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THE CHEMICAL DISTRIBUTING CHARACTERISTICS AND DYNAMICS OF IRON, COBALT AND NICKEL IN 3 DIFFERENT ANAEROBIC DIGESTATES

Mimi Wang, Zhining Zhang, Zixiang Sun, Mengmeng Liu, Chen Sun, Weixing Cao

Green ecology and low-carbon energy technology research center,
Jiaxing University, Jiaxing, Zhejiang Province, 314001, China.

Speaker: Dr. Chen Sun

- Phone: +86 136-7185-0392
- E-mail: sunbeammy@163.com

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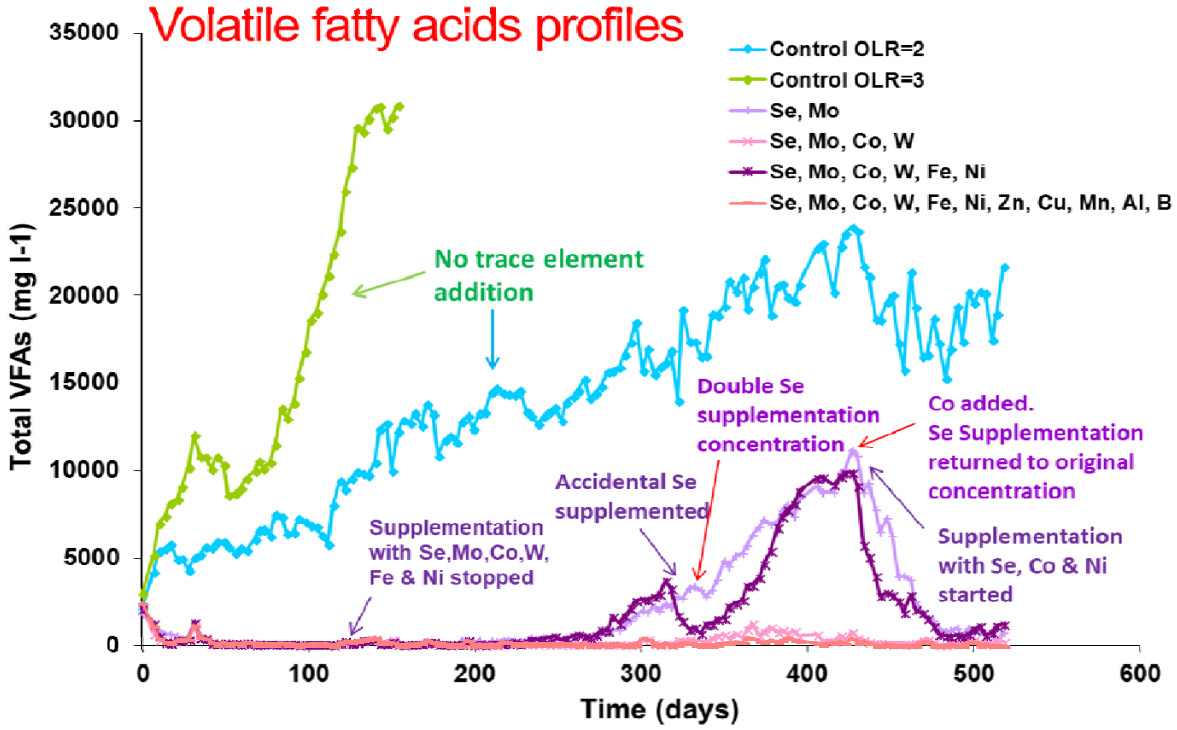
1. Introduction

- Unstable anaerobic digestion (AD) due to trace elements(TEs) deficiency in some feedstocks

  - Food waste
  - Municipal sewage
  - Energy crops
  - Agriculture residues
  - Animal manure
  - ……



Source： Banks, C. J., Y. Zhang, Y. Jiang and S. Heaven (2012). Trace element requirements for stable food waste digestion at elevated ammonia concentrations. Bioresource technology, 104: 127-135.

- The TEs dosage varied from one report to another：

- E.g., The 0.4 g Fe/kg and 0.5 mg Ni/kg benefited the biogas production from municipal solid waste and slaughterhouse waste (Moestedt et al., 2015)

- The 25 mg Fe/L and 5 mg Ni/L contribute to the highest biogas yield in the mesophilic batch AD of sludge (Yang et al., 2017).

