Recovery of Plant Nutrients, Potentially toxic trace and Valuable Elements via Anaerobic Digestion and Acid-Leached Digestate Ash

Presenter:

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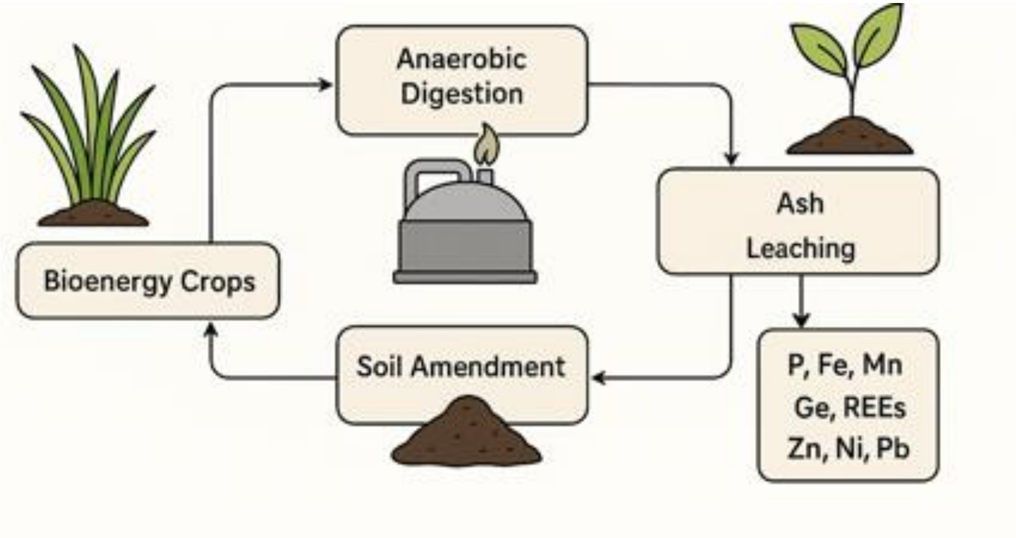
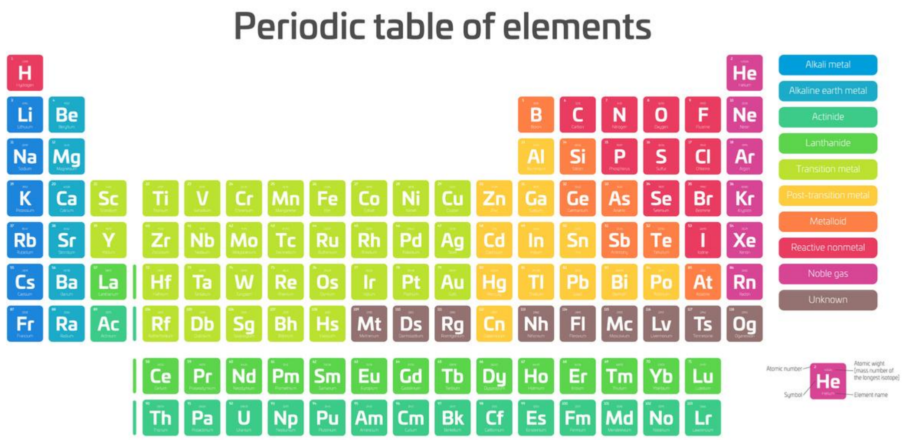
- Institute of Biosciences
- TU Bergakademie Freiberg

- Date 08.05.2025





Background & Problem Statement

- Growing demand for plant nutrients (P, Fe, Mn) potentially toxic elements (Zn, Cr, As, Cd, Cu, Pb) and valuable elements (Ge, REEs)
- High nutrient and metal concentrations in bioenergy crops and biosolids
- Use of *Phalaris arundinacea* as bioenergy crop
- Role of anaerobic digestion (mesophilic vs. thermophilic) bioenergy and circular economy
- Unused potential in digestate and ash for element recovery
- Need for sustainable and safe phytomining, nutrient recovery, and circular use strategies

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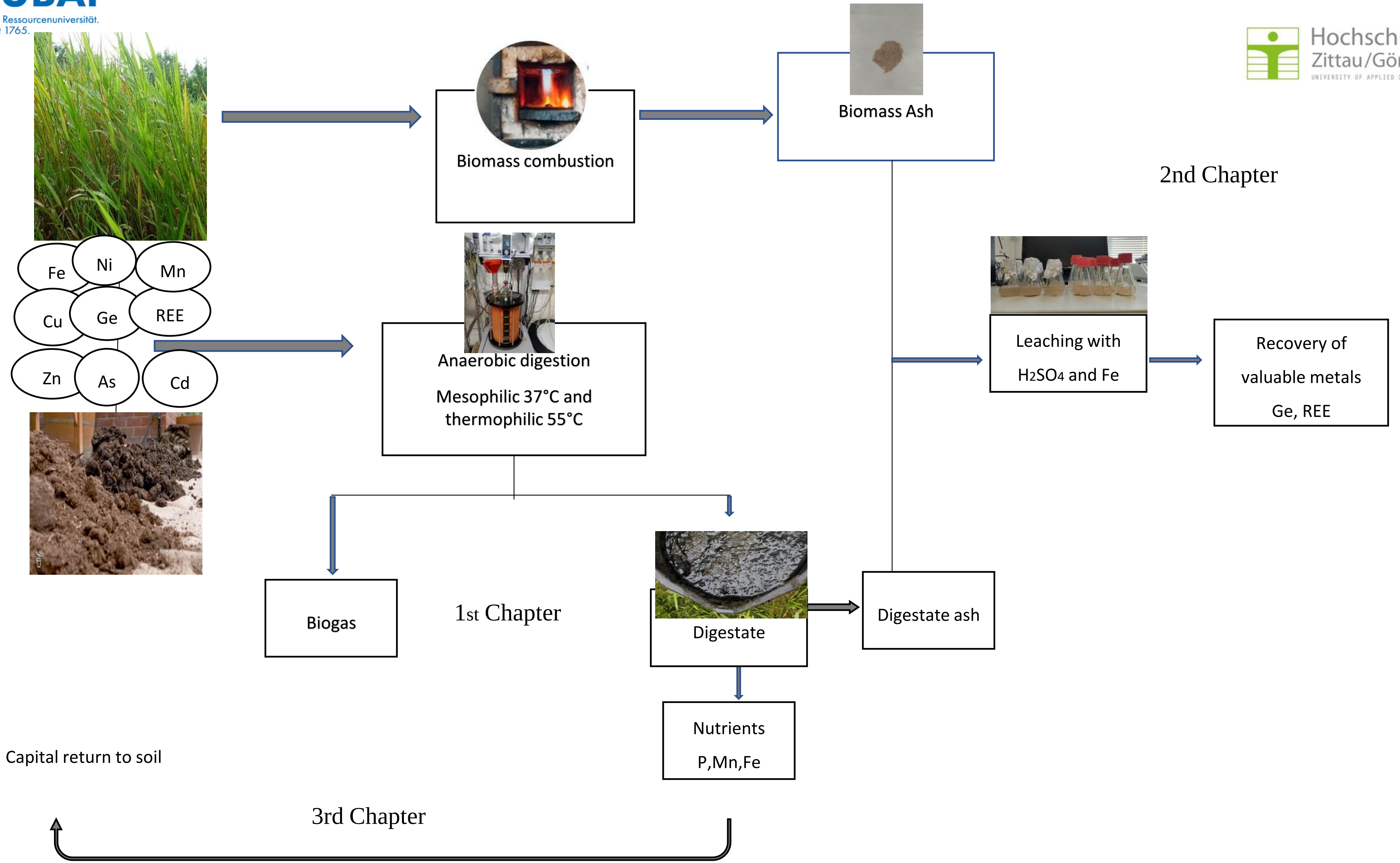
Research Objectives

Compare	study	Evaluate	Focus on
Compare enrichment/fractionation under mesophilic vs. thermophilic digestion	Study thermal and chemical leaching of plant nutrients (P, Mn) potential toxic elements (Zn, Cu, As, Cd) and valuable elements (Ge, REE) in ash	Evaluate effect of biosolids amendment on metal/nutrient mobility and uptake plant nutrients (P, Fe Mn) potential toxic elements (Zn, Cu, As, Cd) and valuable elements (Ge, REE) in ash	Plant nutrient (P, Fe Mn) potential toxic elements (Zn, Cu, As, Cd) and valuable elements (Ge, REE) in ash


Biomass combustion
Biomass Ash
2nd Chapter
Fe
Ni
Mn
Cu
Ge
REE
Zn
As
Cd
Anaerobic digestion
Mesophilic 37°C and thermophilic 55°C
Leaching with
H_2SO_4 and Fe
Recovery of
valuable metals
Ge, REE
Biogas
1st Chapter
Digestate
Digestate ash
Nutrients
P,Mn,Fe
Capital return to soil
3rd Chapter

Methodology Overview

Anaerobic Digestion (Batch Experiments)

•Biomass: *Phalaris arundinacea* (air-dried, ≤1 mm).
•Inoculum: Fresh digestate from prior runs (low TS: 3.5%).

