Evaluation of Fate of Added Copper and Zinc in Prairie Soils Using Chemical Speciation and XANES Spectroscopy

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Justification

Micronutrient deficiency issues in prairies:

- ***Site specific:***
  a patchy distribution related to spatial variability of soil properties

- ***Crop and element specific:***
  - Cu deficiency for cereal crops
  - Zn for pulse crops like pea

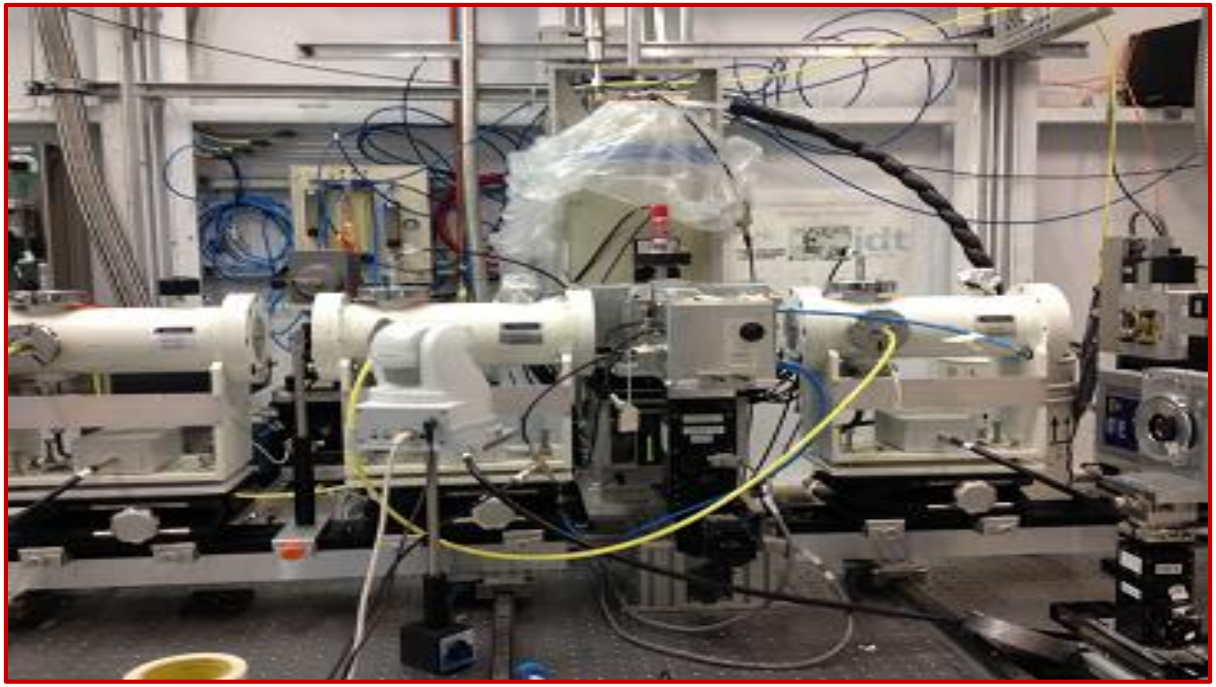
Justification

- Inconsistent yield response to fertilization reported
  - *Uncertainty about soil test critical levels*
- Soil properties can control fate and efficacy
  - *Transformation and complexation*
  - *Redistribution to unavailable pools*

Liang et al., 1990,91; Karamanos and Goh, 2001; Karamanos et al. 2003

Objective

To understand fate of different micronutrient fertilizer formulations added to contrasting soils



Methods and Materials

Whitewood Dark Gray Chernozem (Danbury)
Echo Brown Solodized Solonetz (Central Butte)
Whitefox Dark Gray Chernozem (Nipawin)
Sceptre Orthic Vertisol (Sceptre)
Ukalta Black Chernozem (Alix, AB)

