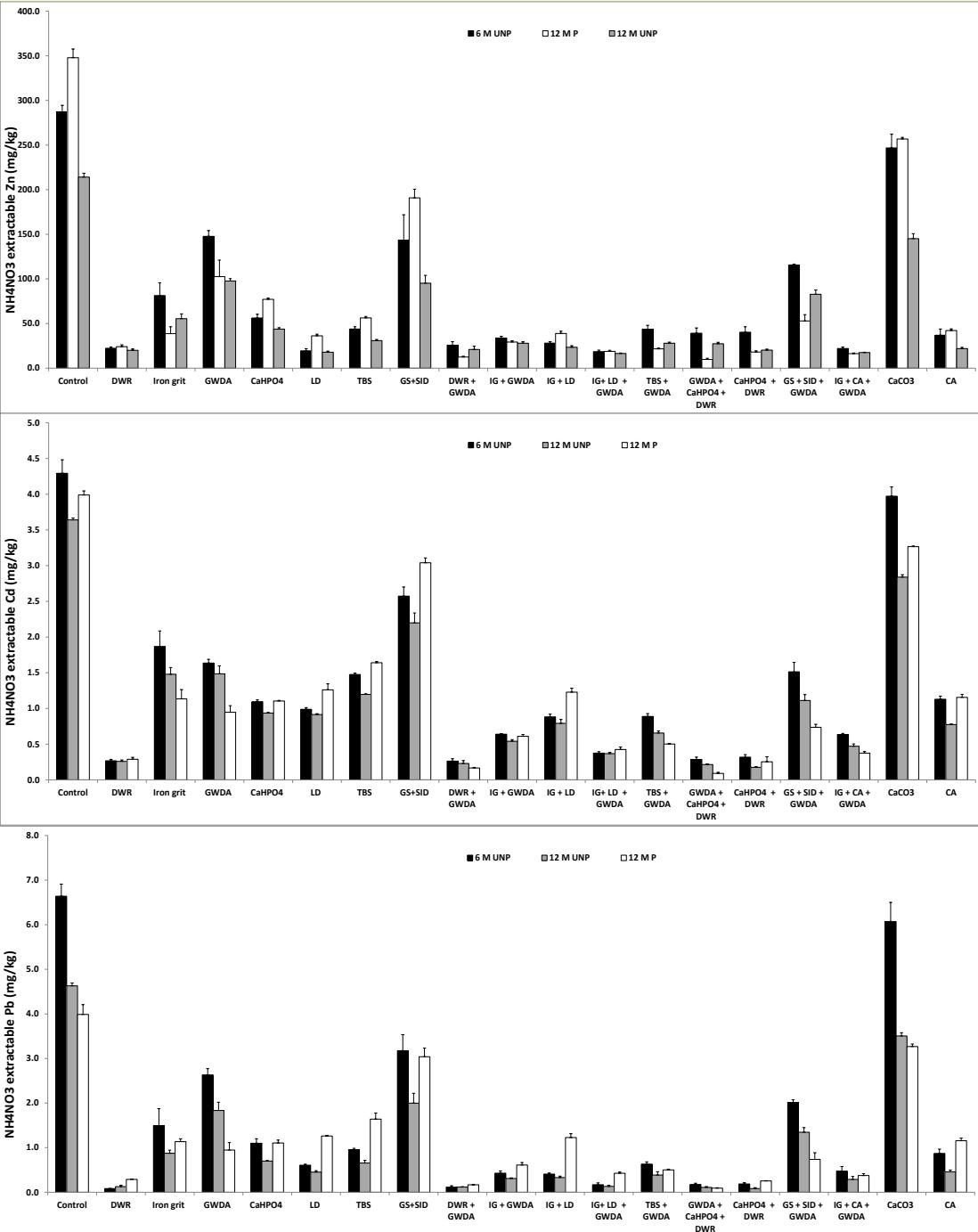


Effect of treatments on:

Zn in shoots

Cd in shoots

Pb in shoots



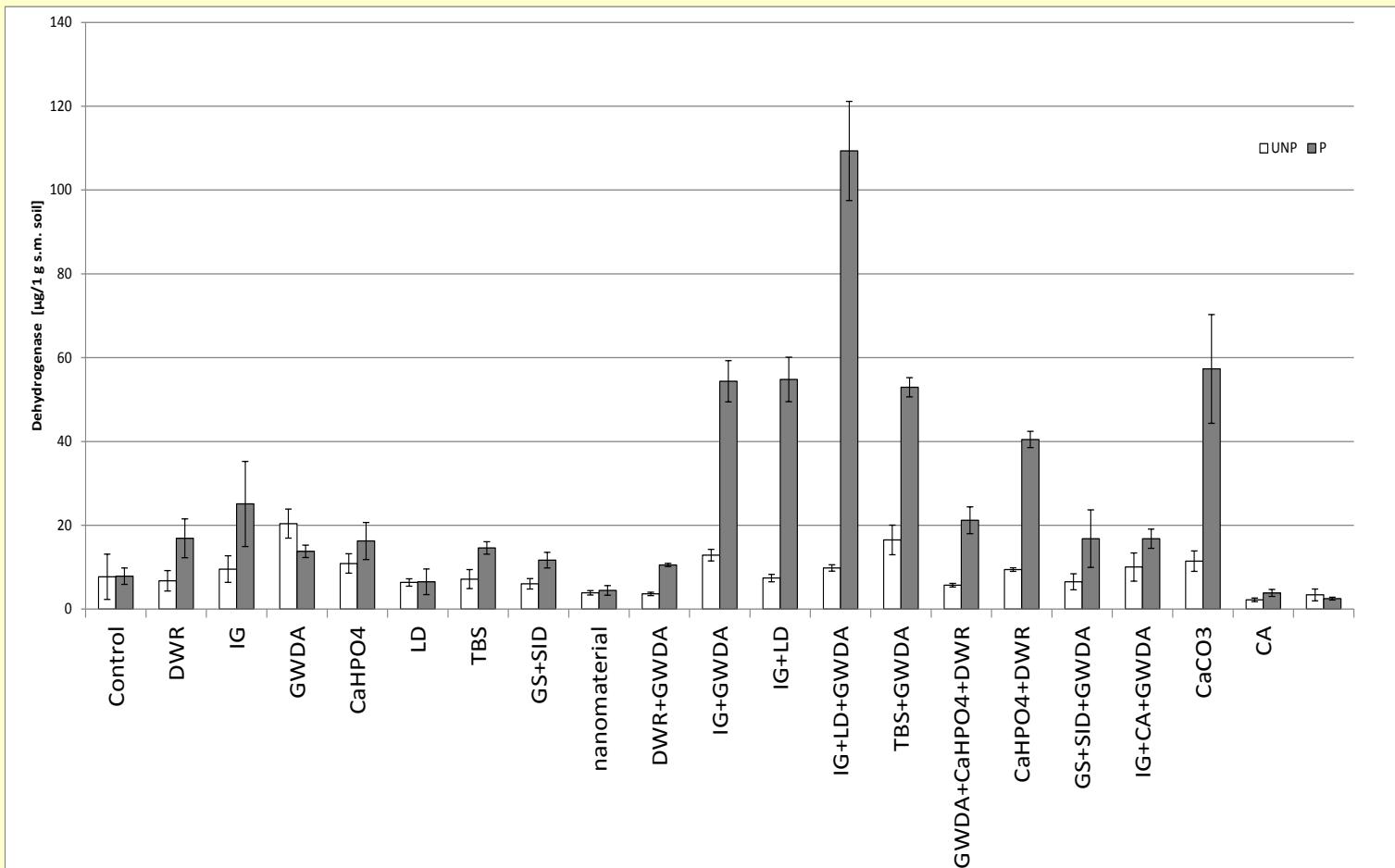
Effect of treatments on:

$\text{NH}_4\text{NO}_3$  extr. Zn

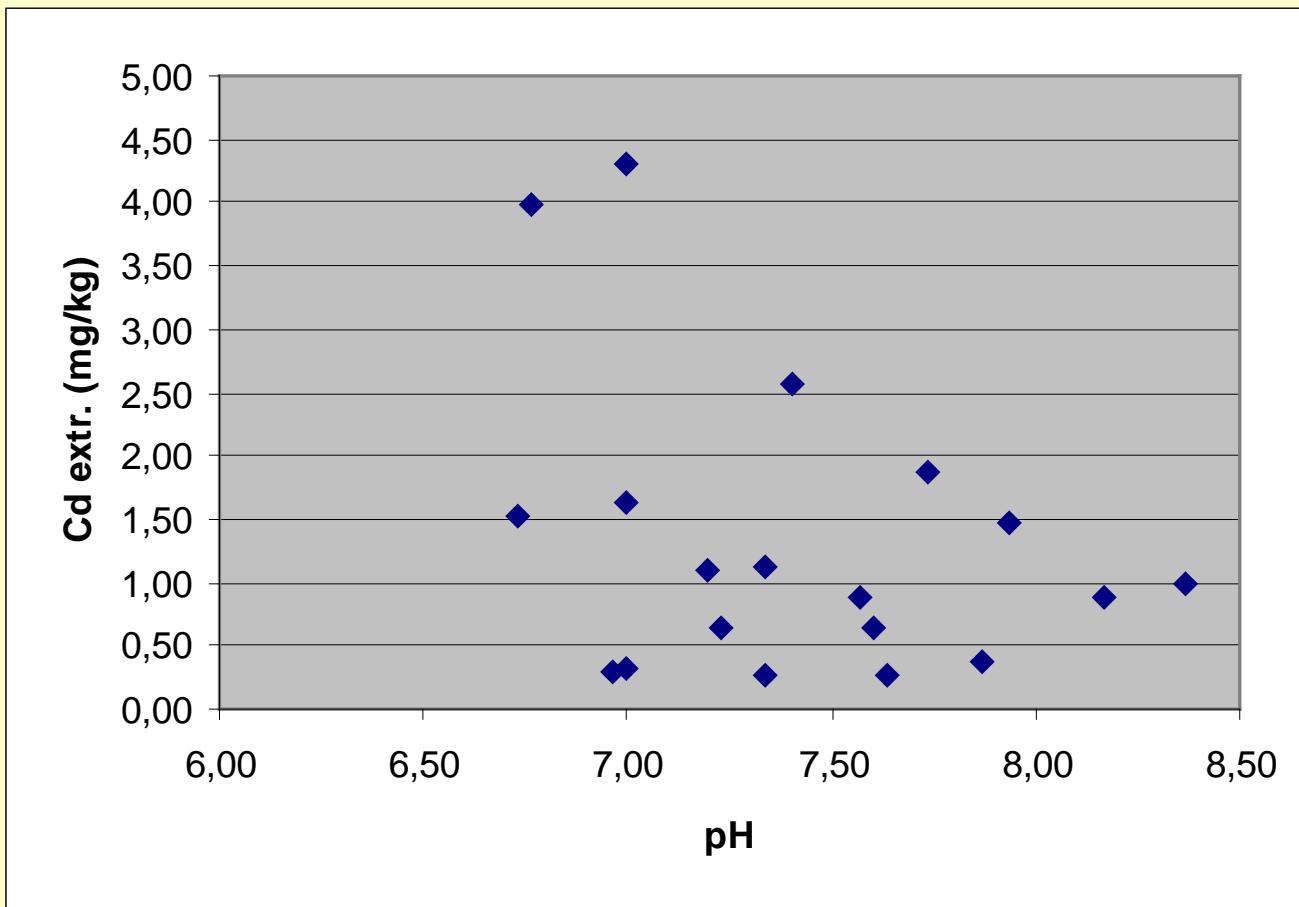
$\text{NH}_4\text{NO}_3$  extr. Cd

$\text{NH}_4\text{NO}_3$  extr. Pb

