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AGH UNIVERSITY OF KRAKOW



The fate of heavy metals during hydrothermal carbonization of sewage sludge with acidic pH

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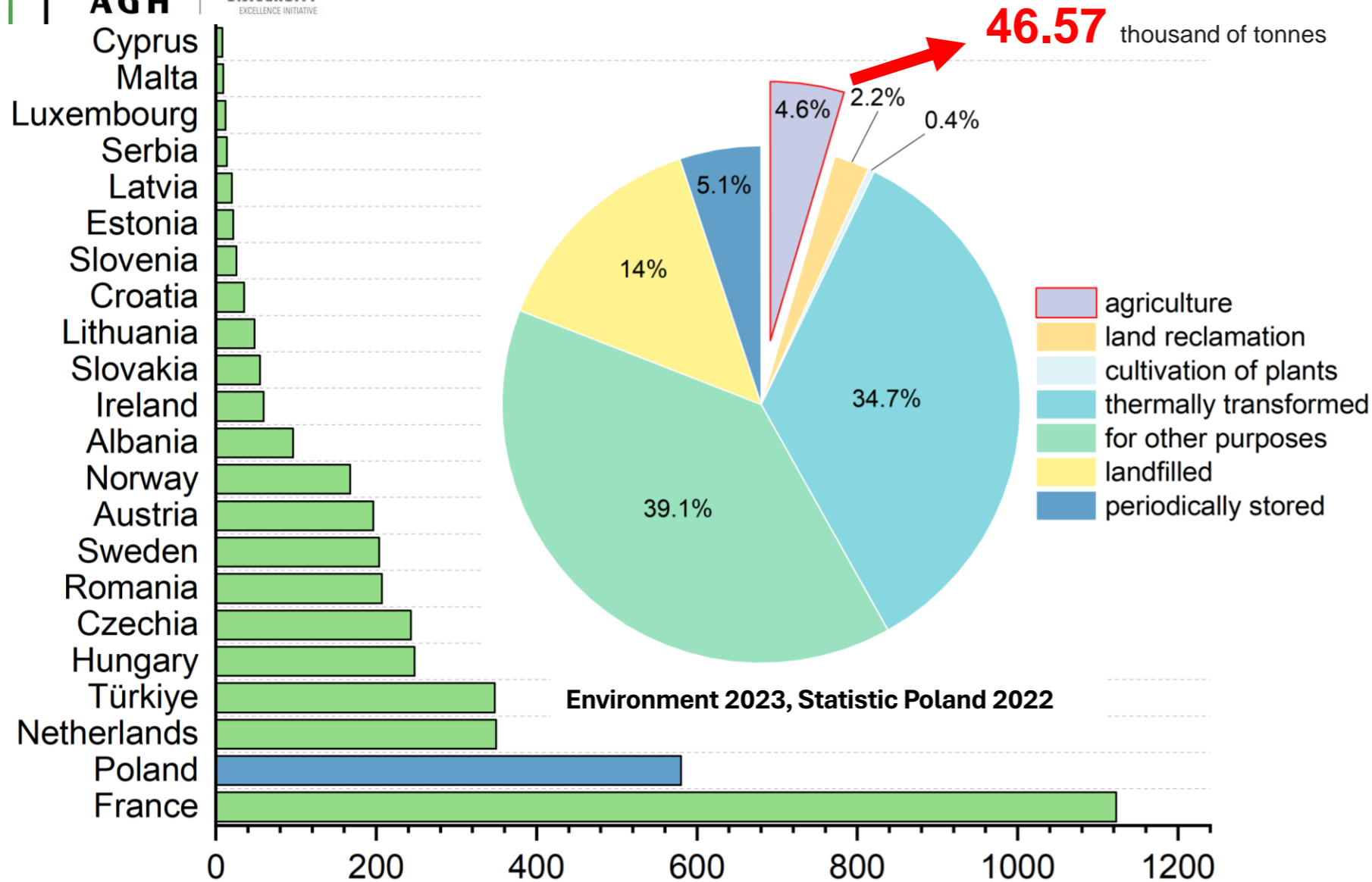
23-26 September 2024, Poland

Presentation plan

- Introduction:
 - sewage sludge,
 - heavy metals,
 - hydrothermal carbonization.
- Experimental procedures.
- Main goal of the study.
- Results.
- Conclusions.