Methods and Materials

Treatments	
Wheat (Cu)	***Pea (Zn)***
T_1: Control	T_1: Control
T_2: soil application @ 5 kg Cu ha^{-1} ($CuSO_4.5H_2O$)	T_2: soil application @ 2 kg Zn ha^{-1} ($ZnSO_4.7H_2O$)
T_3: soil application @ 2 kg Cu ha^{-1} (chelated product)	T_3: soil application @ 1 kg Zn ha^{-1} (chelated product)
T_4: foliar application @ 0.25 kg Cu ha^{-1} (chelated product)	T_4: foliar application @ 0.25 kg Zn ha^{-1} (chelated product)

Why XANES

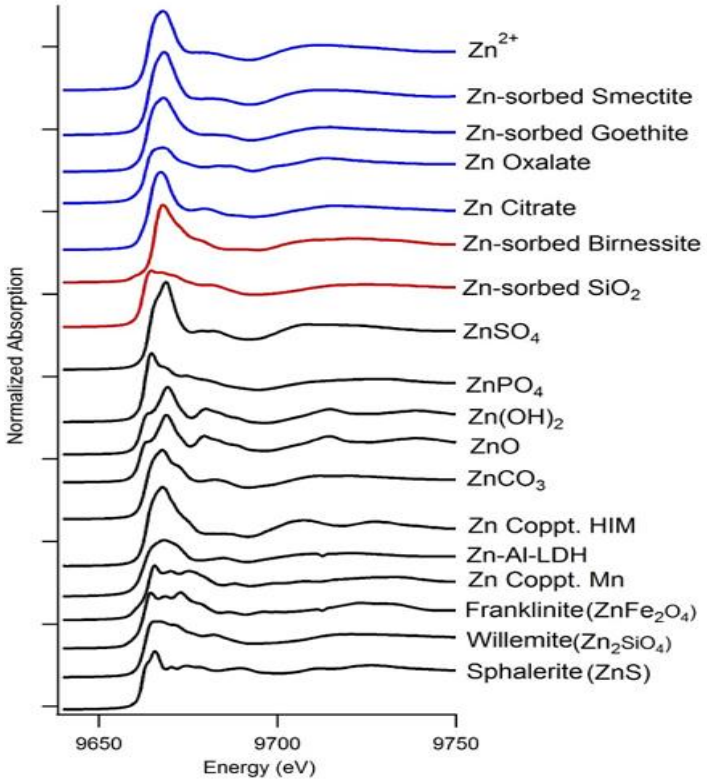
Traditional wet chemical analyses methods

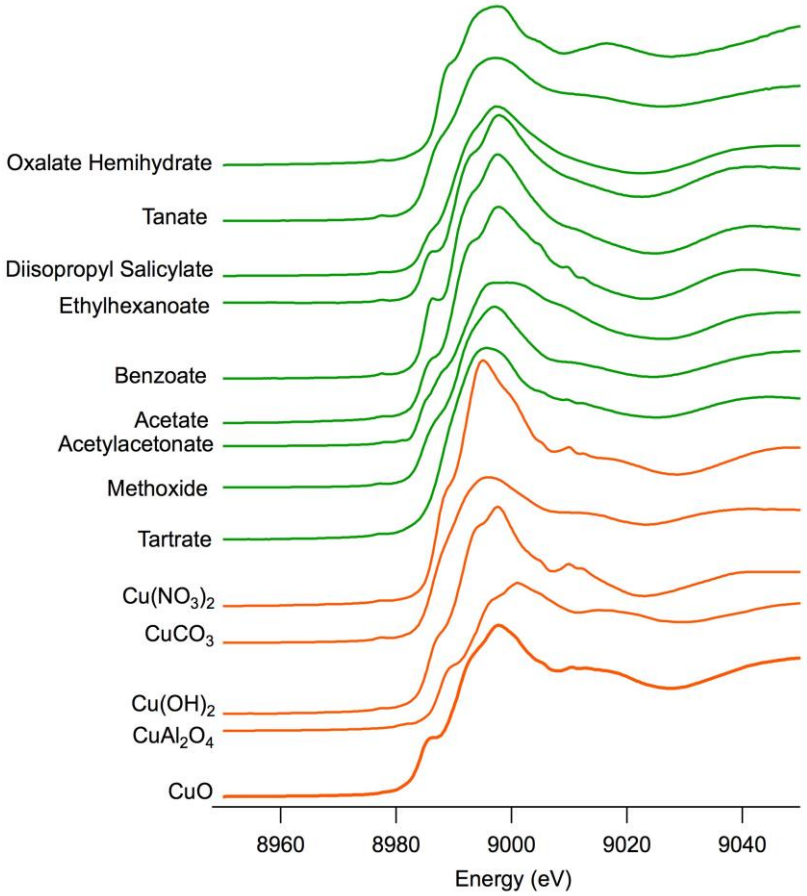
- Unable to identify particular species of Cu and Zn in soil.