- The recommended TEs dosage (Hinken et al., 2008) benificial to corn silage digestion, was unrepeatable in the batch AD study of rice straw (Mancini et al., 2017).

- Facchin et al. (2013) reported that the Co, Mo, Ni, Se, and W addition showed positive effect in food waste AD, while neutral or slightly negative effects in co-digestion of biowaste and waste activated sludge.

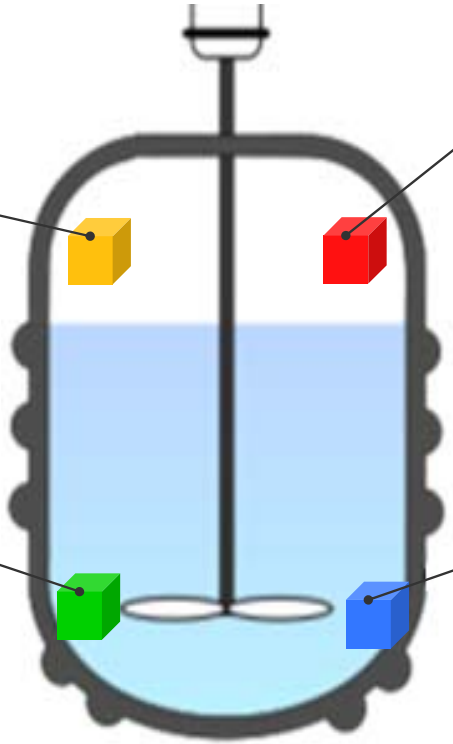
The 4 Reasons for the TEs dosage inconsistency

✓ Feedstock differences

- TEs background values
- TEs distribution patterns

✓ Microflora differences

- Microflora species
- Ecological distribution
- Abilities for obtaining TEs



✓AD process parameter differences

- Diversity of digestate influence chemical forms of TEs:
- pH, alkalinity, redox potential, sulfur, phosphorus, potassium, extracellular polymeric substance (EPS), soluble microbial products(SMP), et al.;

✓ Evaluation methodology

- Emphasis should be put on TEs bioavailability,
- other than total TEs addition

It's important to know the TEs distributing rule & actual bioavailability in different AD

Objective :

To evaluate the effect of pH value, digestate type, TEs dosage and retention time on the dynamical chemical speciation of endogenous and exogenous Fe, Ni and Co in 3 different digestate.

Significance and Prospects :

To provide a basic scientific reference for:

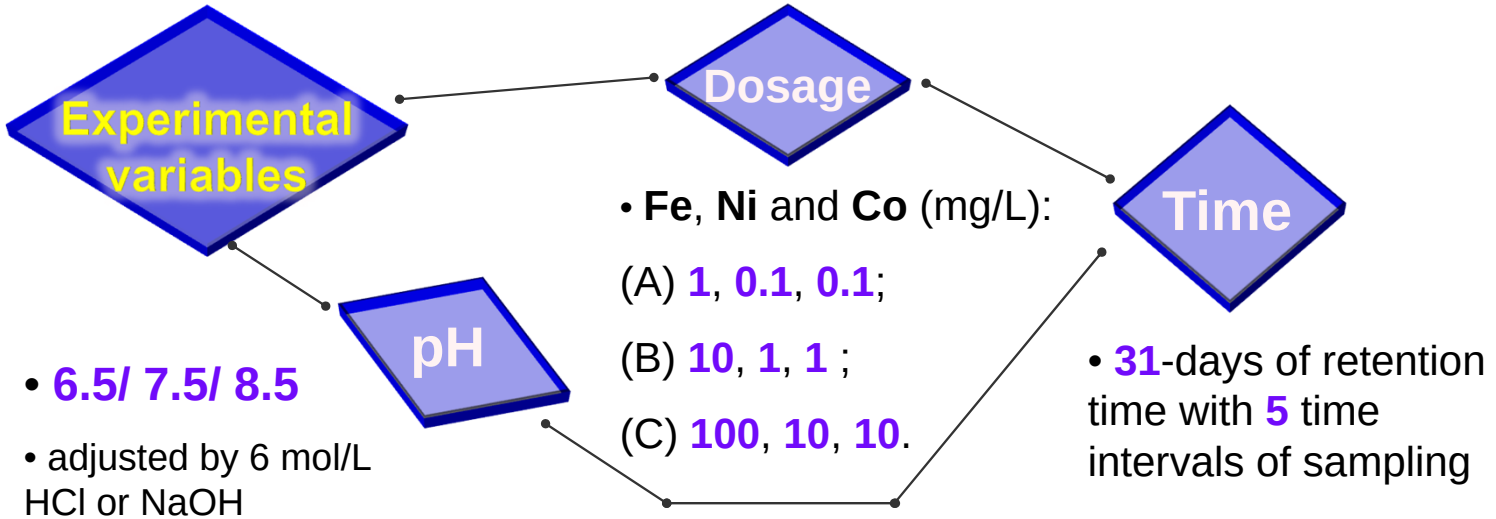
- The optimization of the TEs dosing strategy;
- The exploitation of the endogenous TEs utilization;
- The bioavailability risk assessment of TEs in digestate to its discharging environment.