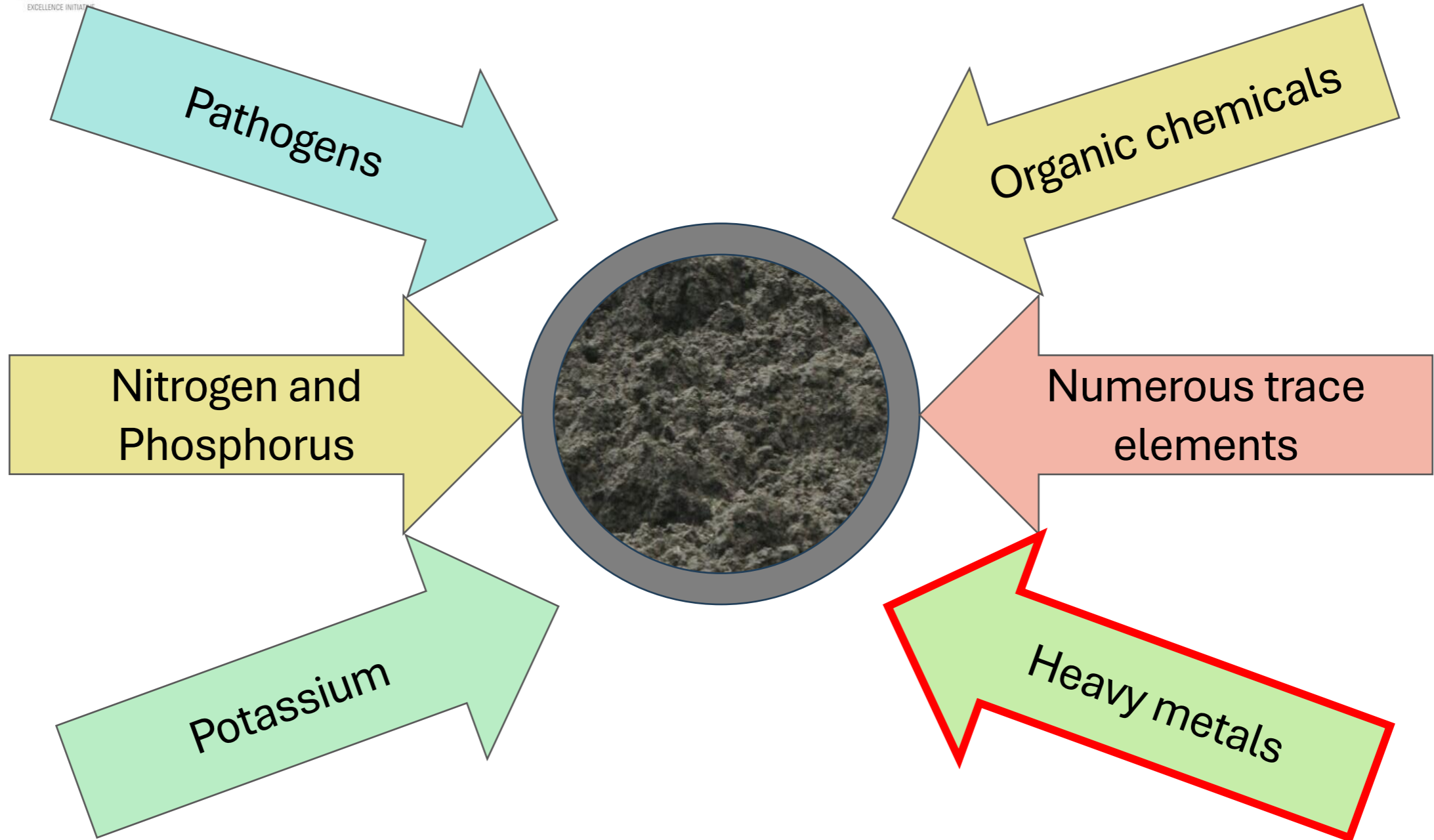
Sewage sludge



Sewage sludge production and disposal from urban wastewater (in thousand tonnes), Eurostat, 2022

*the date for other countries from UE are available.

Sewage sludge

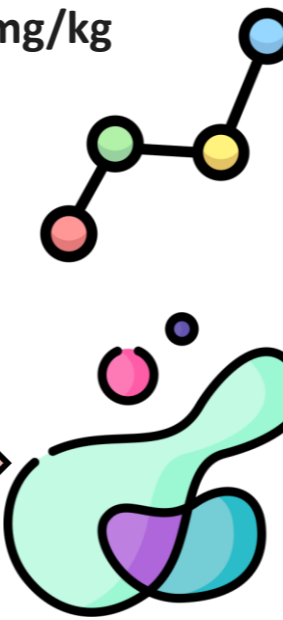


Heavy metals in sewage sludge

Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo, V, W, As, Sb, Se

Permissible content of heavy metals in sewage sludge, mg/kg

	Soil reclamation applications	Agricultural uses
Hg	20	16
Cd	25	20
Cr	1000	500
Cu	1200	1000
Ni	400	300
Pb	1000	75
Zn	3500	2500



Conditions: precipitated, dissolved, absorbed or assimilated with biological residues, co-precipitated with metal oxides.

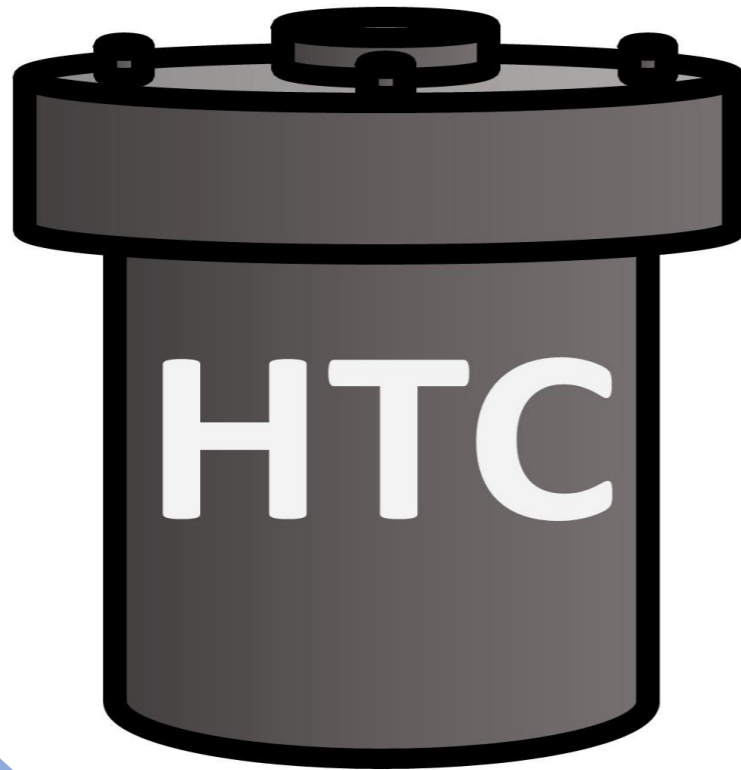
Forms: oxides, phosphates, hydroxides, sulphates, sulphides, silicates, compounds with complex sugars and organic compounds in the form of humus complexes.



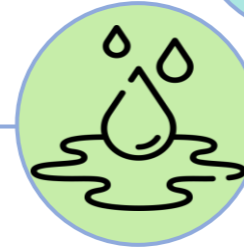
Mobility fractions: exchangeable (F1), bound to carbonates (F2), bound to Fe–Mn oxides (F3), bound to organic matter (F4).

Journal of Laws of 2015 I, vol. 257.; Rozporządzenie ministra środowiska z dnia 6 lutego 2015 r. w sprawie komunalnych osadów ściekowych (in english: Regulation of the Minister of the Environment of 6 February 2015 on municipal sewage sludge)

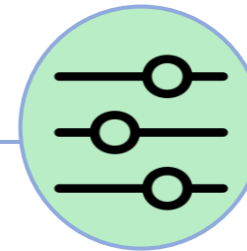
What is the HydroThermal Carbonization?



The process of converting wet sewage sludge into biofuel.



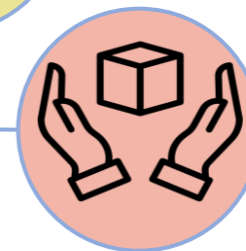
HTC is carried out in an aqueous environment.



Process parameters: temperature, time, heating rate, biomass to water ratio.