- ***XANES spectroscopy can distinguish different oxidation states of an element***

- ***Offers unique ability to follow transformation of fertilizers through different forms.***

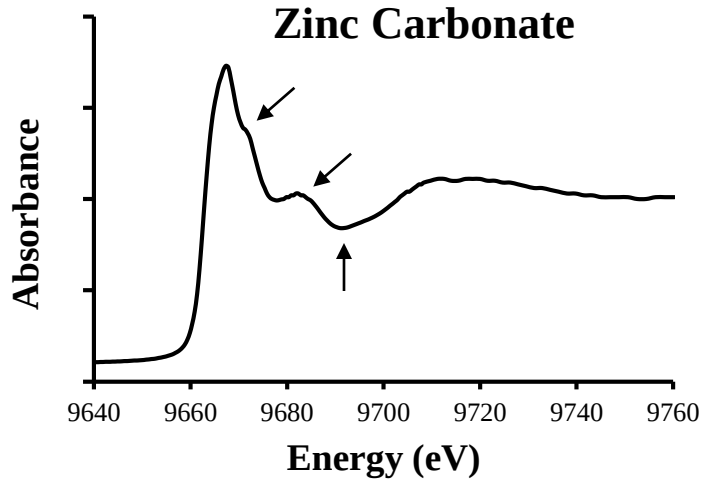
XANES spectra of Cu and Zn reference compounds



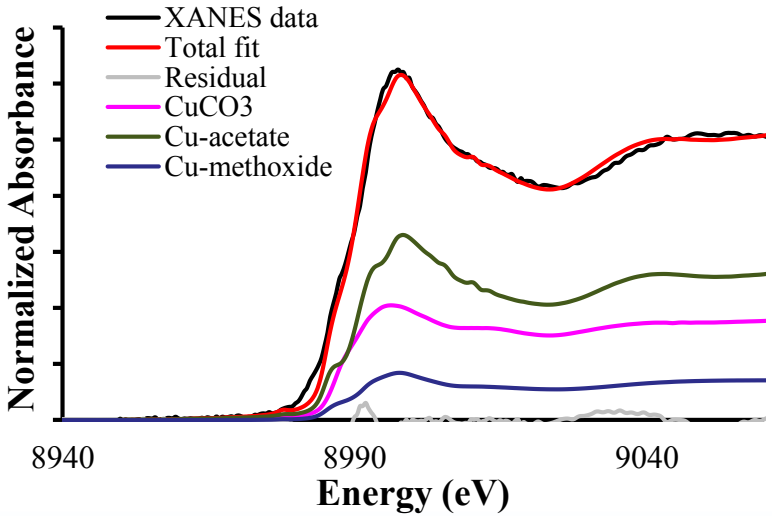


XANES Data Analysis Approaches

- **Qualitative analysis**
  - Fingerprint technique



- **Quantitative analysis**
  - LC fitting technique



Results

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Observed increased plant available Cu and Zn in soil after harvest with soil applied fertilizer could have rotational benefits