2. Materials and Methods

- 3 types of anaerobic digestates：

maize stalk (MS); pig slurry (PS); waste water from chocolate factory (WW)

- Targeted TEs: Fe, Ni, & Co (Endogenous or exogenous)
- Evaluation method: Sequential extraction



2. Materials and Methods

1.


2.


3.

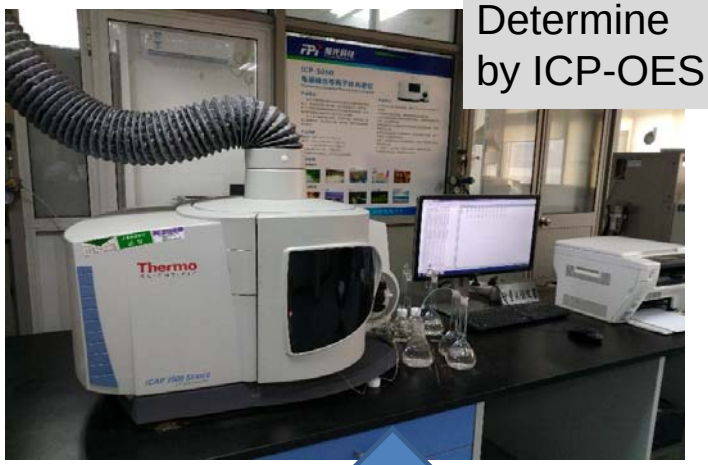

4.


BCR method		Modified Tessier's method	
1. Acid Extractable	HOAc	**1. Water-soluble**	distilled water
		2. Ion-exchangable	$MgCl_2$
		3. Carbonate	NaAc
		4. Weak organic combination (humic acid)	$Na_4PO_7 \cdot 10H_2O$
2. Reducible	$NH_2OH \cdot HCl + HNO_3$	**5. Fe-Mn Oxidates**	$NH_2OH \cdot HCl + HCl$
3. Oxidizable	H_2O_2	**6. Strong organic combination**	$NH_4OAC + HNO_3 + H_2O_2$
4. Residual	$HNO_3 + HF + HClO_4$	**7. Residual**	$HNO_3 + HF + HClO_4$

Quantitative TEs determination

Pre-digestion

Strong acid+ microwave digestion



Determine by ICP-OES

3. Results and Discussion

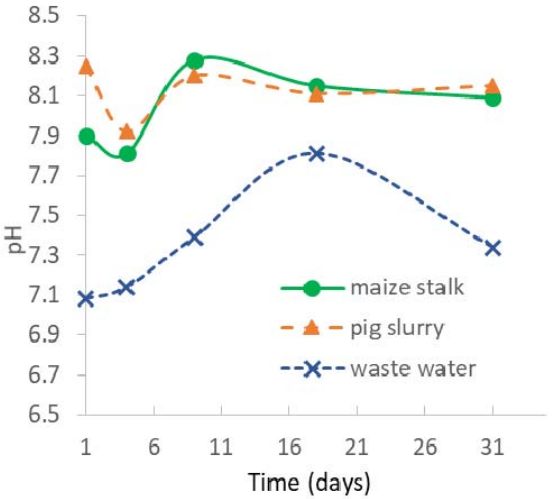
3.1 Characteristics of 3 different digestates