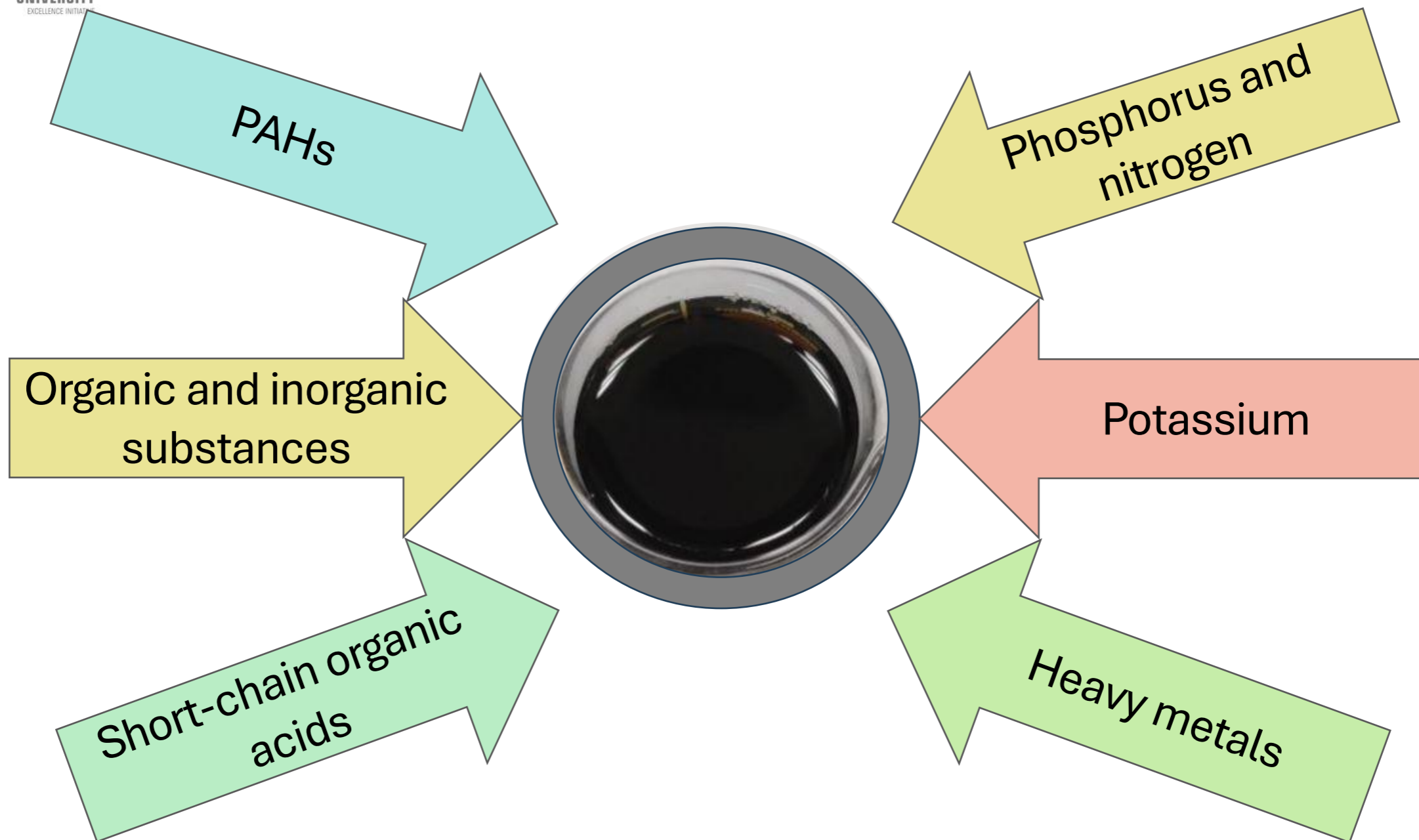


Research material: organic and inorganic material.

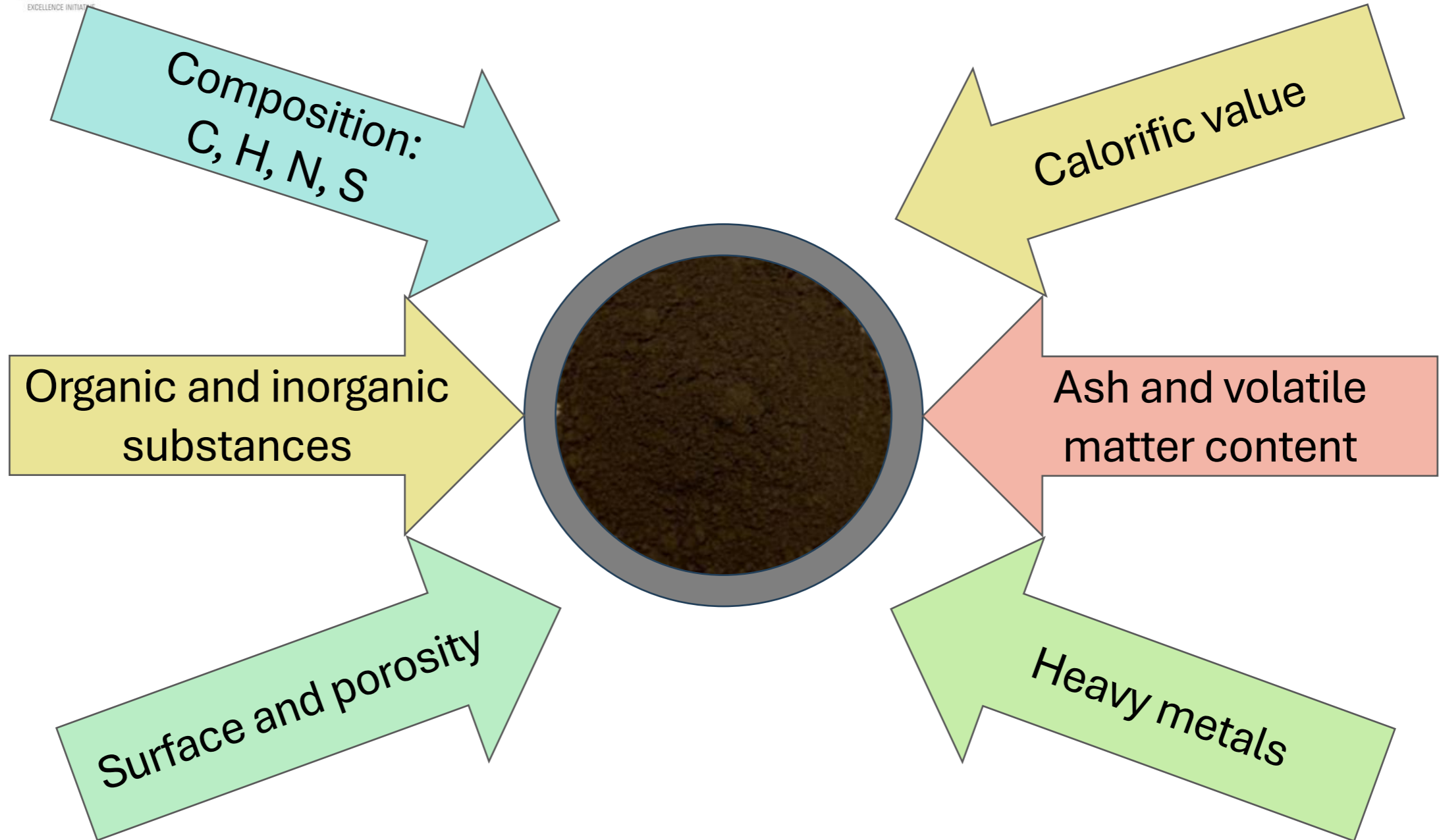


Reaction products:
→ **post-processing liquid**
→ **hydrochar**
→ **gas.**

Post-processing liquid



Hydrochar



The main aim of the study

1

Investigation the HTC of sewage sludge in a different acidic pH.