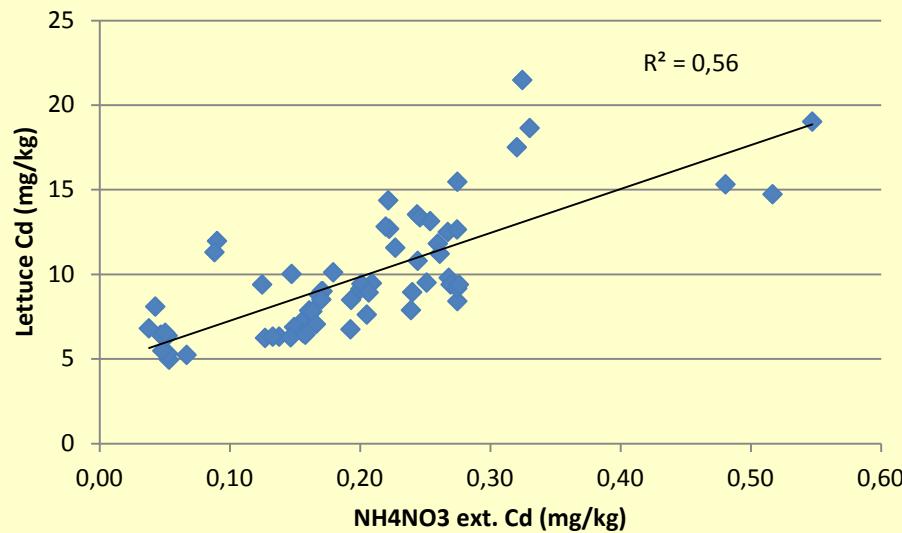
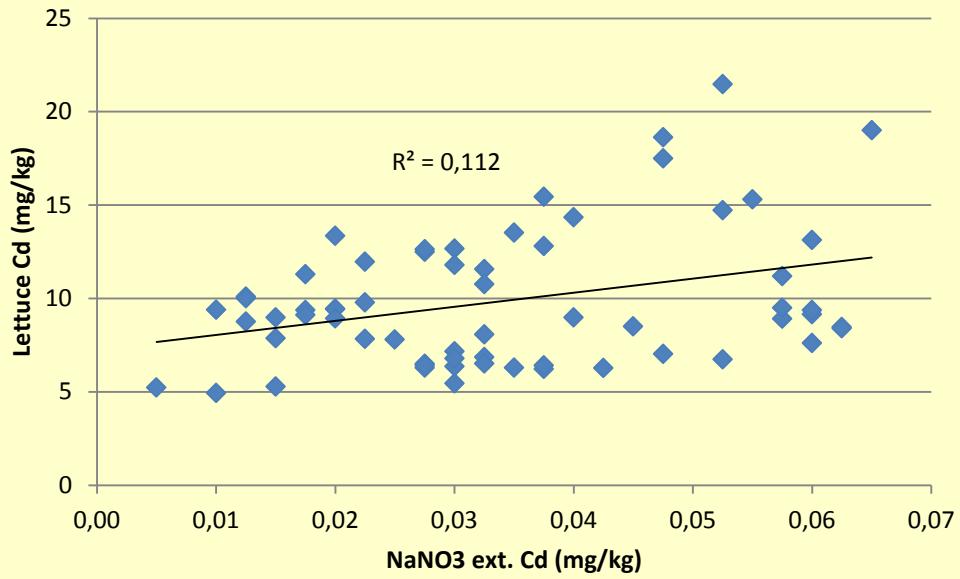
## Effect of treatments on dehydrogenase activity of soil B:



## Metal solubility not a simple effect of pH



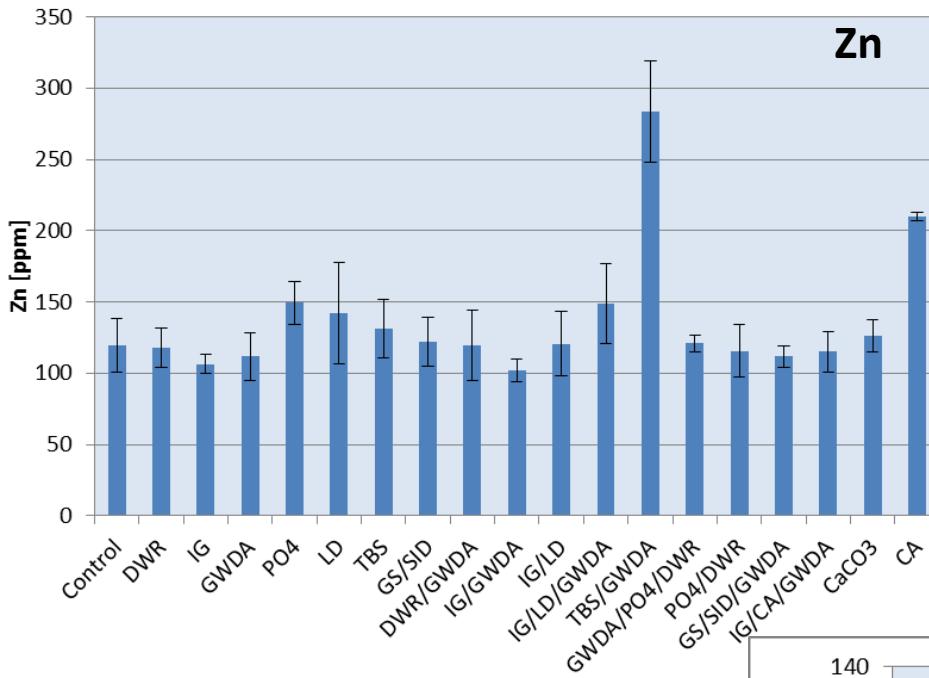
Soil PL-B – Ammonia nitrate extraction



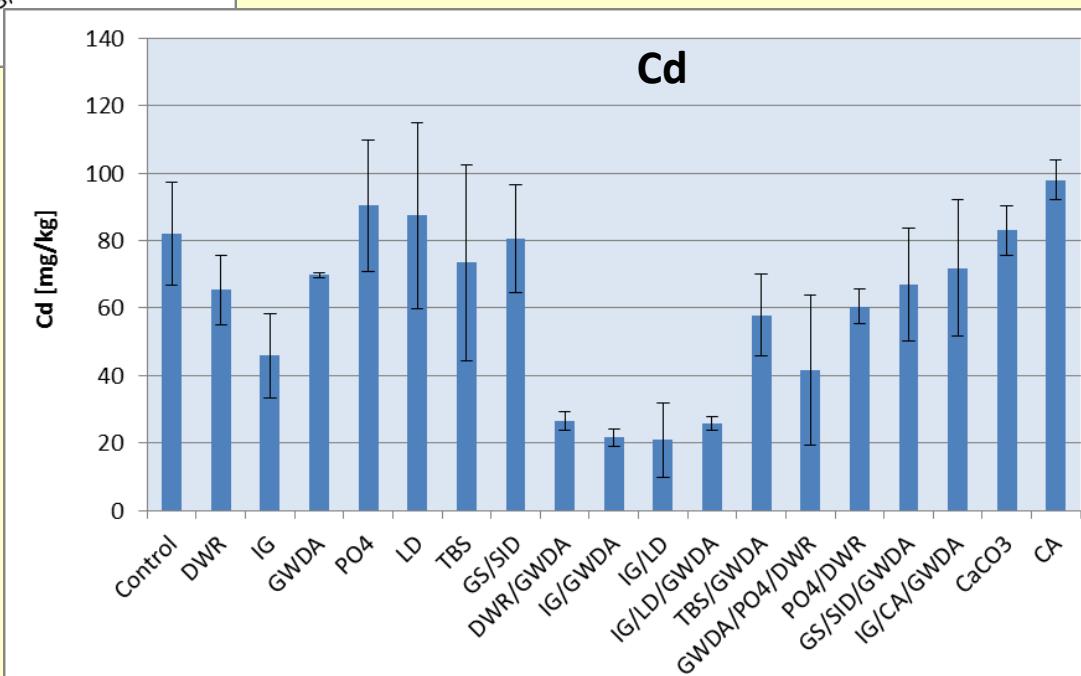
Relationship between 0.1M NaNO<sub>3</sub> or 1MNH<sub>4</sub>NO<sub>3</sub> extractable Cd and Cd in lettuce (soil PL-A; Month 6)

# Effect of treatments on metal accumulation in earthworm (*Eisenia veneta*)





**TE in earthwoms**



## Inoculation study

We tested whether effect of selected amendment combinations can be enhanced by bacterial inoculation of plants (*Festuca arundinacea*). Eight amendment combinations were tested at 2 rates and with 2 types of inoculants.

Amendment	Rate of addition
Control soil	Unamended
DWR	2.5%
DWR	5.0%
DWR + GWDA	2.5% (DWR), 2.5% (GWDA)
DWR + GWDA	5% (DWR), 5% (GWDA)
LD slag	0.25%
LD slag	0.5%
LD slag + IG + GWDA	0.25% (LD slag), 0.5% (IG), 2.5% (GWDA)
LD slag + IG + GWDA	0.5% (LD slag), 1.0% (IG), 5% (GWDA)

For each treatment:

- No inoculation
- Strain P87 (*Massilia niastensis*)
- P35 (*Pseudomonas koreensis*)