Post-Harvest Soil Residual DTPA extractable Cu and Zn

Treatment	Soil type				
	Whitewood	Echo	Whitefox	Sceptre	Ukalta
	----------mg Cu kg^{-1} soil----------				
T_1 (Con)	0.84a	0.70b	1.31c	1.83c	0.38b
T_2 (Soil)	3.07a	1.79a	4.56a	3.80a	1.77a
T_3 (Soil)	2.02a	1.35a	2.34b	3.47ab	0.60ab
T_4 (Foliar)	1.11a	0.74b	1.45bc	1.95bc	0.30b
p-values	0.057	<.0001	<.0001	0.009	0.013
	----------mg Zn kg^{-1} soil----------				
T_1 (Con)	1.44c	1.18b	1.73b	0.79b	2.43b
T_2 (Soil)	2.43a	1.89a	2.66a	2.03a	3.58a
T_3 (Soil)	1.86b	1.54a	2.01ab	1.20b	2.60b
T_4 (Foliar)	1.42c	1.15b	1.67b	0.92b	2.29b
p-values	<.0001	<.0001	0.012	<.0001	<.0001

Chemical speciation results

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Residence of **added Cu** in the **soil solution-carbonate-exchangeable** (F_1) and **oxyhydroxide** fractions (F_2)

Soil	Treat.	mg Cu kg^{-1} soil				
		F_1	F_2	F_3	F_4	F_5
Whitefox	T_1	0.61c	0.58c	1.65b	4.65a	7.49c
	T_2	**2.30a**	**2.05a**	**3.30a**	4.50a	12.2a
	T_3	**1.23b**	**1.13b**	1.91b	5.27a	9.64b
	T_4	0.60c	0.65c	1.72b	4.23a	7.19c
p-values		<.0001	<.0001	<.0001	0.064	<.0001
Ukalta	T_1	0.31b	0.09c	1.57b	4.29a	6.26b
	T_2	**1.27a**	**0.69a**	**3.10a**	2.80a	7.86a
	T_3	**0.72a**	**0.39b**	2.34ab	4.00a	7.45a
	T_4	0.28b	0.11c	1.68b	3.83a	5.91b
p-values		<.0001	<.0001	0.003	0.109	<.0001