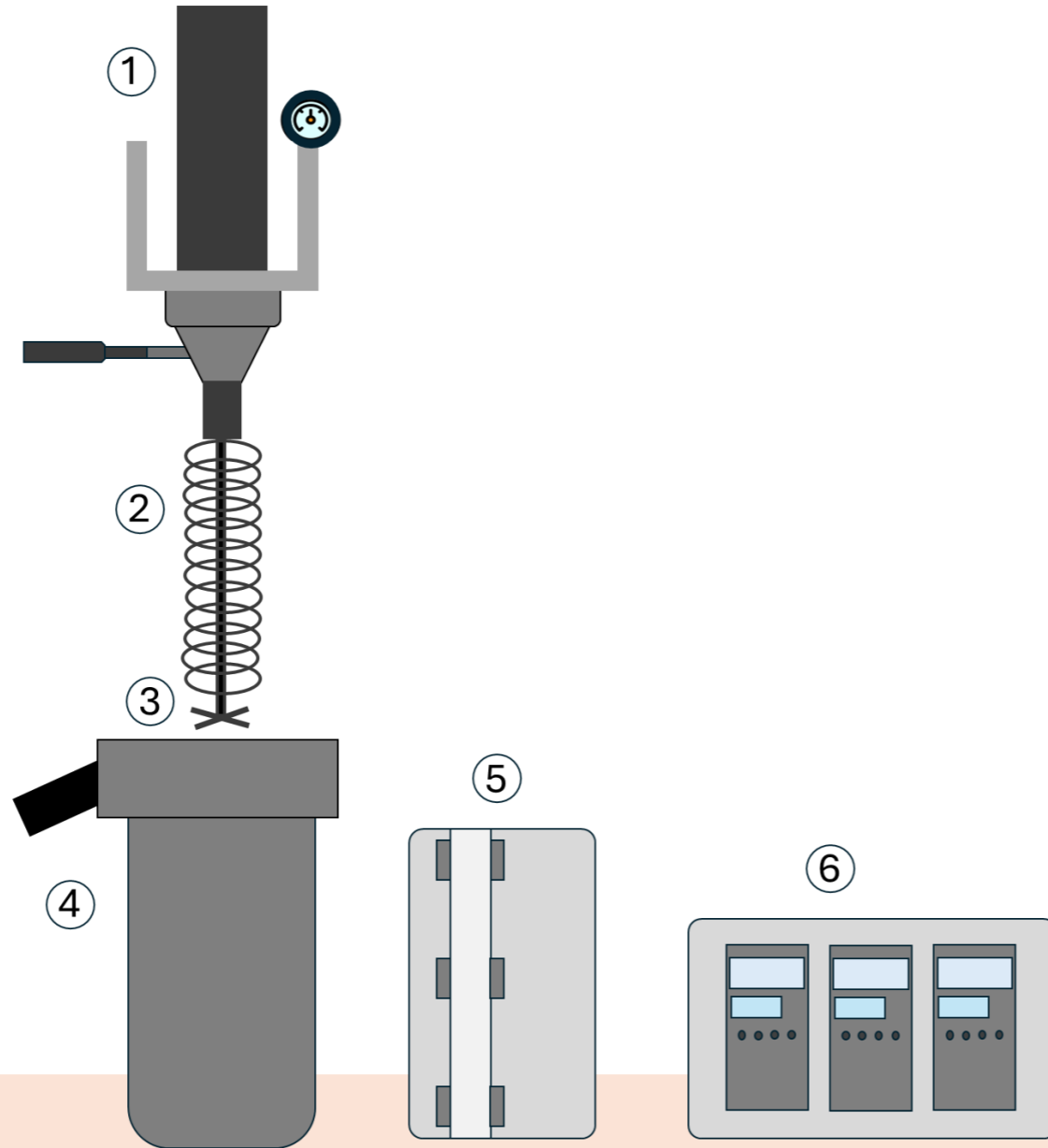
2

Chemical and physical analysis of hydrochar and post-processing liquid.

3

Investigation of the effects of pH on various aspects including heavy metal stability.

Parameters of the experiment



1 – MagneDrive;

2 – cooling coil;

3 – mixer;

4 – reactor;

5 – heating jacket;

6 – control panel.

Parameters of the experiment



Sewage sludge from the Central Wastewater Treatment Plant in Gliwice (Poland) after the anaerobic digestion process



Reactor: Zipperclave Stirred Reactor, 1000 ml.



Sewage sludge to water ratio to ensure free mixing.



Residence time: 2 h.