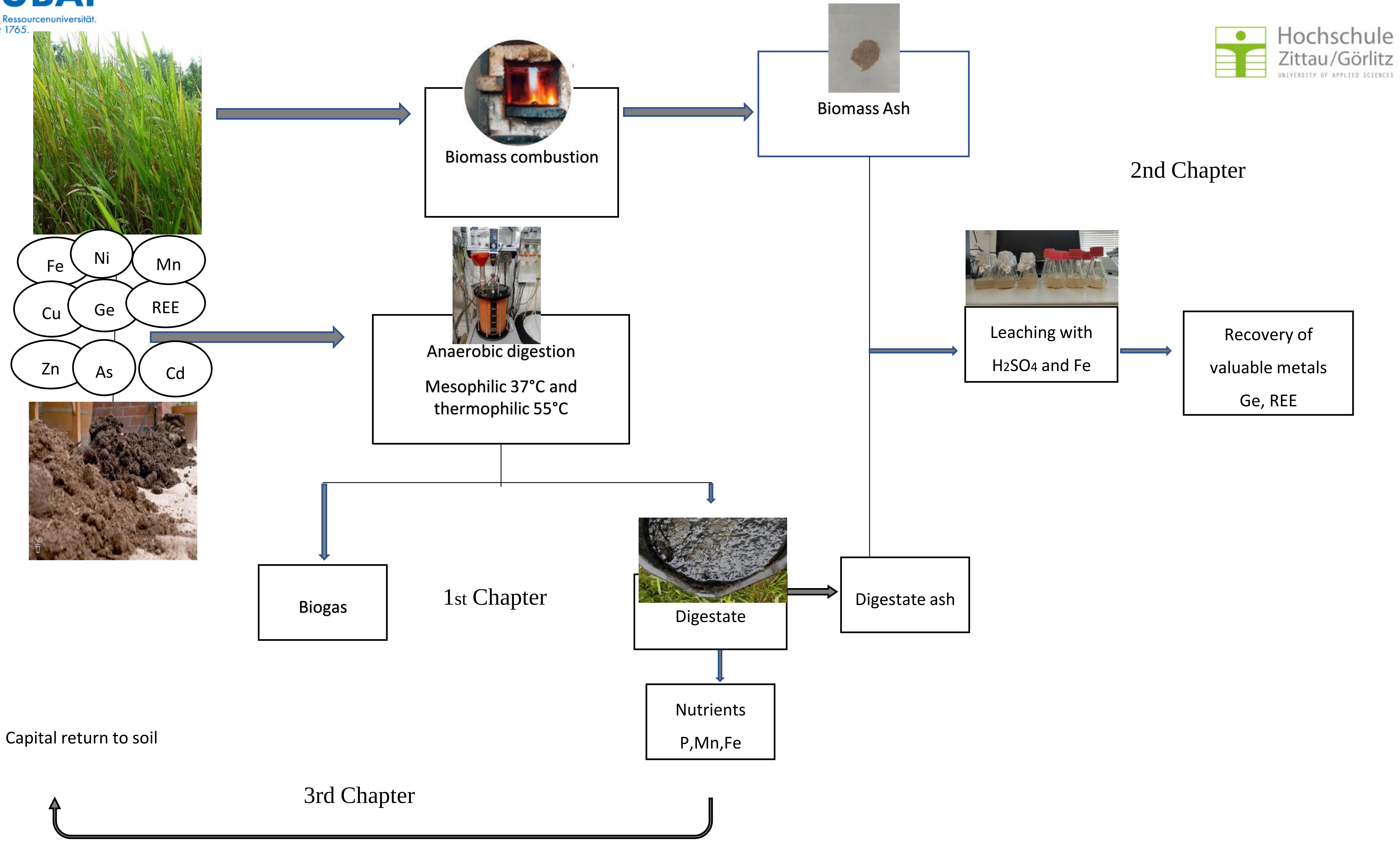
- Setup:
  - 2 L glass reactors (1.5 L working volume)
  - Mesophilic temp (~37°C) Thermophilic (55 °C)
  - Batch reactors, 40-day digestion

Digestate analyzed for:

- Total and dissolved elements
- Exchangeable/acid-soluble fractions
- Digestion & ICP-MS Analysis:
  - Microwave digestion with HNO_3, HF
  - ICP-MS for P, Fe, Mn, Zn, CuAs, Cd, Cr, Ge, REEs, etc

- **Pot Experiment with Biosolids**
- Soil: Luvisol (0–20 cm depth) from TU Freiberg campus.
- Treatments:
  - Soil only (control)
  - Soil + Sewage sludge (40:60 fw, ≈24% dm)
  - Soil + Digestate (15:85 fw, ≈3% dm)
- Plants:
  - *Alyssum murale*, *Lupinus albus*, *Carthamus tinctorius*, *Fagopyrum esculentum*
  - Surface-sterilized, germinated seedlings (n = 5 replicates/species/treatment)
- Harvest & Sample Prep:
  - Shoots cut, dried (60°C), milled, stored at 4°C

- **Ash Characterization & Leaching**
- Ash Production:
  - Biomass & digestate ash (1–4 g) heated at 550–950°C
  - Ground & homogenized
- Leaching Setup:
  - 500 mg ash + 50 mL solution (1 M H_2SO_4, DI water, Fe^{3+})
  - Incubated at 30°C, 200 rpm (1 month)
  - Separation via centrifugation (20,000 rpm), stored at 4°C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Results Chapter 1: Enrichment and chemical fractionation of plant nutrients, potentially toxic and economically valuable elements in digestate from mesophilic and thermophilic fermentation

Concentration µg/g of plant nutrients, potentially toxic trace and valuable elements in fresh (fw) and dried (dw) digestate after 40 days of mesophilic and thermophilic digestion (mean ± sd (n = 14 (Meso) – 10 Thermo).

Elements	Mesophilic (37 °C)	Thermophilic	Mesophilic	Thermophilic
	$\mu g\ g^{-1}$ fw		$\mu g\ g^{-1}$ dw	
P	481 ± 127	827 ± 150**	14667 ± 3252	18434 ± 3495*
Mn	14 ± 5	20 ± 4**	419 ± 57	438 ± 47ns
Fe	190 ± 42	432 ± 98***	6376 ± 2031	9572 ± 1133***
Co	0.05 ± 0.01	0.27 ± 0.16**	2.0 ± 0.2	6.0 ± 3.4*
Ni	0.37 ± 0.09	1.6 ± 0.9**	16 ± 4	34 ± 19*
Cu	3.9 ± 1.1	10.5 ± 4.5**	164 ± 32	226 ± 88ns
Zn	22 ± 9	40 ± 8***	700 ± 109	894 ± 88***
Cr	0.36 ± 0.09	0.97 ± 0.31***	15 ± 3	21 ± 4***
As	0.22 ± 0.07	0.51 ± 0.13***	7.1 ± 1.2	11.3 ± 1.3***
Cd	0.09 ± 0.01	0.28 ± 0.05***	3.9 ± 0.6	6.2 ± 0.6***
Pb	0.87 ± 0.37	1.7 ± 0.4***	26 ± 5	37 ± 4***
Ge	0.017 ± 0.005	0.031 ± 0.007***	0.56 ± 0.09	0.70 ± 0.14*
REEs	0.33 ± 0.12	0.59 ± 0.11***	10.4 ± 2.5	13.1 ± 1.6**

ns denoted as non-significant * denoted as $p < 0.05$ ** denoted as $p < 0.01$ *** denoted as $p < 0.001$.