	digestate source		
items	maize stalk	pig slurry	waste water of chocolate factory
pH	8.16	8.46	7.20
TS, g/kg	147.8	113.1	21.23
VS, g/kg	56.79	69.20	10.68
COD, g/kg	52.95	72.49	9.38
VFAs, mg/kg	1282	1766	unfound
TP, mg/kg	132.4	117.6	2.12
TN, mg/kg	2600	3083	141.3
S, mg/kg	1274	1231	139.5
TA, g CaCO3/kg	24.70	26.40	12.31
PA, g CaCO3/kg	18.81	19.63	10.32
IA, g CaCO3/kg	5.89	6.76	1.99
IA/PA	0.31	0.34	0.19
Total Fe, mg/kg	673.7	652.8	652.7
Total Ni, mg/kg	2.242	1.947	0.946
Total Co, mg/kg	0.672	0.513	0.119

MS, PS>WW

Similar

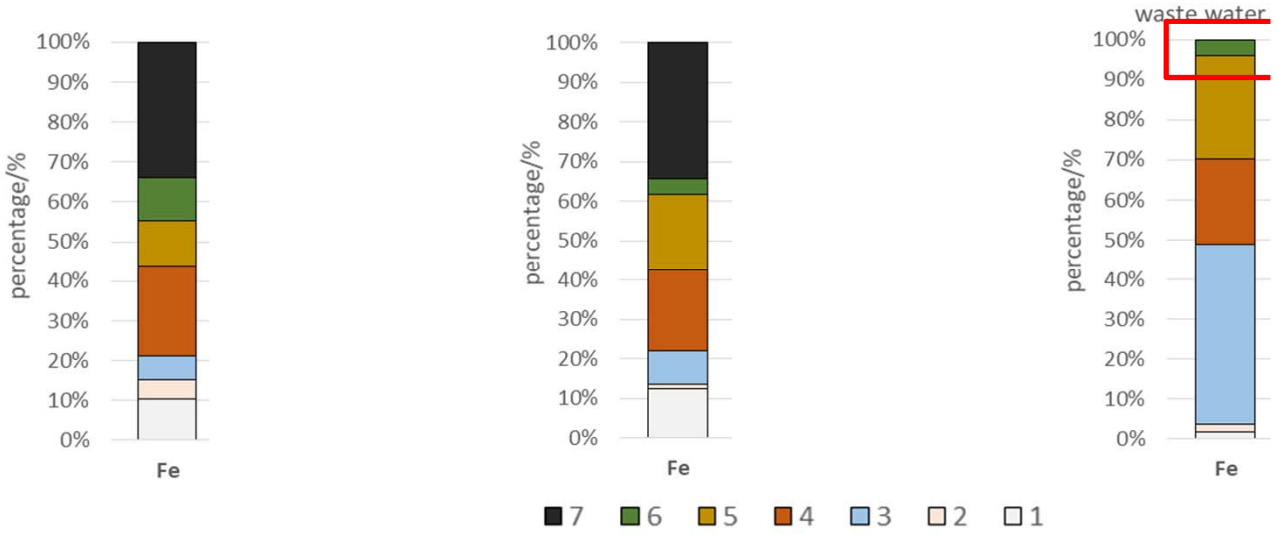
MS, PS>WW



The pH variation of maize stalk, pig slurry and waste water digestate during AD

3. Results and Discussion

3.1 Characteristics of 3 different digestates



The chemical forms distribution of Fe, Ni and Co in the 3 digestates (mg/kg ww)

1: water-soluble fraction; 2: ion-exchangable fraction; 3: carbonate fraction; 4: weak organic combination fraction;
5: Fe-Mn oxides fraction; 6: strong organic combination fraction; 7: residue fraction.