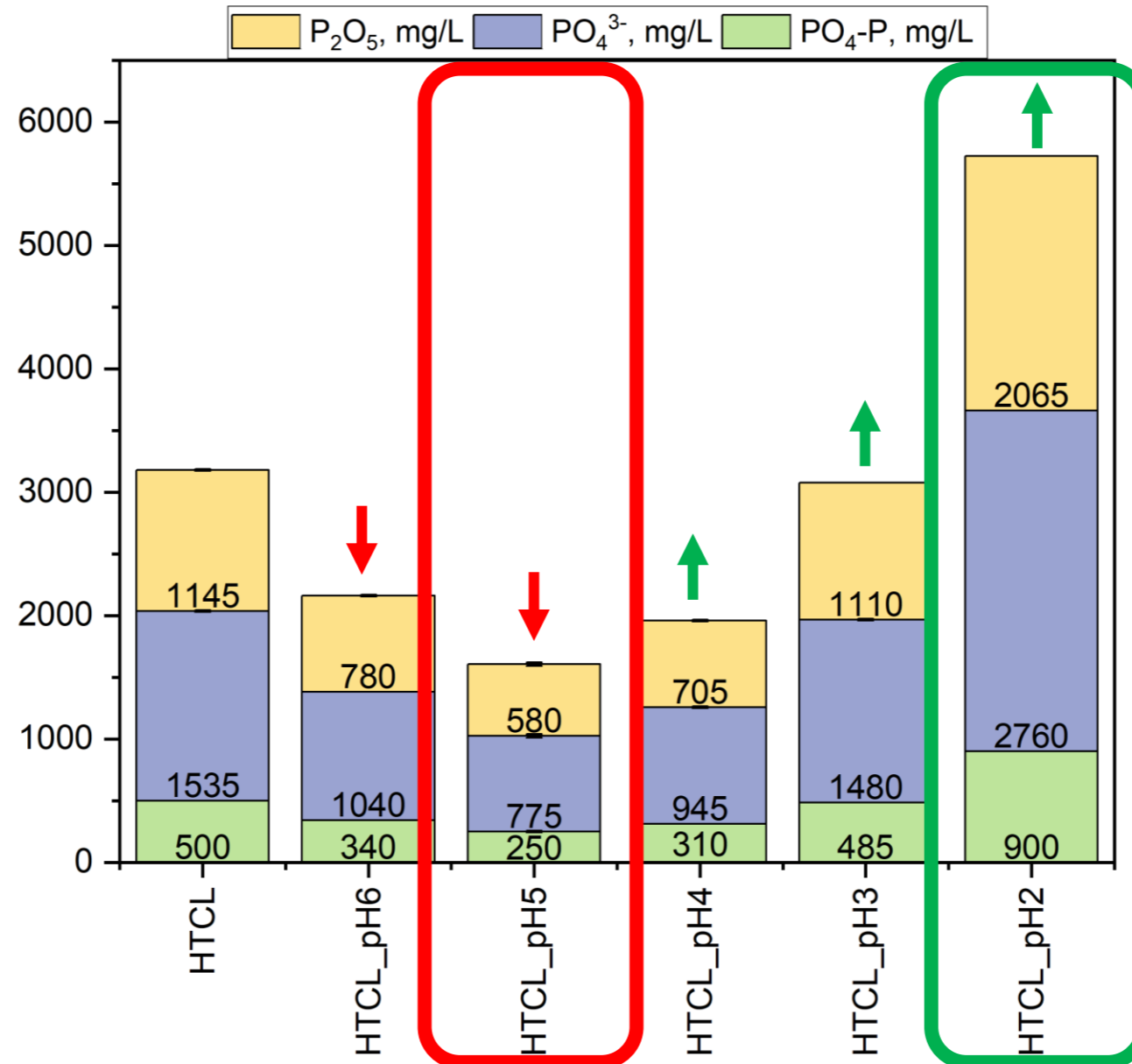


Temperature: 200 °C.