P, Mn and Fe show significantly higher concentrations under thermophilic digestion, especially Fe (432 µg/g fw vs 190 µg/g fw)

Cu, Zn):increased concentrations in thermophilic digestion, often statistically significant indicates higher solubilization/mobilization at higher temperatures

Pb, Cd, Cr show higher concentrations under thermophilic conditions, raising considerations for environmental management

Ge and REEs are more enriched in thermophilic digestate

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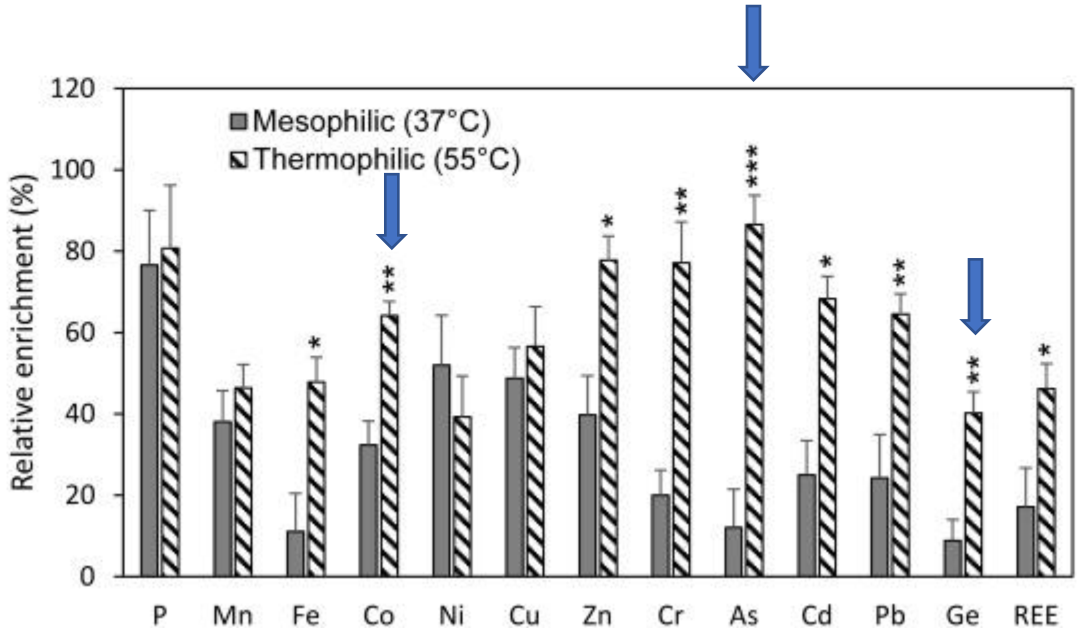

Effect of mesophilic and thermophilic digestion on the relative enrichment (percentage increase of concentrations in digestate relative to the initial concentrations) of plant nutrients, potentially toxic trace and valuable elements in digestate. Means ± sd (n = 24); * denoted as $p < 0.05$ ** denoted as $p < 0.01$.

- Thermophilic digestion significantly enriched:
  - Ge: +193%, REEs: +90%
  - Fe, Co, As, Cd, Pb: all >50% increase
- Over 70% of elements bound in solid phase

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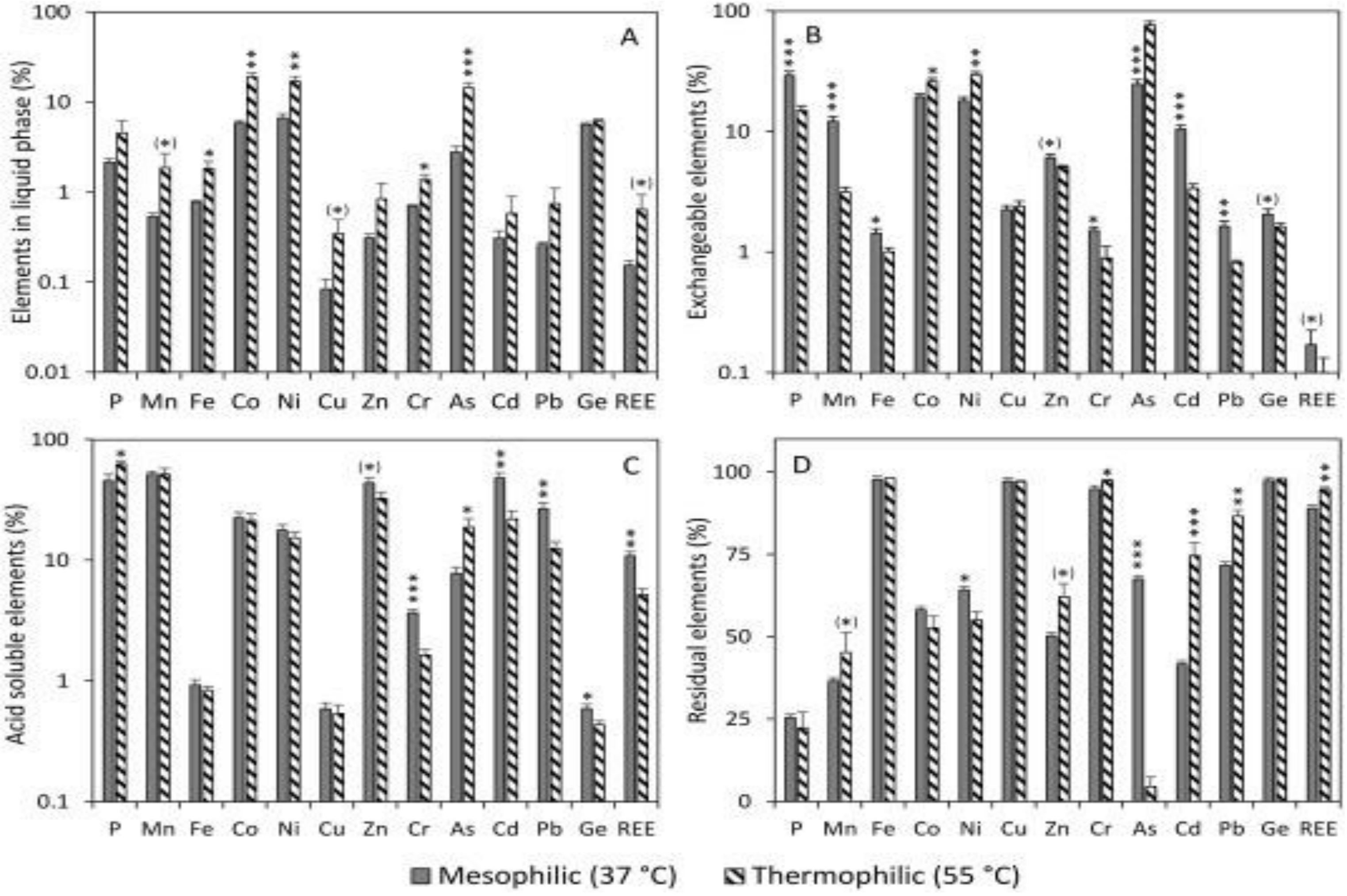

Effect of mesophilic and thermophilic digestion on distribution of plant nutrients (%), potentially toxic, trace and valuable elements (%) in water-soluble (5A), mobile/exchangeable (5B), acid soluble (5C), and residual (5D) (*) denoted as $p < 0.1$, * denoted as $p < 0.05$, ** denoted as $p < 0.01$, *** denoted as $p < 0.001$.

Elements distribution

- Compared to mesophilic digestions, thermophilic conditions increased the percentage share of all elements in the liquid phase; however, this increase was only statistically significant for Mn, Fe, Co, Ni, Cu, Cr, As and REE, while there was no significant effect on P, Zn, Cd
- More specifically, in mesophilic, P (2%), Co (6%), Ni (7%), As (3%) and Ge (6%) showed the highest portion of dissolved forms, whereas the dissolved portion of other elements was substantially lower and ranged between 0.1% (Cu) and 0.8% (Fe).
- Moreover, in the ammonium acetate-soluble element fraction (F2) which largely integrates elements adsorbed onto particulate substances the concentrations of P, Mn Cu and Zn were significantly lower in thermophilic
- Considering the percentage share of elements in the different fractions, digestate from both operating conditions contained on average less than 5% of the investigated elements in dissolved forms, less than 30% were present in exchangeable and acid soluble forms and more than 70% were present in the residual fraction.