3.2 The pH effect on the chemical distribution of Fe, Ni, and Co

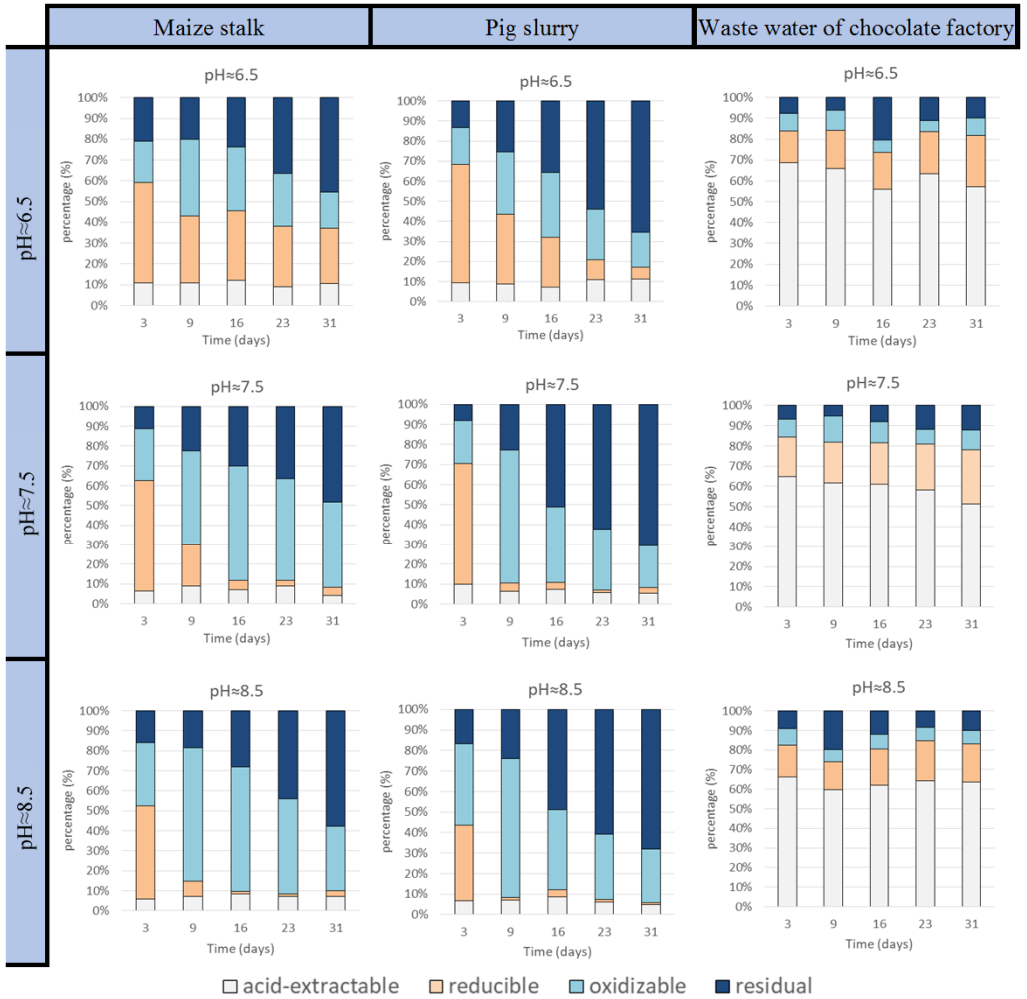
3.2.1 The chemical fractions of **Fe** under different pH

- WW digestate showed different distribution pattern ;
- The pH affected Fe distribution:

✓ pH 6.5 enhanced acid-extractable and reducible Fe;

✓ pH 8.5 enhanced the oxidizable and residual Fe.