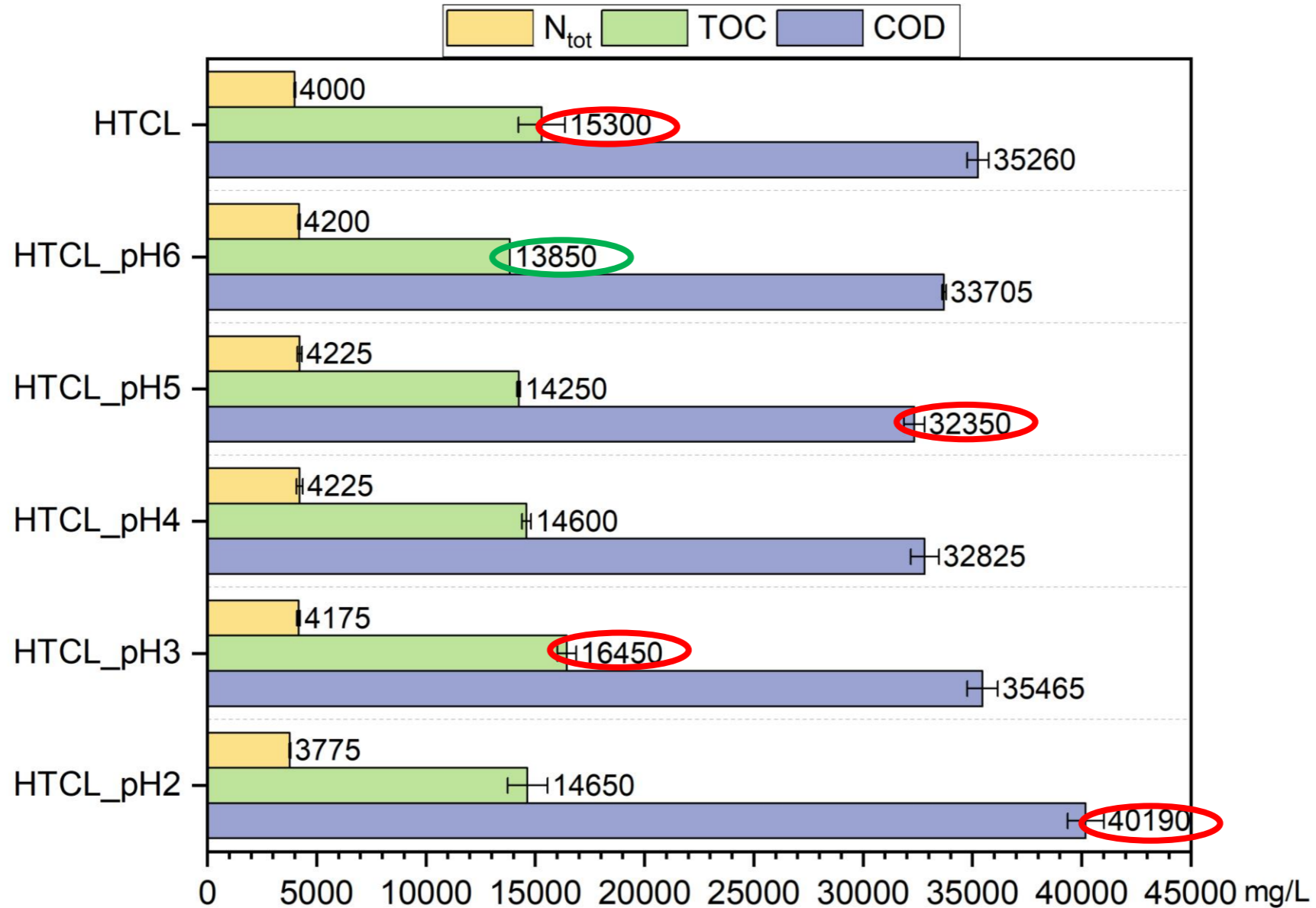


pH=2, 3, 4, 5, and 6

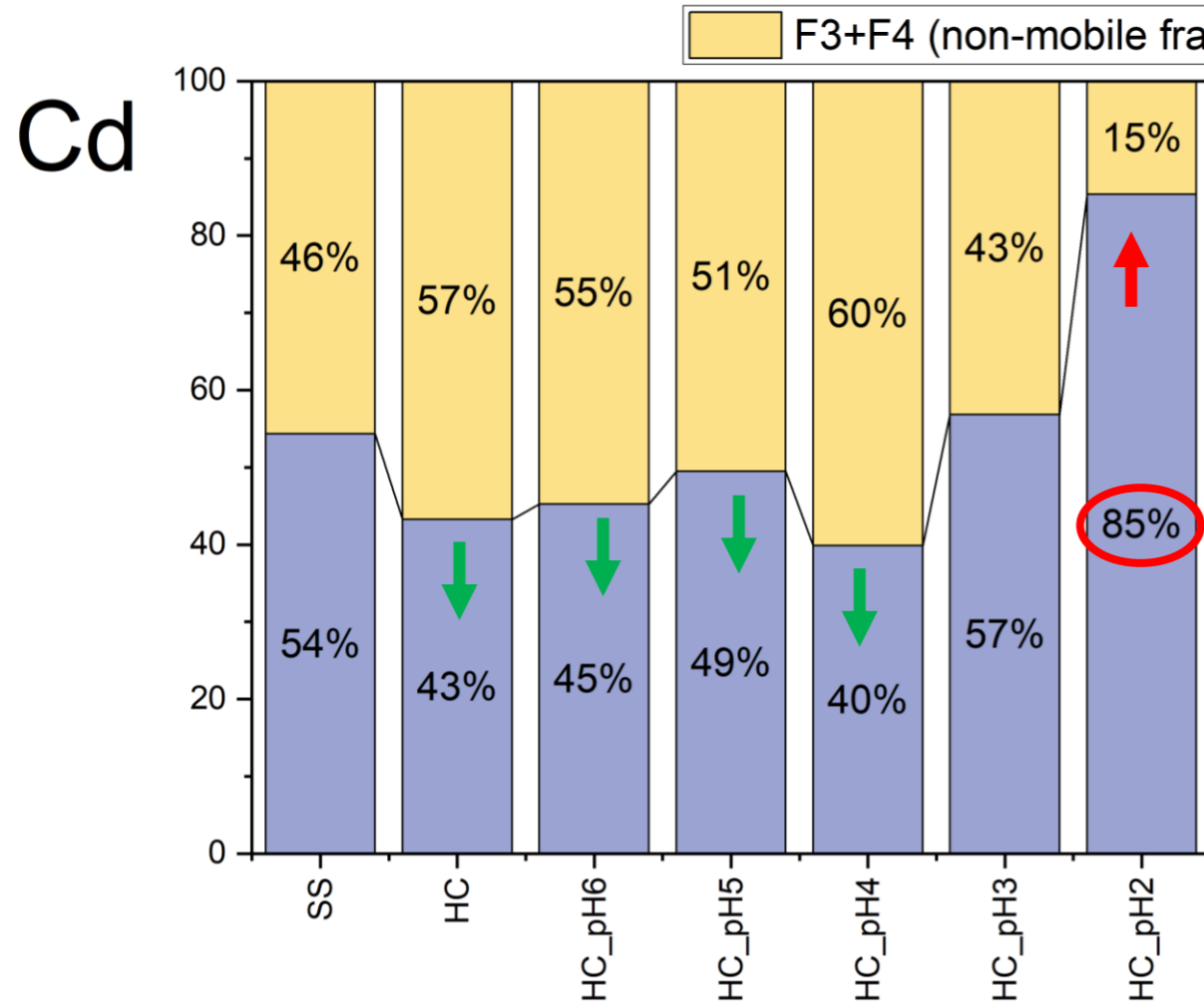
Post- processing liquid: $\text{PO}_4\text{-P}$, PO_4^{3-} , P_2O_5