1 harvest



## 2 harvest



LD 0,5%+IG 1%+GWDA 5%

LD 0,25%+IG 0,5%+GWDA 2,5%



DWR 5%

DWR 5% -  
INOCULATION

DWR 5% -  
INOCULATION 1

DWR 5% -  
INOCULATION 2

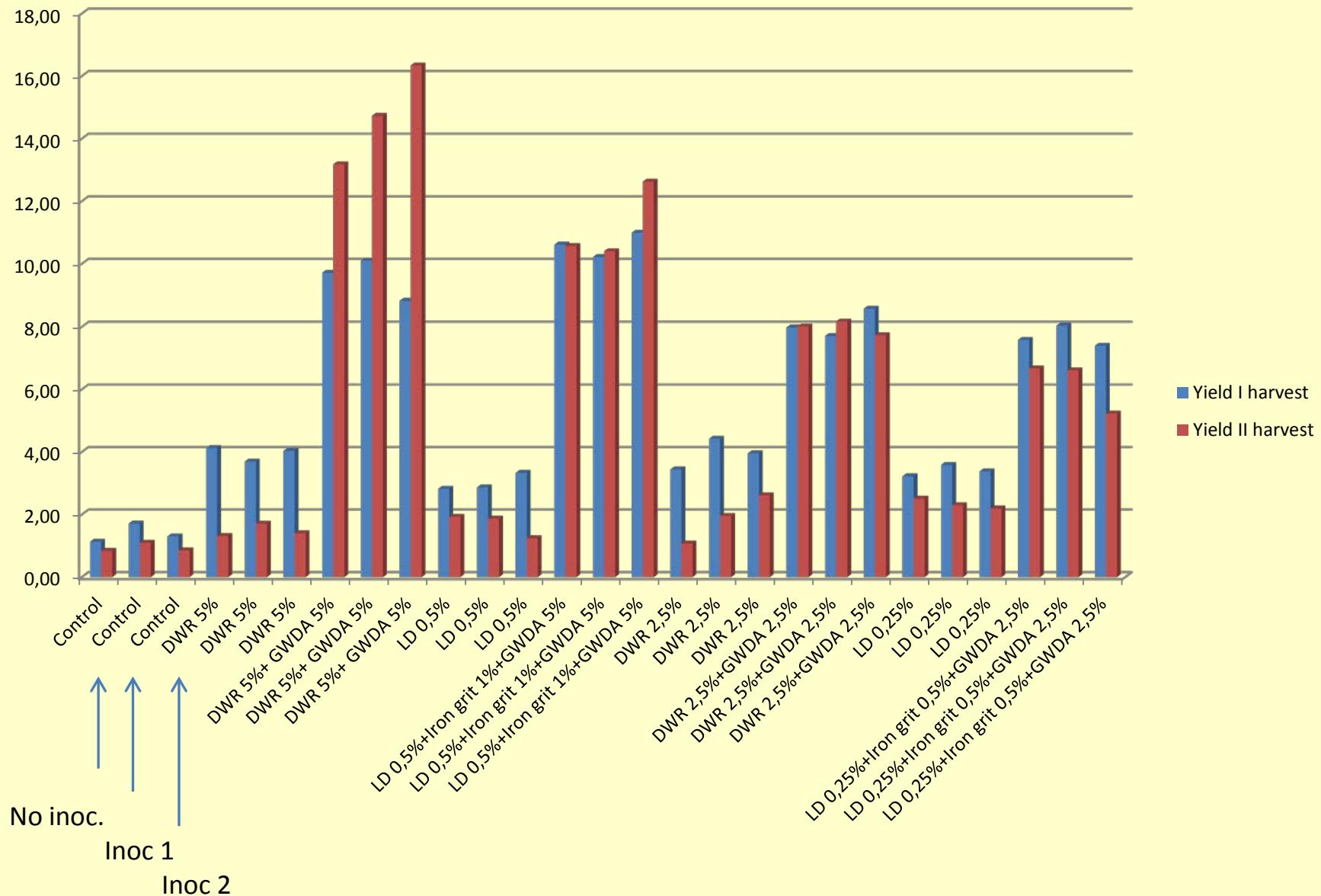
DWR 5% + GWDA 5% -  
NO INOCULATION

DWR 5% + GWDA 5% -  
INOCULATION 1

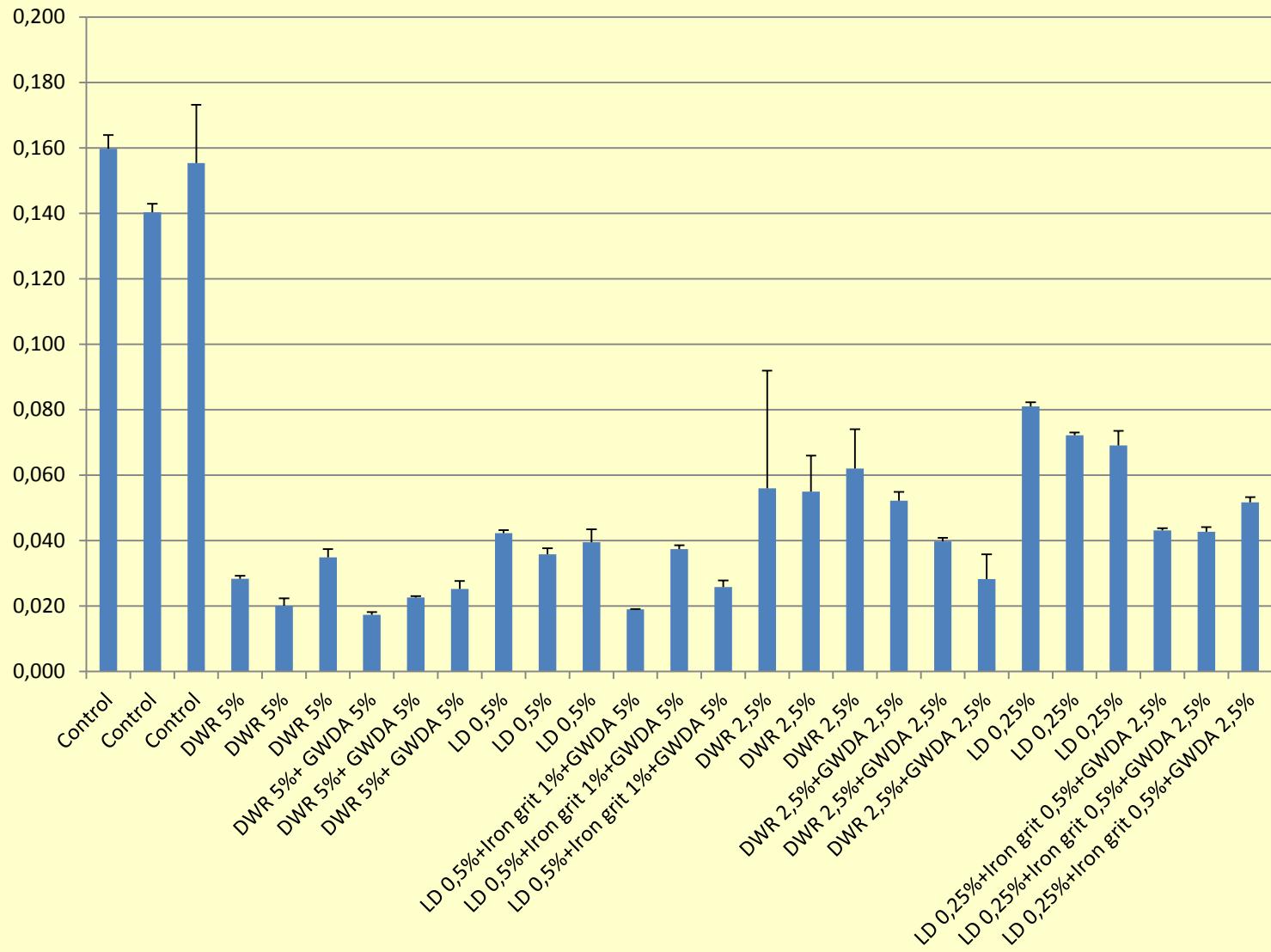
DWR 5% + GWDA 5% -  
INOCULATION 2

DWR 5% + GWDA 5%

## Effect of inoculation and rate on grass yield



## Effect of inoculation and rate on Cd water solubility at 1 harvest



*Tagetes patula*, no sediment, no inoculation 22.09.2014

*Tagetes patula*, no sediment (RP92)  
22.09.2014

*Tagetes patula*, no sediment (P87)  
22.09.2014



*Tagetes patula*, sediment, no inoculation  
22.09.2014

*Tagetes patula*, sediment (RP92)  
22.09.2014

*Tagetes patula*, sediment (P87)  