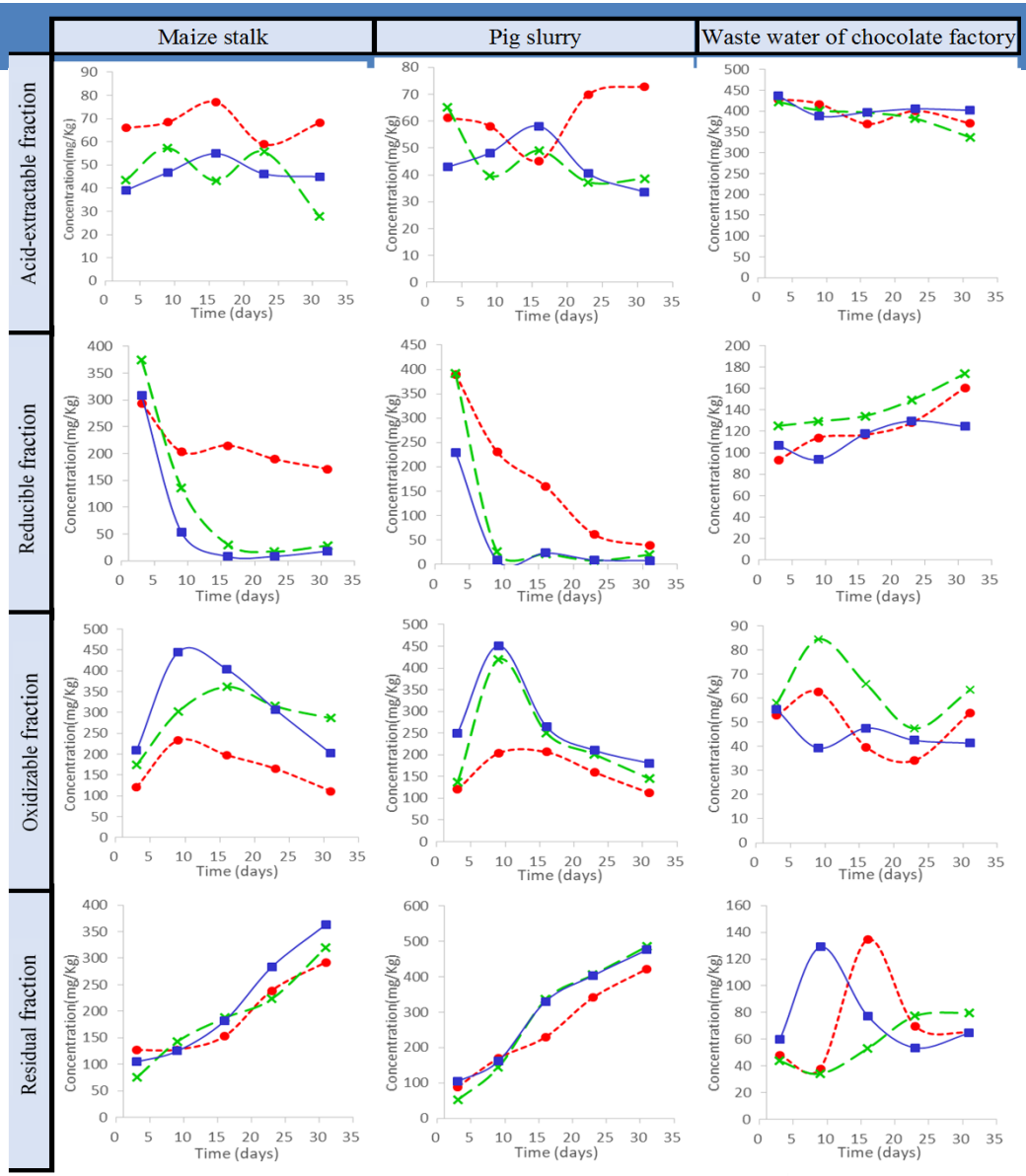
- AD and higher pH reduced Fe bio-availability.



The chemical fraction proportions of endogenous Fe in the three digestate under different pH