Post- processing liquid: COD, TOC, N_{tot}

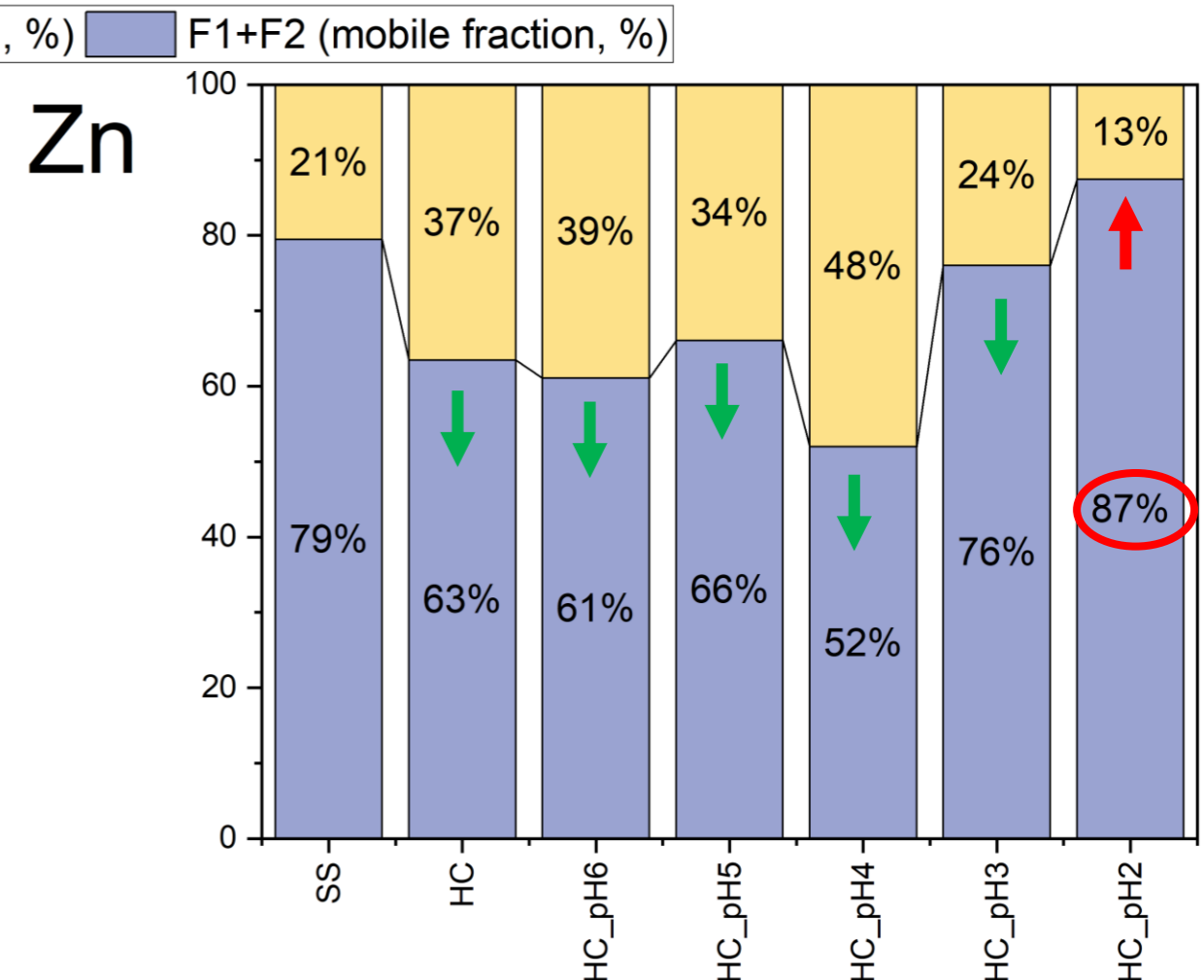


Heavy metals in hydrochar by Tessier and the Community Bureau of Reference (BCR)



$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	2.58	4.03	3.91	4.13	4.37	4.54	5.48

HIGHER 

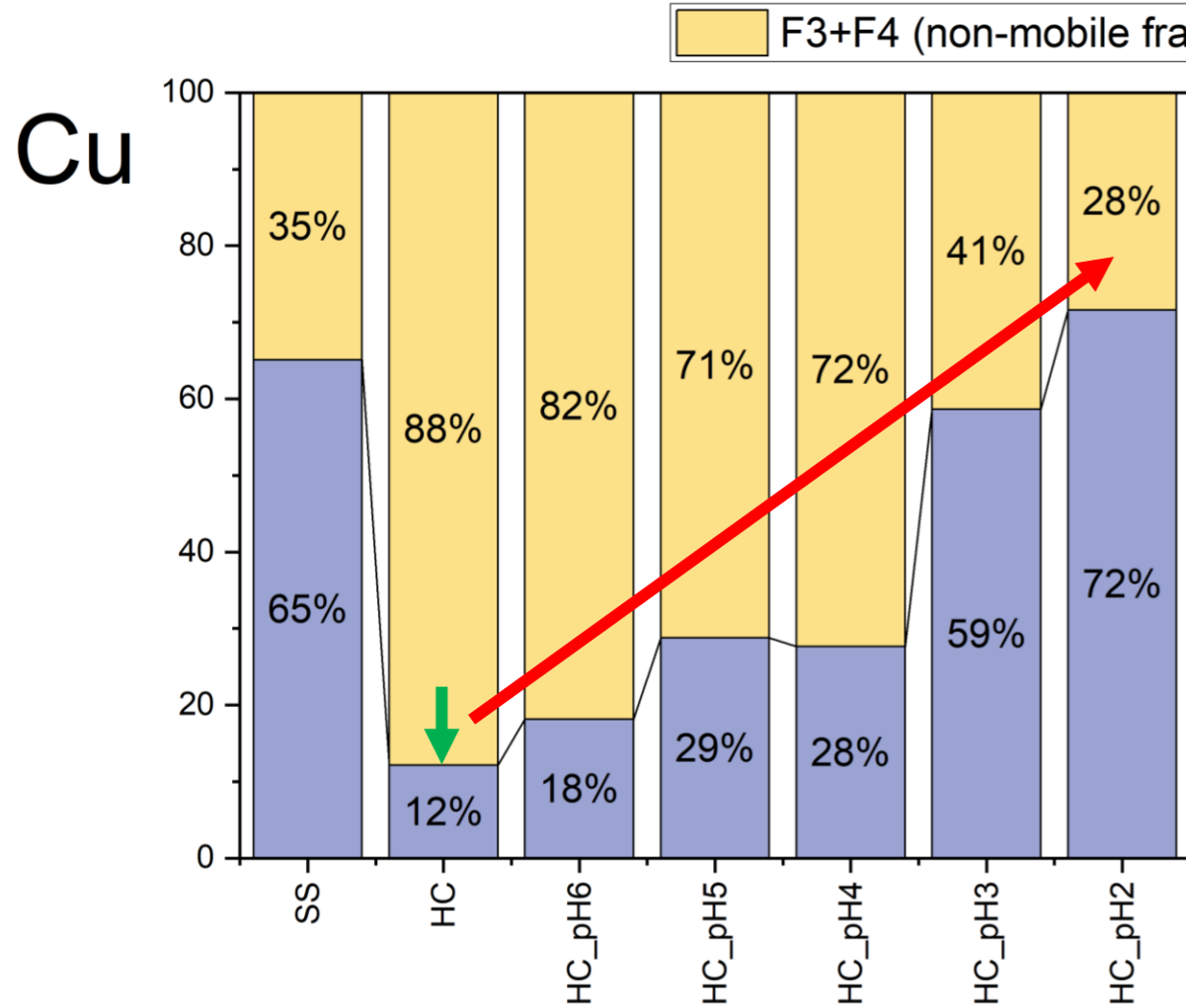


$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	1382.8	2241.7	2216.8	2204.7	2224.3	1927.7	1709.0