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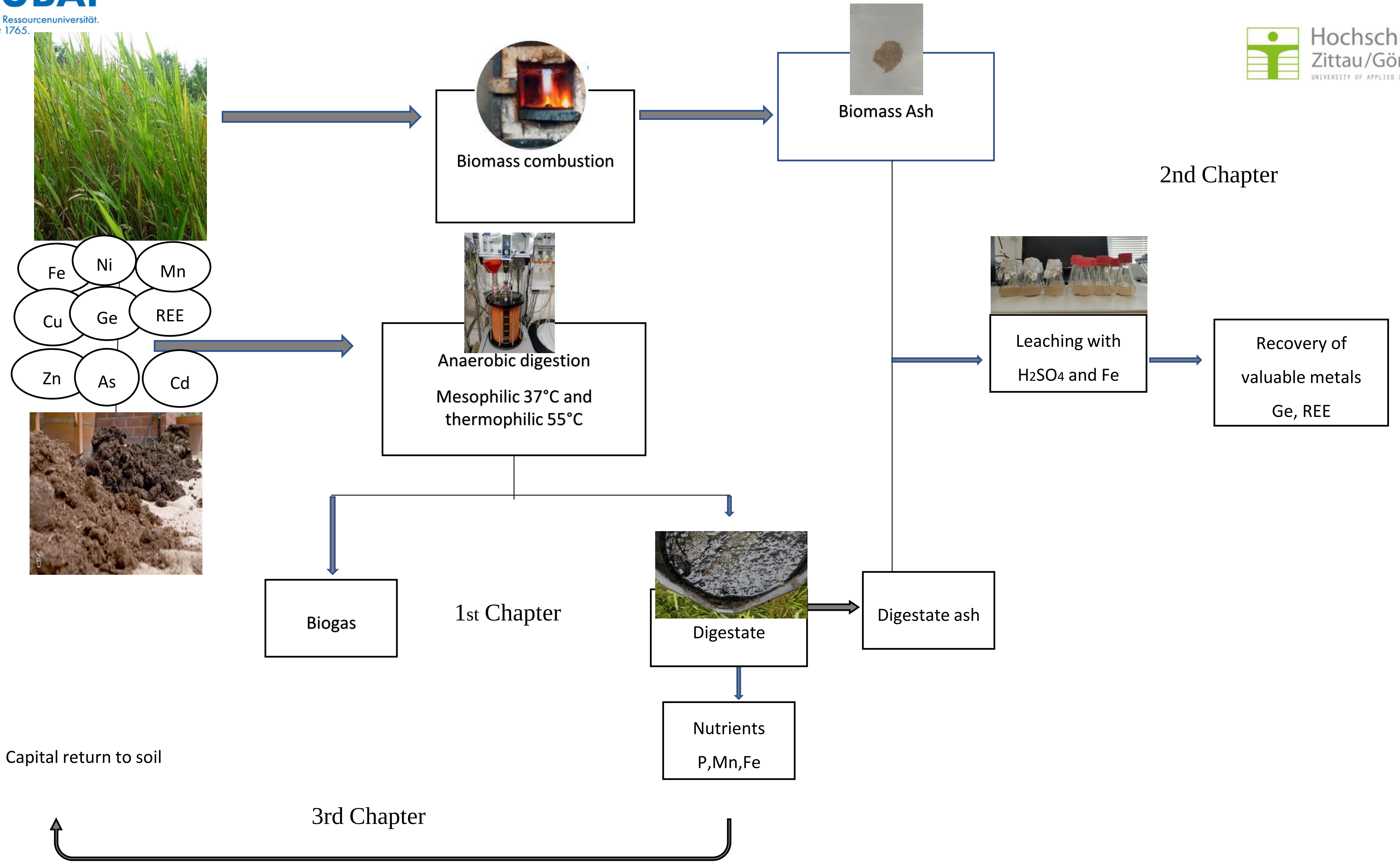
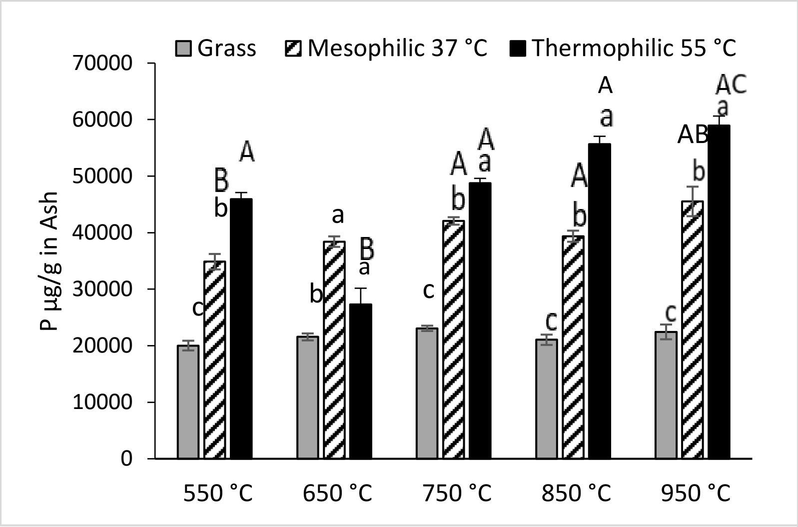
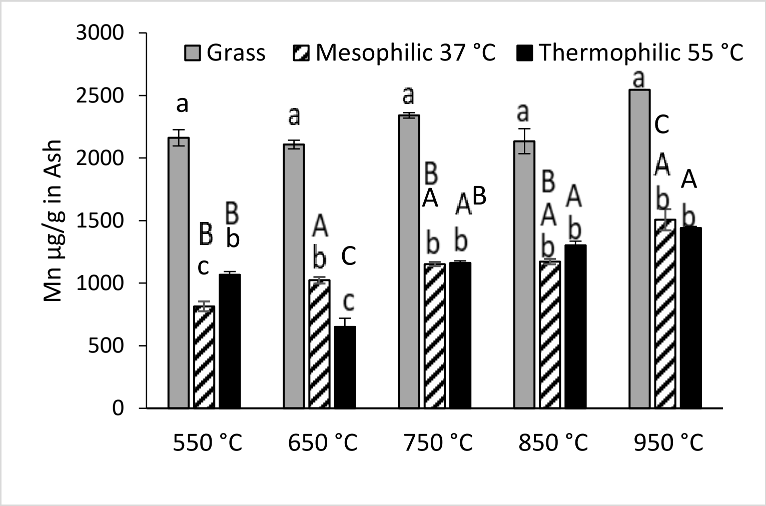
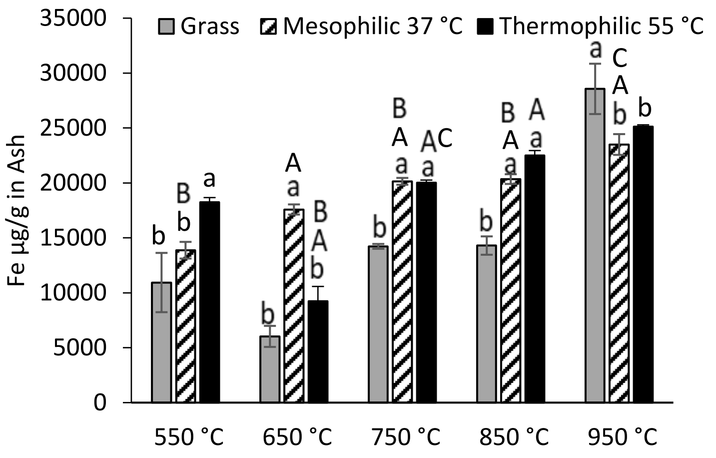