3.2.1 Chemical fractions of **Fe** under different pH

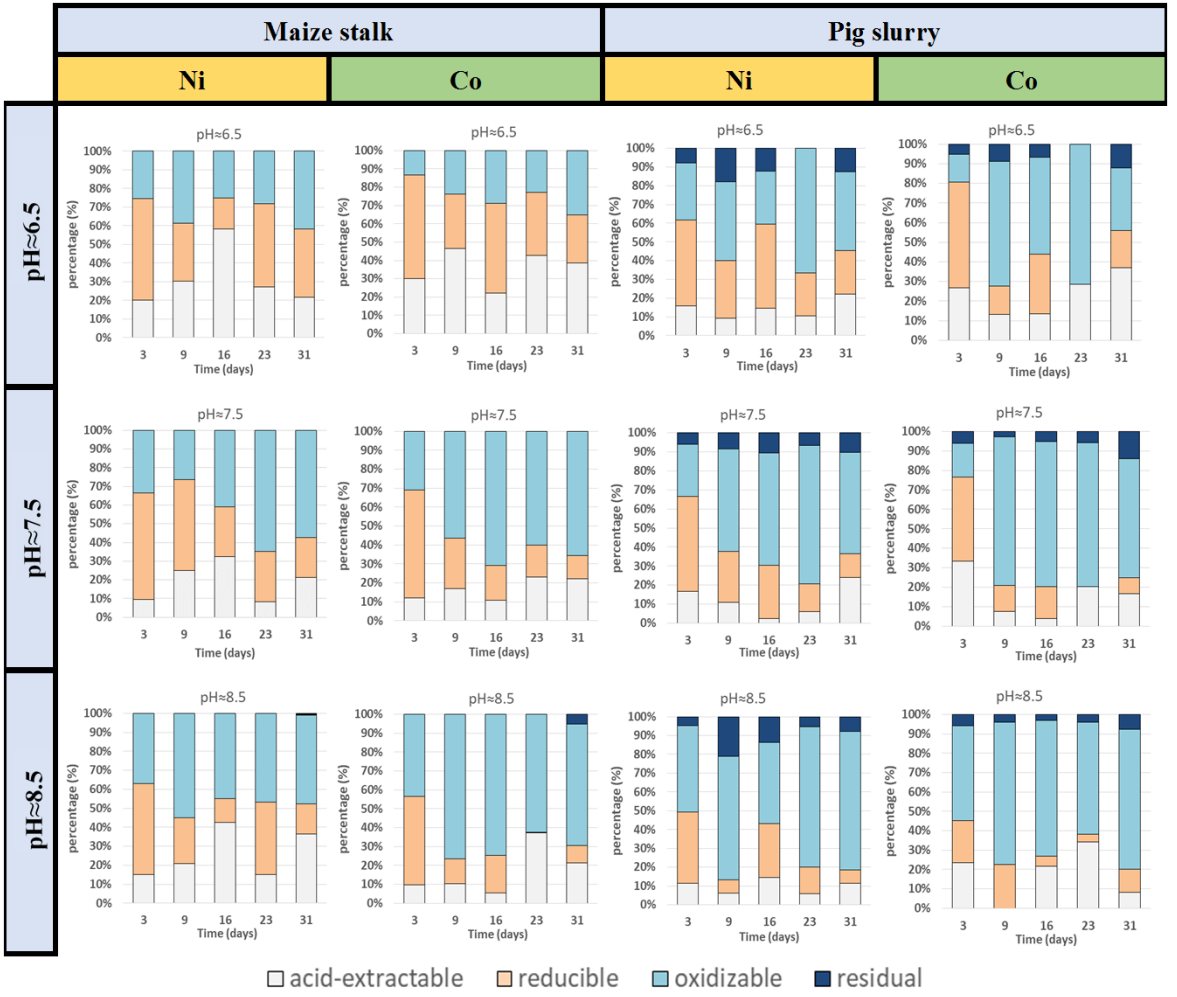
- WW digestate showed different dynamic pattern;
- pH exerts effects mainly on MS and PS digestate;
- pH 6.5 slowed down the decrease of reducible Fe and the increase of oxidizable Fe in MS and PS, indicating that acidic pH increased the Fe bio-availability.



The chemical form distrition dynamics of endogenous Fe in the three digestate under different pH