Chemical speciation results

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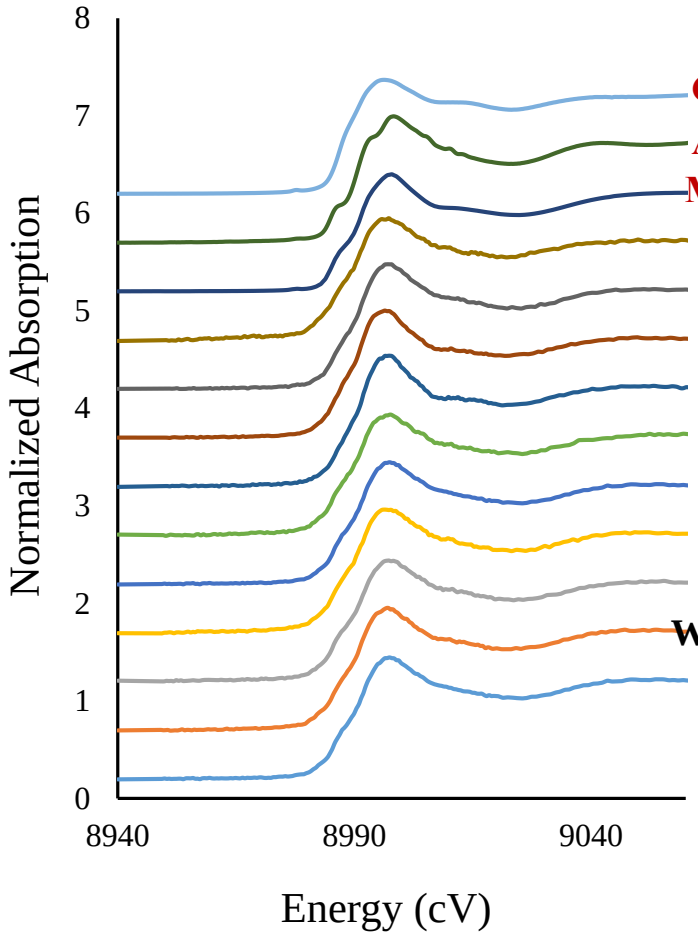
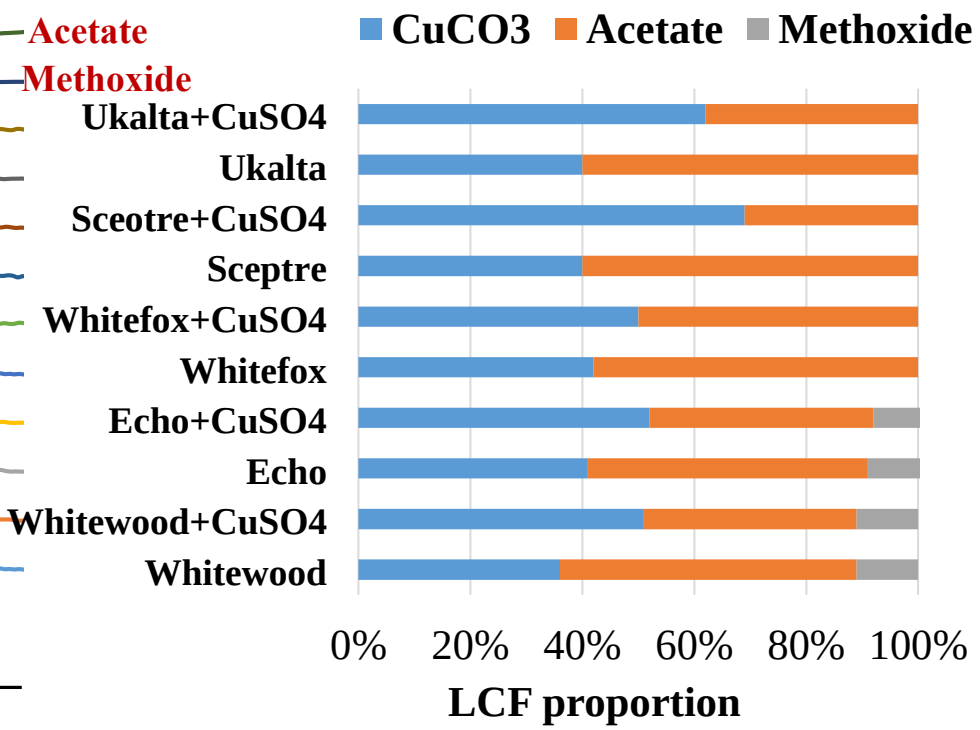
Residence of **added Zn** in the **soil solution-carbonate-exchangeable** (F_1) and **oxyhydroxide fractions** (F_2)