22.09.2014

**Bottom sediment contaminated soil**

## SOIL A – Summary table

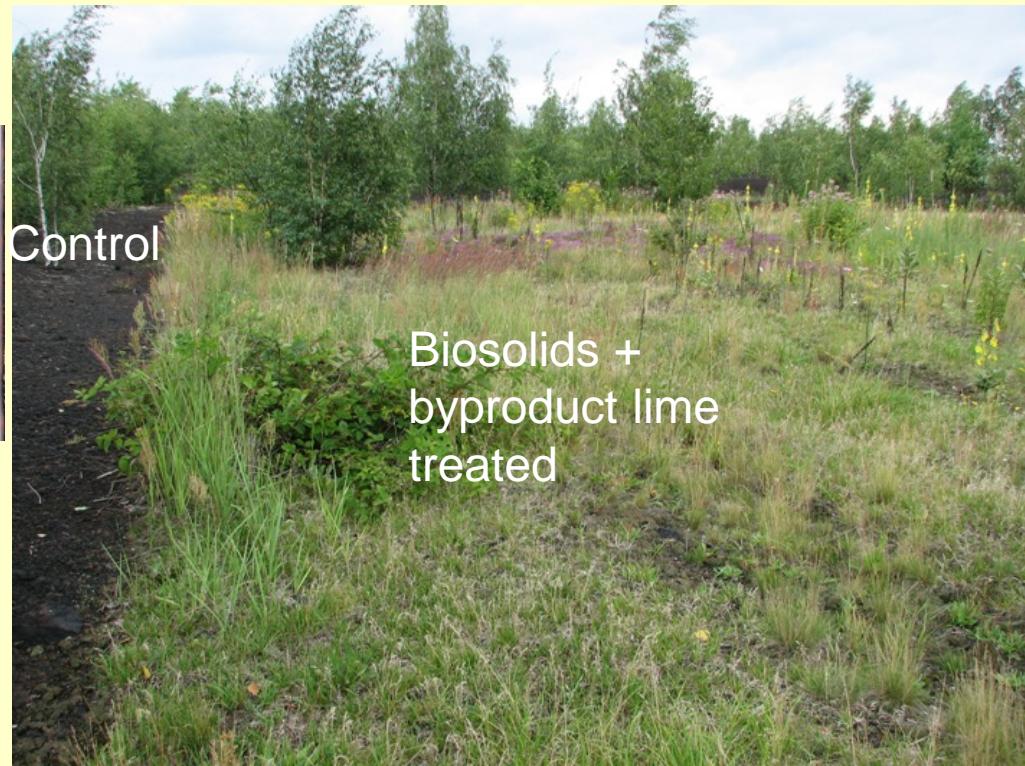
Treatment	Plant growth	Plant metal bioaccumulation		Soil metal availability			Soil enzymes	Metal leaching	Earthworm metal bioaccumulation		Scoring
		Cd	Pb	Zn	Cd	Pb			Cd	Pb	
Control	2	2	1	2	2	0	2	1	2	1	15
CaCO <sub>3</sub>	2	2	1	1	2	0	1	2	2	1	14
CaHPO <sub>4</sub>	2	2	1	2	2	1	2	1	2	1	16
IG	2	1	0	1	1	1	1	0	1	0	8
CA	2	2	2	1	2	0	0	2	2	2	15
LDslag	1	1	1	1	1	1	1	0	2	1	10
TBS	2	1	1	1	1	1	1	0	2	1	11
DWR	2	1	1	0	0	1	2	0	2	0	9
GWDA	0	1	0	1	1	1	1	1	2	0	8
GS+SID	2	2	1	1	2	1	1	0	2	1	13
IG+GWDA	1	1	1	1	1	1	0	1	0	0	7
IG+LDslag	1	1	0	1	1	1	1	0	0	1	7
TBS+GWDA	1	1	0	1	1	0	0	1	1	2	8
DWR+GWDA	0	0	0	0	0	1	0	1	0	0	2
CaHPO <sub>4</sub> +DWR	1	1	1	0	0	0	1	0	1	0	5
GS+SID+GWDA	0	1	1	1	1	0	0	2	2	0	8
IG+LDslag+GWDA	1	0	1	1	1	0	0	1	0	1	6
IG+CA+GWDA	1	0	0	1	1	0	0	2	2	0	7
CaHPO <sub>4</sub> +DWR+GWDA	0	0	0	0	0	0	0	0	1	0	1

## SOIL B – Summary table

## Conclusions

- Among single amendments Drinking Water Residue, compost GWDA and Iron Grit were the most effective in improving plant growth and reducing metal solubility and bioavailability
- In the phytoexclusion strategy where TE bioavailable pool in soil is smaller: only combinations give any effect
- In the phytostabilisation strategy single treatments reduce risk but combinations of treatments are much more effective
- The most effective combinations: DWR/compost combinations, IG/compost combinations

Thank you for your attention  
and GREENLAND friends for the collaboration



Piekary site 17y after  
reclamation