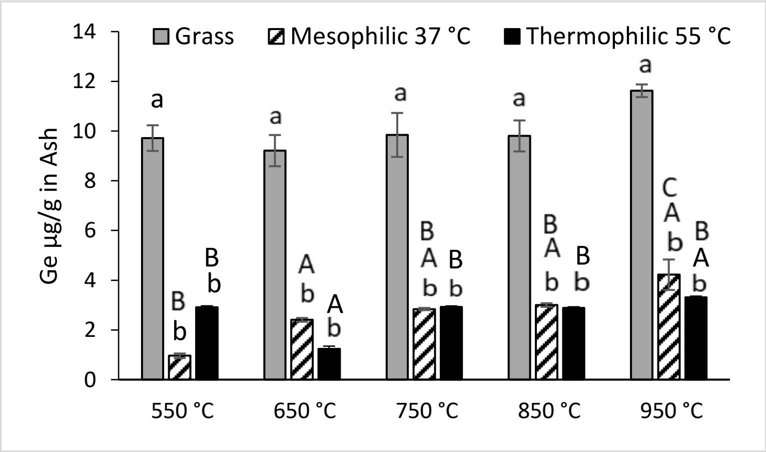
Chapter 2 results: Effect of Burning Temperature on plant nutrients, potentially toxic and economically valuable elements and leaching of selected elements in Biomass and anaerobic digestate Ash

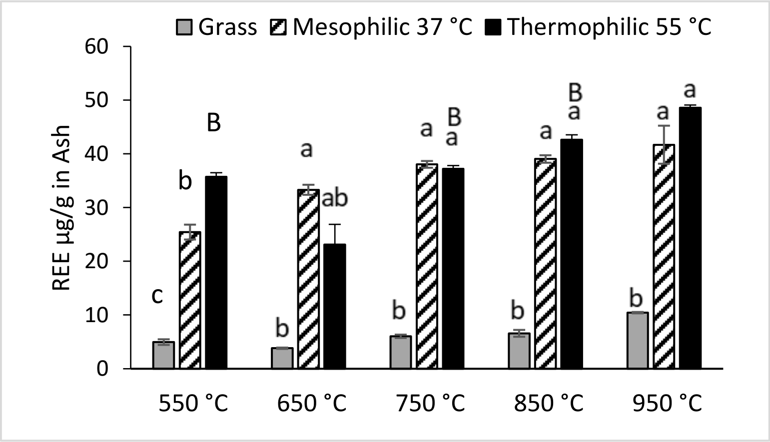
Small letters show concentration differences among different substrate and treatment within a specific Temperature. Capital letters denote differences between same substrate and treatment within a different Temperature.











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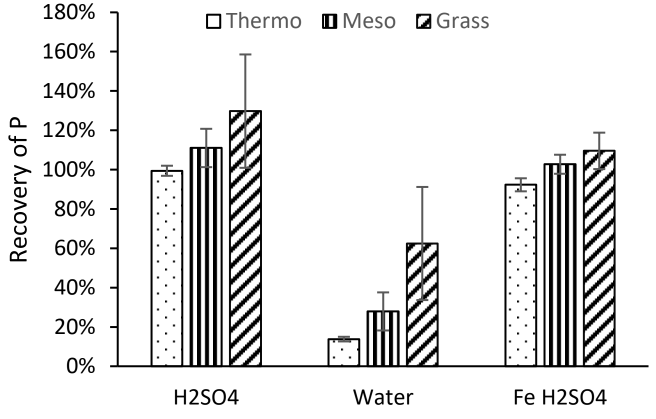