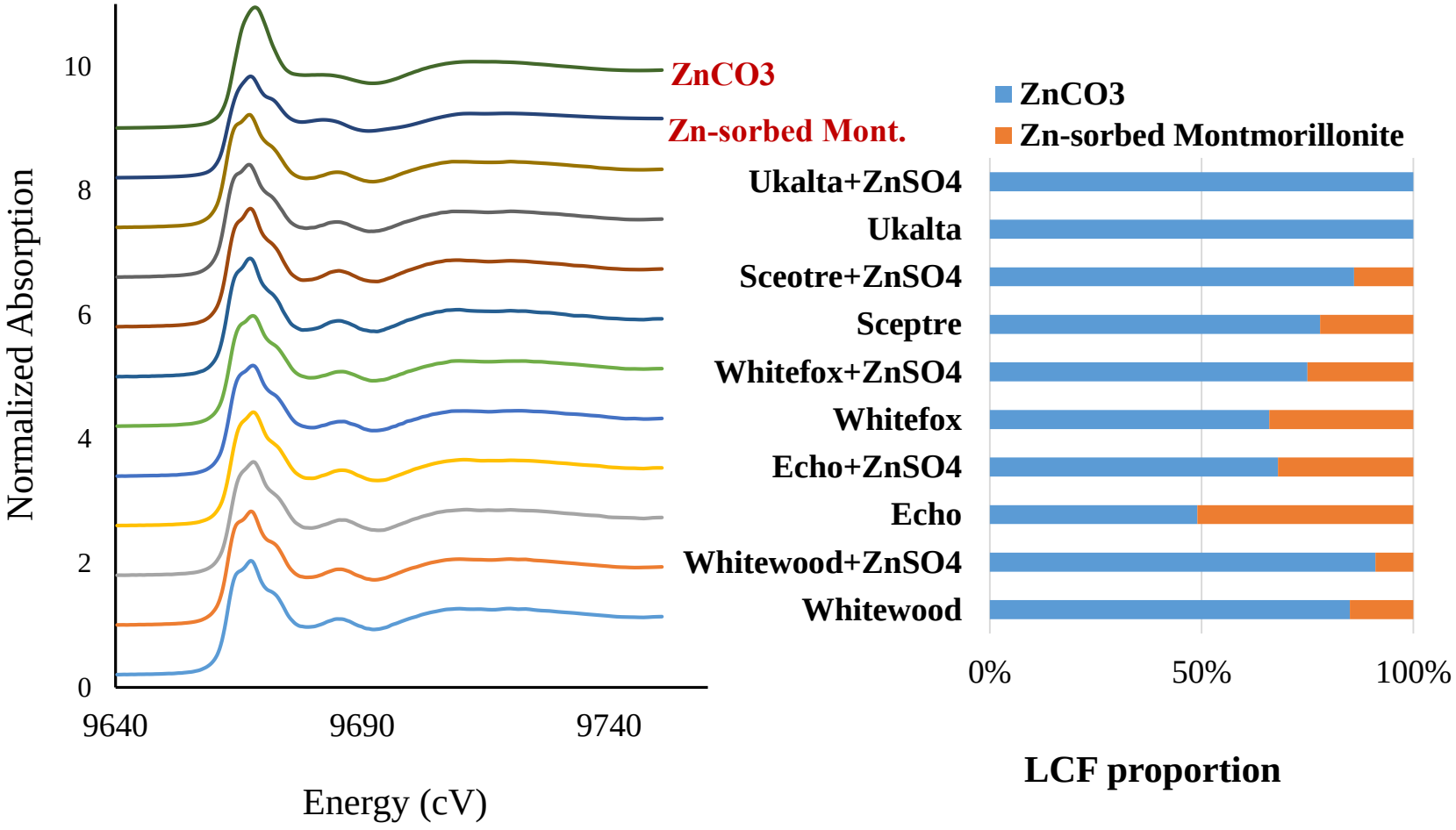
Soil	Treat	mg Zn kg^{-1} soil				
		F_1	F_2	F_3	F_4	F_5
Echo	T_1	0.77bc	4.24b	6.27a	33.9a	45.2a
	T_2	**1.11a**	**5.04a**	6.75a	34.4a	47.3a
	T_3	**0.90b**	4.33b	6.92a	35.8a	47.9a
	T_4	0.71c	4.13b	6.46a	34.3a	45.6a
p-values		0.003	0.002	0.05	0.788	0.477
Sceptre	T_1	0.41b	6.85c	12.3a	61.3a	80.9b
	T_2	**1.31a**	**8.68a**	12.9a	61.6a	84.5a
	T_3	**1.04a**	**7.52b**	12.8a	63.0a	84.3a
	T_4	0.39b	7.19bc	12.2a	59.8a	79.6b
p-values		<.0001	<.0001	0.197	0.160	0.009

Cu XANES spectra and LC Fit Results





Zn XANES spectra and LC Fit Results



Summary

- Carbonate is the dominant form of Cu and Zn, and adsorption to carbonates is likely the dominant process that determines fate of added fertilizer
- Organic forms of Cu (acetate) and Zn-sorbed montmorillonite can contribute to maintain bioavailability through chelation and cation exchange, respectively
- Applied $CuSO_4$ is mostly distributed to soil carbonates and oxyhydroxide fraction; but also to the organic fractions (e.g. Whitefox and Ukalta soils)
- Residual micronutrients from soil-applied fertilizer may favor performance of following crops grown in rotation

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Thank you

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