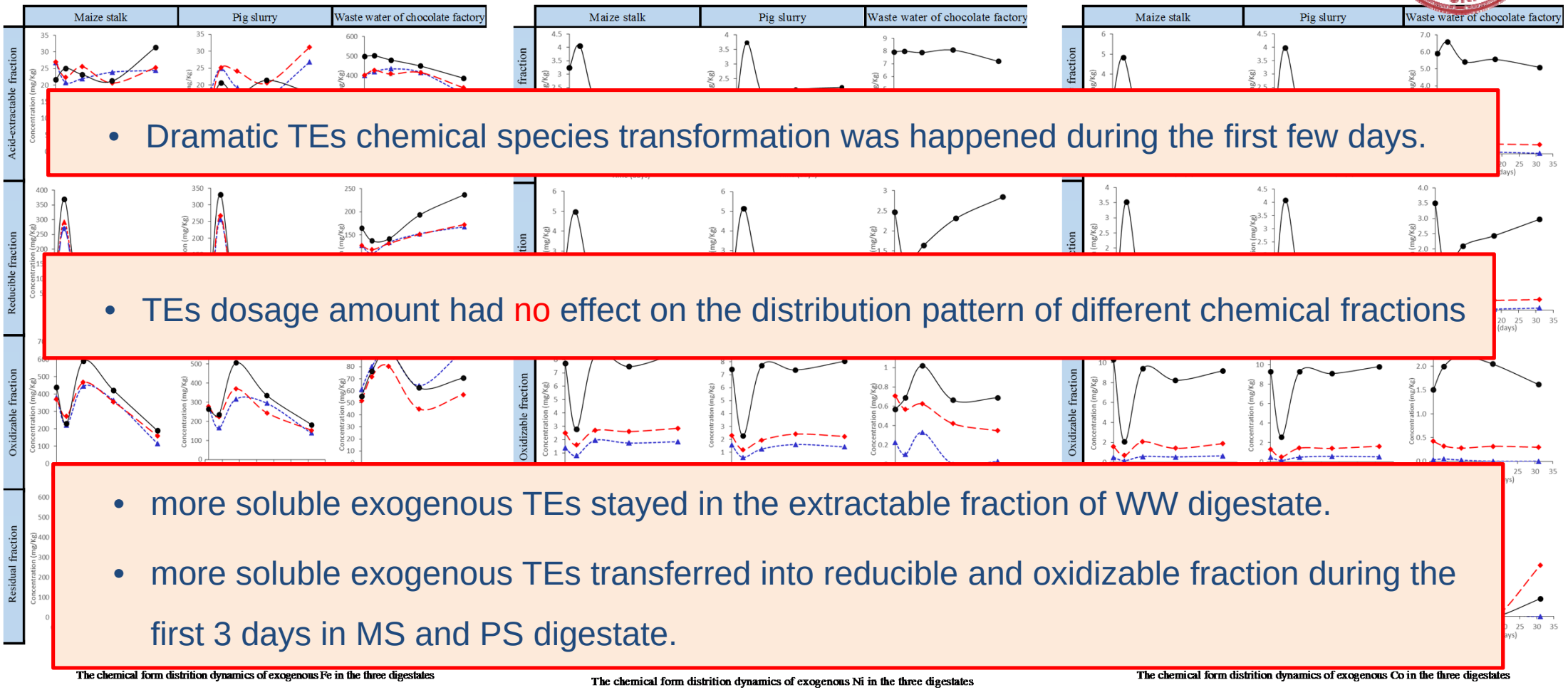
3.2.2 Chemical fractions of **Ni** and **Co** under different pH

- Similar to Fe, pH 6.5 enhanced extractable and reducible Ni & Co, and decreased oxidizable Ni & Co in MS and PS digestate;
- Unlike Fe, the Ni and Co distributing patterns in MS and PS are different;
- acidic pH increased the TEs bio-availability



The chemical fraction proportions of endogenous Ni and Co in MS and PS digestate under different pH

3.3 Chemical distribution dynamics of exogenous Fe, Ni &Co



- Dramatic TEs chemical species transformation was happened during the first few days.
- TEs dosage amount had no effect on the distribution pattern of different chemical fractions
- more soluble exogenous TEs stayed in the extractable fraction of WW digestate.
- more soluble exogenous TEs transferred into reducible and oxidizable fraction during the first 3 days in MS and PS digestate.

The chemical form distrition dynamics of exogenous Fe in the three digestates

Fe

The chemical form distrition dynamics of exogenous Ni in the three digestates

Ni

The chemical form distrition dynamics of exogenous Co in the three digestates

Co

4. Conclusions

1) The chemical distribution patterns of Fe, Ni and Co was not influenced by the amount of exogenous TEs dosage, but by the pH and digestate type.

2) The pH 6.5 showed negative effect on the recovery of high proportion of reducible TEs fraction formed in the first few days, which was beneficial for the bioavailability.

3) The pH value exerted different effects on different digestate. There were more effects showed on MS and PS digestate, while less on WW digestate.

4) AD process contributed to TEs transforming into less bioavailable state.

Thank you for your attention !

Dr. Chen Sun
Green ecology and low-carbon energy technology research center,
Jiaxing University, Jiaxing, Zhejiang Province, 314001, China.
Phone： +86 136-7185-0392
E-mail: sunbeammy@163.com