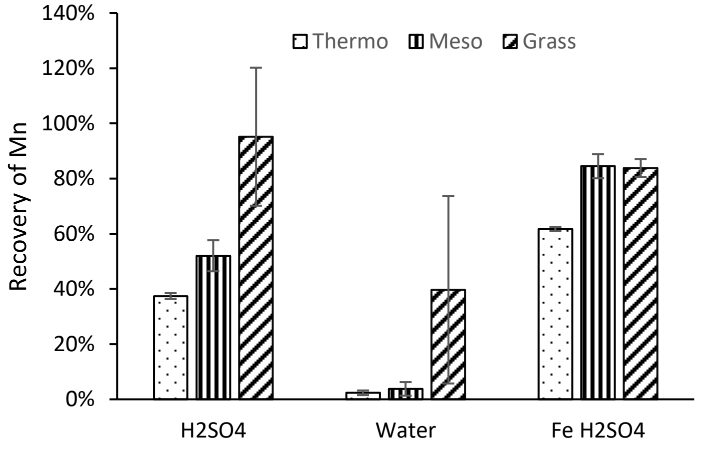

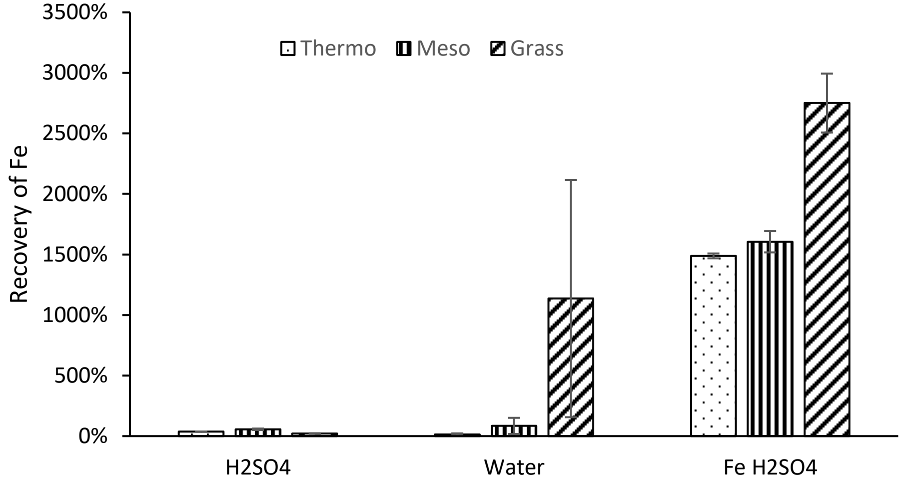

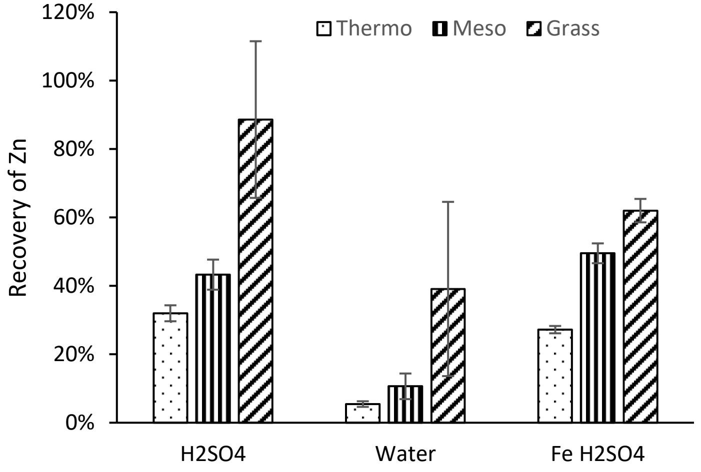

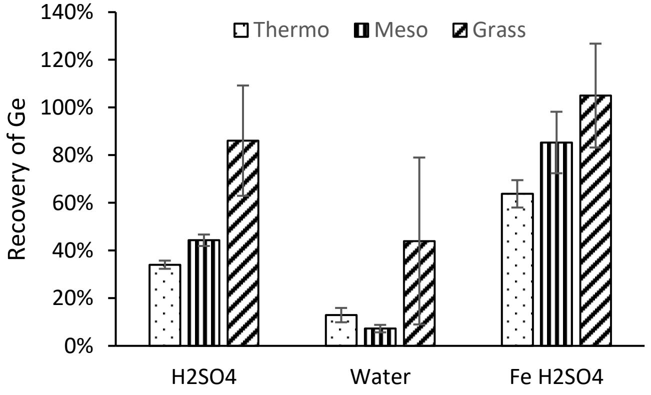

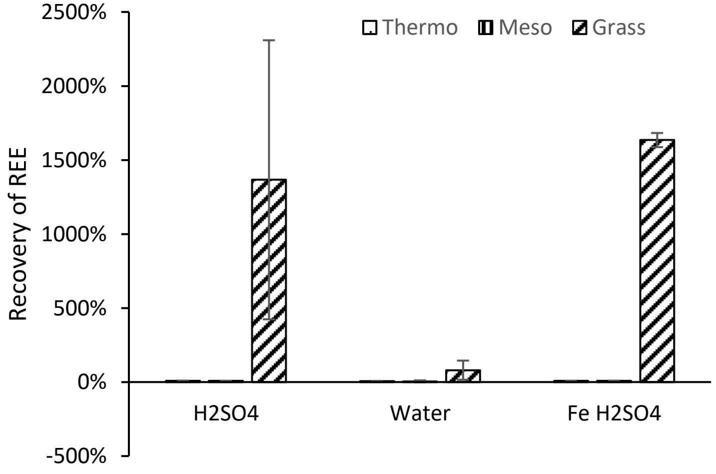

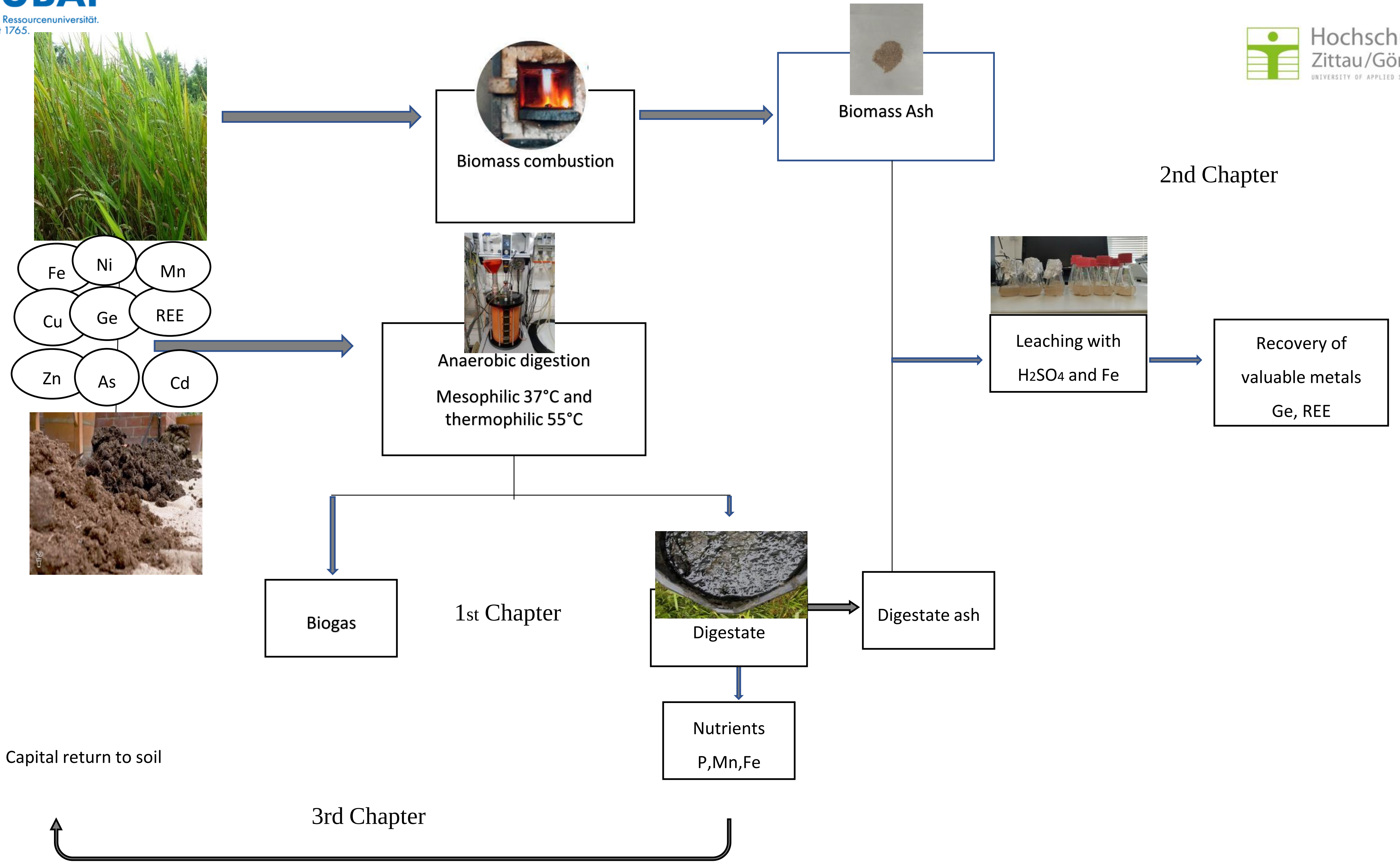
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Chapter 3 results: Effect of sewage sludge and digestate from anaerobic fermentation on the mobility of cadmium (Cd), gallium (Ga), germanium (Ge) and rare earth elements (REEs) in soil and uptake by plants with different nutrition strategies

Total and NH_4-acetate extractable concentrations (mg/kg dw) of plant nutrients and potentially toxic in soil, soil amended with digestate (soil + DG) and soil amended with sewage sludge (soil + SS).

Element	Fraction	Soil	Soil + DG	Soil+ SS
	mg/kg dw			
P	Total	745 ± 46b	889 ± 92b	4006 ±648a
	Labile	6.3 ± 0.6c	14 ± 4b	53 ± 6a
Fe	Total	31465 ± 2718a	33256 ± 4644a	28870 ± 1647b
	Labile	4.7 ± 1.1c	10.1 ± 2.1a	7.2 ± 0.9b
Mn	Total	720 ± 44a	847 ± 68a	593 ± 29b
	Labile	17 ± 2c	107 ± 12a	60 ± 4b
Zn	Total	214 ± 32b	279 ± 62ab	358 ± 41a
	Labile	9.1 ± 0.8c	13 ± 1b	22 ± 1a

- Total P was significantly higher in soil + sewage sludge (SS) compared to other treatments.
- Labile P (plant-available) also increased in SS treatment, showing high P availability.
- the addition of digestate did alter the total concentrations of the plant nutrients Fe, Mn
- Digestate improved micronutrient availability (Mn, Fe).
- Sewage sludge increased total nutrient content but also elevated toxic elements (Zn).

Chapter 3 results: Effect of sewage sludge and digestate from anaerobic fermentation on the mobility of cadmium (Cd), gallium (Ga), germanium (Ge) and rare earth elements (REEs) in soil and uptake by plants with different nutrition strategies

Total and NH_4-Ac extractable concentrations (mg/kg dw) of essential elements in soil, soil amended with digestate (soil + DG) and soil amended with sewage sludge (soil + SS).

Element	Fraction	Soil	Soil + DG	Soil + SS
	mg/kg dw			
Cd	Total	1.8 ± 0.6ns	1.3 ± 0.4ns	1.9 ± 1.0ns
	Labile	0.62 ± 0.04b	0.75 ± 0.16ab	0.81 ± 0.05a
Ge	Total	1.87 ± 0.05a	2.14 ± 0.27a	1.57 ± 0.24b
	Labile	0.0049 ± 0.0009 ns	0.0037 ± 0.0015ns	0.0036 ± 0.0002ns
Ga	Total	14.1 ± 0.2b	16.5 ± 2.1a	12.5 ± 0.1c
	Labile	0.0037±0.0008c	0.0103±0.0012a	0.0067±0.0012b
LREE	Total	125 ± 3a	137 ± 16a	109 ± 4c
	Labile	0.39 ± 0.02b	0.45 ± 0.03a	0.28 ± 0.01c
HREE	Total	44 ± 2ab	52 ± 6a	34 ± 7b
	Labile	0.16 ± 0.01b	0.18 ± 0.02a	0.12 ± 0.01c
LREE/HREE	Total	2.86 ± 0.06ns	2.82 ± 0.09ns	3.26 ± 0.70ns
	Labile	2.46 ± 0.02b	2.52 ± 0.04a	2.27 ± 0.04c

- the portion of labile Ge, Ga, and REE did not exceed 0.5% of the total concentrations.
- Based on results from NH_4-acetate extracts, the potential availability decreased in the order Cd > LREE > HREE > Ge, Ga.

- This is in accordance with the findings of Tyler and Olsson (2001), who demonstrated that compared to Cd and REE, the solubility of Ge and Ga in soils is low, and their mobilization requires substantial changes in physicochemical soil properties

Chapter 3 results .Effect of sewage sludge and digestate from anaerobic fermentation on the mobility of cadmium (Cd), gallium (Ga), germanium (Ge) and rare earth elements (REEs) in soil and uptake by plants with different nutrition strategies

Shoot biomass and concentrations of nutrients in plants cultivated on soil (reference), soil amended with digestate (Soil + DG), and soil amended with sewage sludge (Soil + SS); mean ± sd, n = 5. Small letters show concentration differences among different substrates within a specific plant species. Capital letters denote differences between plant species within a specific substrate.

Species	Treatment	Biomass	P	Mn	Fe	Zn	Ni
		g	g/kg	mg/kg			
A. murale	Reference	0.41 ± 0.17C	2.4 ± 0.2bA	24 ± 4bB	78 ± 23bAB	107 ± 87b	1.6 ± 0.3b
	Soil + DG	0.14 ± 0.09B	2.5 ± 0.6b	224 ± 91aB	252 ± 117aA	173 ± 86bA	2.5 ± 1.4b
	Soil + SS	0.25 ± 0.16C	4.5 ± 0.9aA	231 ± 36aB	135 ± 57abA	1071 ± 639aA	6.2 ± 2.6aA
	p-value	0.08	<0.01	<0.01	0.03	<0.01	0.03
F. esculentum	Reference	7.4 ± 1.0bA	2.5 ± 0.4bA	40 ± 22bB	31 ± 10bB	54 ± 10bB	1.1 ± 0.2b
	Soil + DG	3.6 ± 3.0bA	2.2 ± 0.7b	163 ± 159bB	100 ± 81bB	38 ± 16bB	1.3 ± 0.1b
	Soil + SS	13.9 ± 2.1aA	6.9 ± 1.4aA	632 ± 262aA	132 ± 63aA	482 ± 133aA	4.0 ± 0.9aA
	p-value	<0.001	<0.001	<0.001	0.04	<0.001	<0.001
C. tinctorius	Reference	1.2 ± 0.9bB	2.0 ± 0.4bAB	27 ± 5cB	98 ± 75A	79 ± 13b	2.0 ± 1.3
	Soil + DG	1.8 ± 0.6abAB	2.3 ± 0.1b	82 ± 5bB	68 ± 49B	71 ± 10bB	2.7 ± 2.4
	Soil + SS	3.1 ± 1.5aB	3.0 ± 0.5aB	216 ± 22aB	55 ± 10B	152 ± 25aB	1.1 ± 0.3B
	p-value	0.05	<0.01	<0.001	0.4	<0.001	0.37
L. albus	Reference	2.7 ± 1.0bB	1.5 ± 0.2bB	996 ± 353aA	79 ± 15abAB	48 ± 5b	2.4 ± 1.1
	Soil + DG	1.3 ± 0.5bB	1.9 ± 0.3b	1412 ± 805aA	103 ± 38aB	42 ± 9bB	1.7 ± 0.3
	Soil + SS	4.9 ± 1.0aB	2.5 ± 0.4aB	404 ± 149bB	46 ± 7bB	94 ± 21aB	1.8 ± 0.3B
	p-value	<0.001	<0.01	0.05	0.01	<0.001	0.45

Chapter 3 results : Effect of sewage sludge and digestate from anaerobic fermentation on the mobility of cadmium (Cd), gallium (Ga), germanium (Ge) and rare earth elements (REEs) in soil and uptake by plants with different nutrition strategies

Concentrations of non-essential elements in plants cultivated on soil (reference), soil amended with digestate (Soil + DG) and soil amended with sewage sludge (Soil + SS); mean ± sd, n = 5).

	Treatment	Cd	Ge	Ga	LREE	HREE
		mg/kg	µg/kg	µg/kg	µg/kg	µg/kg
A. murale	Reference	0.6 ± 0.1bB	6 ± 3bA	18 ± 14b	198 ± 94bA	84 ± 34b
	Soil+DG	2.8 ± 2.1bA	22 ± 5aA	92 ± 54aA	858± 376aA	280 ± 122a
	Soil+SS	10 ± 6aA	8 ± 4b	45 ± 27bA	378 ± 265bA	152 ± 61ab
	p-value	<0.01	<0.01	0.04	0.02	0.02
F. esculentum	Reference	1.1 ± 0.3bBC	<1B	7 ± 3b	237 ± 151A	93 ± 65A
	Soil+DG	0.8 ± 0.6bB	<1B	6 ± 4bB	204 ± 78B	82 ± 38B
	Soil+SS	7.1 ± 1.4aAB	<1	14 ± 4aB	281 ± 139A	104 ± 57A
	p-value	<0.001	n.a.	<0.01	0.68	0.84
C. tinctorius	Reference	4.7 ± 1.4A	12 ± 7aA	11 ± 8	207 ± 152aA	79 ± 48a
	Soil+DG	3.6 ± 1.0A	<1	4 ± 2B	96 ± 20abB	44 ± 12ab
	Soil+SS	4.3 ± 1.0B	2 ± 1b	8 ± 2B	70 ± 22bB	35 ±10b
	p-value	0.33	0.02	0.11	0.03	0.05
L. albus	Reference	0.09 ± 0.03bC	7 ± 4A	9 ± 1ab	39 ± 13bB	18 ± 4b
	Soil+DG	0.16 ± 0.05bB	4 ± 1B	16 ± 6aB	65 ± 22aB	19 ± 5b
	Soil+SS	0.24 ± 0.07aC	8 ± 7	8 ± 3bB	31 ± 10bB	26 ± 5a
	p-value	<0.01	0.70	0.05	0.01	0.04

- Cd: High mobility and bioavailability with sewage sludge; NH_4-acetate extraction reliably predicts plant uptake.
- Ga & REEs: Uptake not directly linked to soil extractability; influenced by plant traits:
  - *Lupinus albus*: carboxylate release
  - *Fagopyrum esculentum*: rhizosphere acidification
- Ge: Minimal uptake across all plant species.

Conclusions

- Thermophilic digestion significantly enhances the enrichment of valuable elements like germanium (Ge) and rare earth elements (REEs) in the digestate compared to mesophilic conditions.
- Alongside valuable elements, toxic elements like arsenic (As), cadmium (Cd), and lead (Pb) are also enriched—posing potential risks if the digestate is used as fertilizer.
- Chemical fractionation revealed that most toxic As became more mobile under thermophilic conditions, while Ge and REEs remained largely in the stable residual fraction (>94%).
- Temperature plays a critical role in both element enrichment and speciation—highlighting the potential for process optimization to enhance selective recovery and reduce environmental risks.

- Fe–H_2SO_4 is the most effective extractant across all sample types, especially for Fe and REE, showing extremely high recovery (up to ~3200% for Fe and ~1800% for REE).This suggests that Fe addition improves the acid solubilization of metals, possibly due to enhanced redox-driven solubilization or complexation.
- P and Zn recovery is relatively efficient across all digestate ash types, with acid treatments (H_2SO_4 and Fe–H_2SO_4) achieving near or over 100% recovery.
- This suggests P is highly leachable, especially under acidic conditions. Mn recovery is also enhanced in thermophilic and grass digestates ash, with acidic extractants performing better than water. Water alone results in poor recovery of all elements, especially REE and Ge, highlighting the need for chemical treatment for efficient element recovery.

- Digestate and sewage sludge application affect nutrient mobility and the availability of Ge, Ga, and REEs in soils, but this effect is element- and plant-specific.
- Cd mobility and plant uptake increase significantly with sewage sludge, showing that NH_4-acetate-extractable Cd is a reliable proxy for plant uptake.
- Ga and REE uptake are not directly correlated with their extractable (mobile) soil fractions, implying that physiological plant traits and nutrient interactions play a key role.
- Soil–plant transfer of Ga is likely driven by specific uptake mechanisms, while REE uptake is also influenced by phosphorus-related root traits and the plant’s nutritional status.

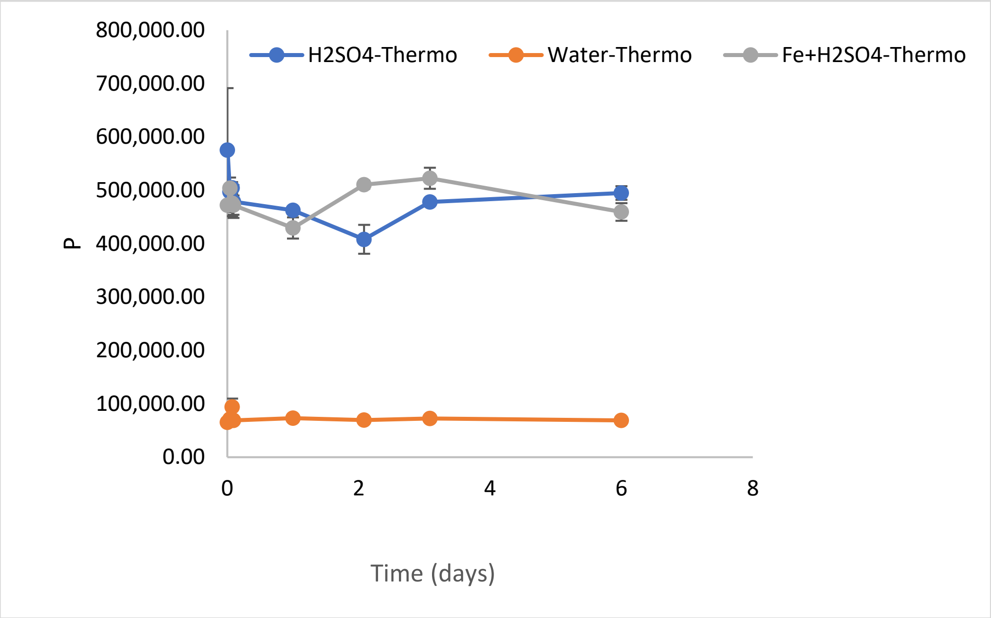
Thank You

For Your Attention!

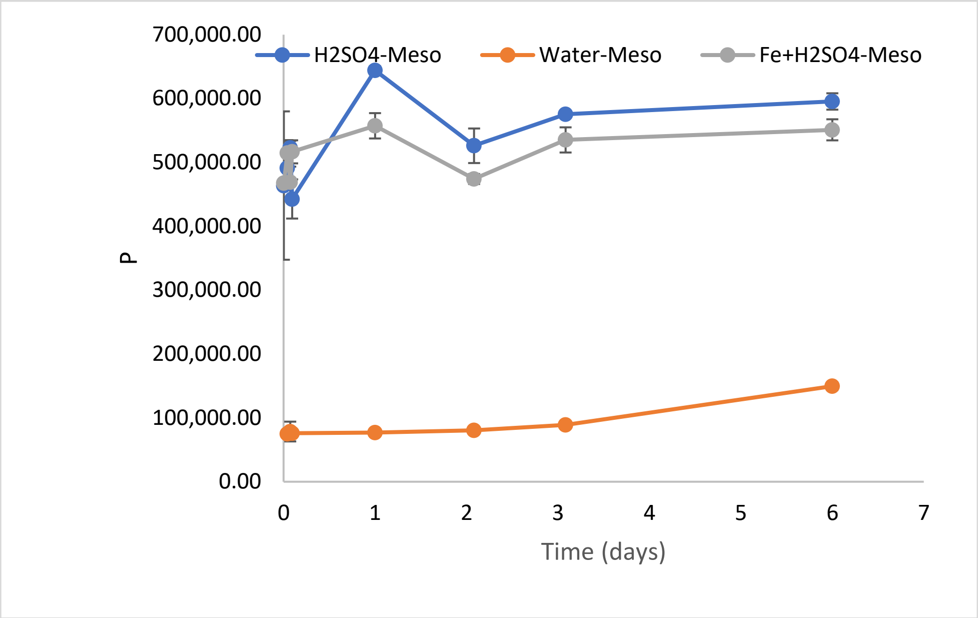
Any Questions

Future research

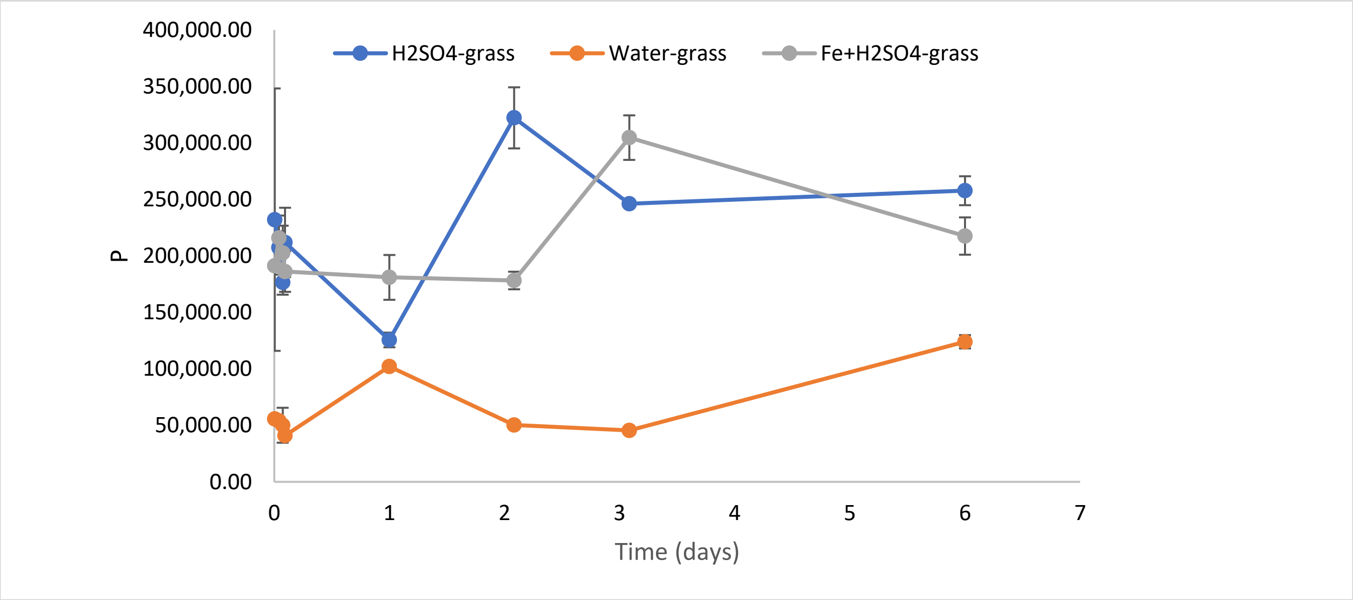
1. Explore how thermophilic conditions alter chemical speciation and binding of Ge, REE, and toxic elements (As, Cd).
2. Conduct long-term studies on element accumulation in thermophilic digestate from various feedstocks, including hyperaccumulator plants and waste streams.
3. Develop optimized protocols using eco-friendly and cost-effective reagents for selective leaching of valuable vs. toxic elements.
4. Examine the fate of enriched elements (especially toxic ones like As, Cd) when digestate is applied to soil.
5. Study plant uptake mechanisms, especially for Ga and REE, under different soil amendments and plant species, integrating physiological and rhizospheric traits.



H2SO4-Thermo
Water-Thermo
Fe+H2SO4-Thermo
800,000.00
700,000.00
600,000.00
500,000.00
400,000.00
300,000.00
200,000.00
100,000.00
0.00
P
0
2
4
6
8
Time (days)



H2SO4-Meso
Water-Meso
Fe+H2SO4-Meso
700,000.00
600,000.00
500,000.00
400,000.00
300,000.00
200,000.00
100,000.00
0.00
P
0
1
2
3
4
5
6
7
Time (days)



H2SO4-grass
Water-grass
Fe+H2SO4-grass
400,000.00
350,000.00
300,000.00
250,000.00
200,000.00
150,000.00
100,000.00
50,000.00
0.00
P
0
1
2
3
4
5
6
7
Time (days)