HIGHER 

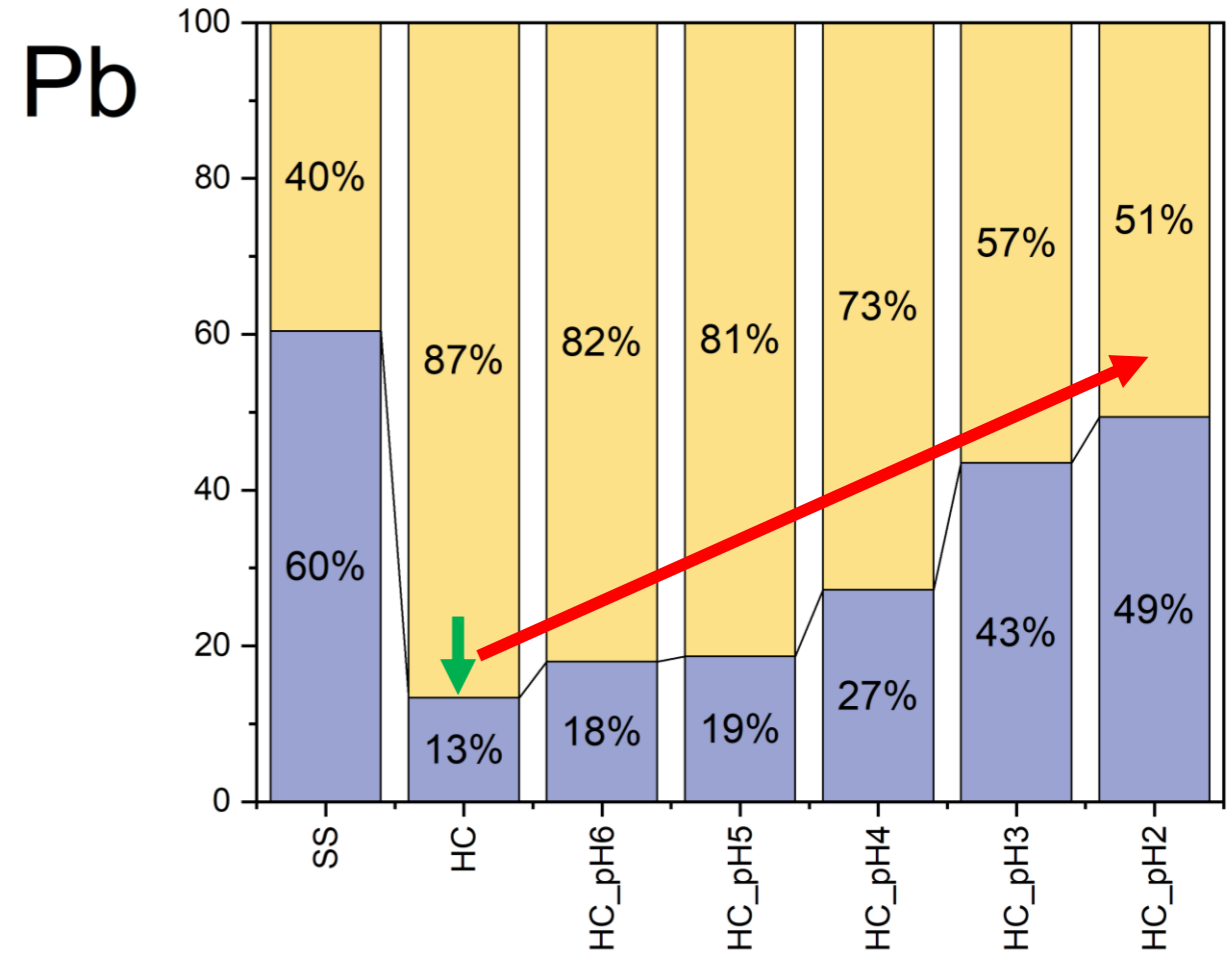
LOWER 

Heavy metals in hydrochar by Tessier and the Community Bureau of Reference (BCR)



$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	155.77	285.75	304.17	282.39	292.80	249.73	312.44

HIGHER →

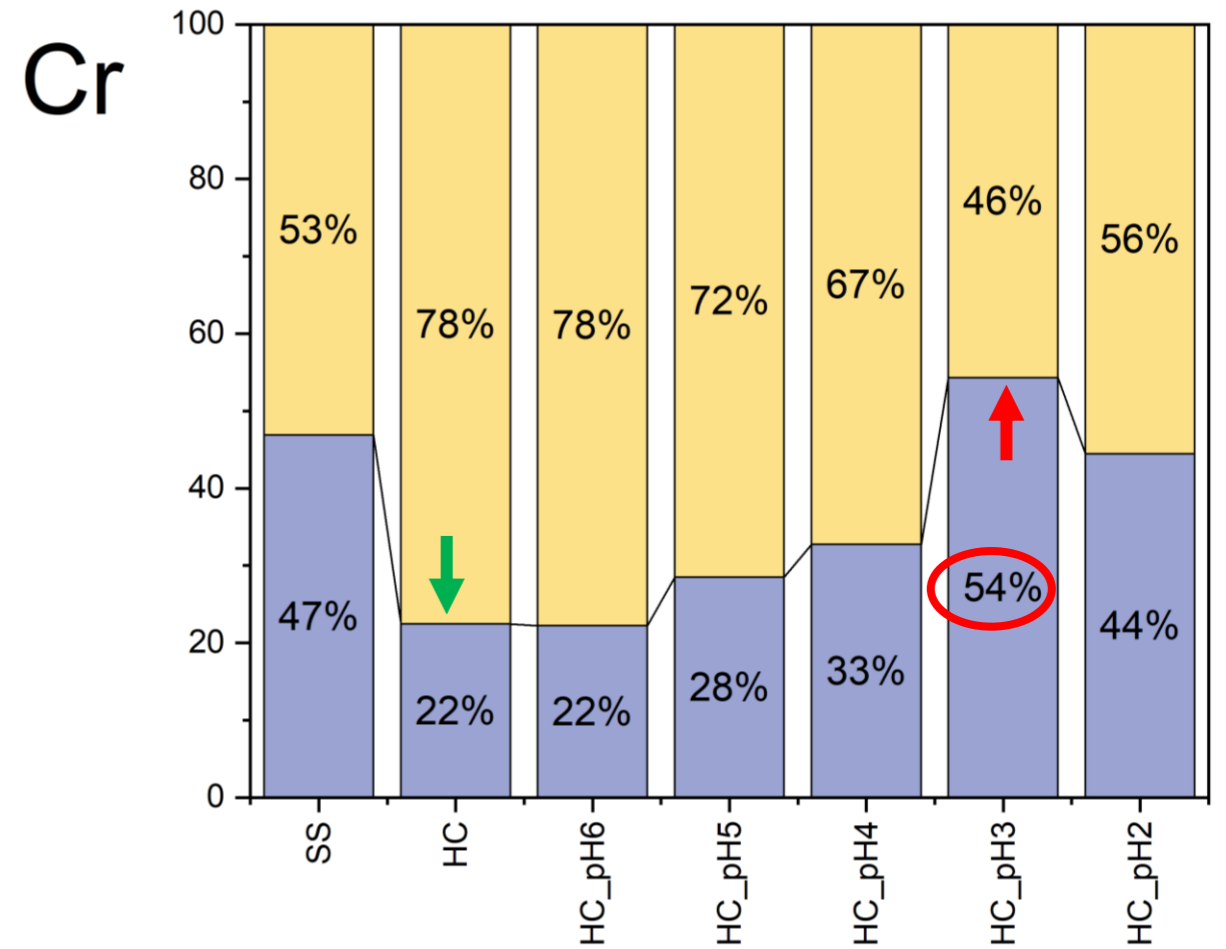
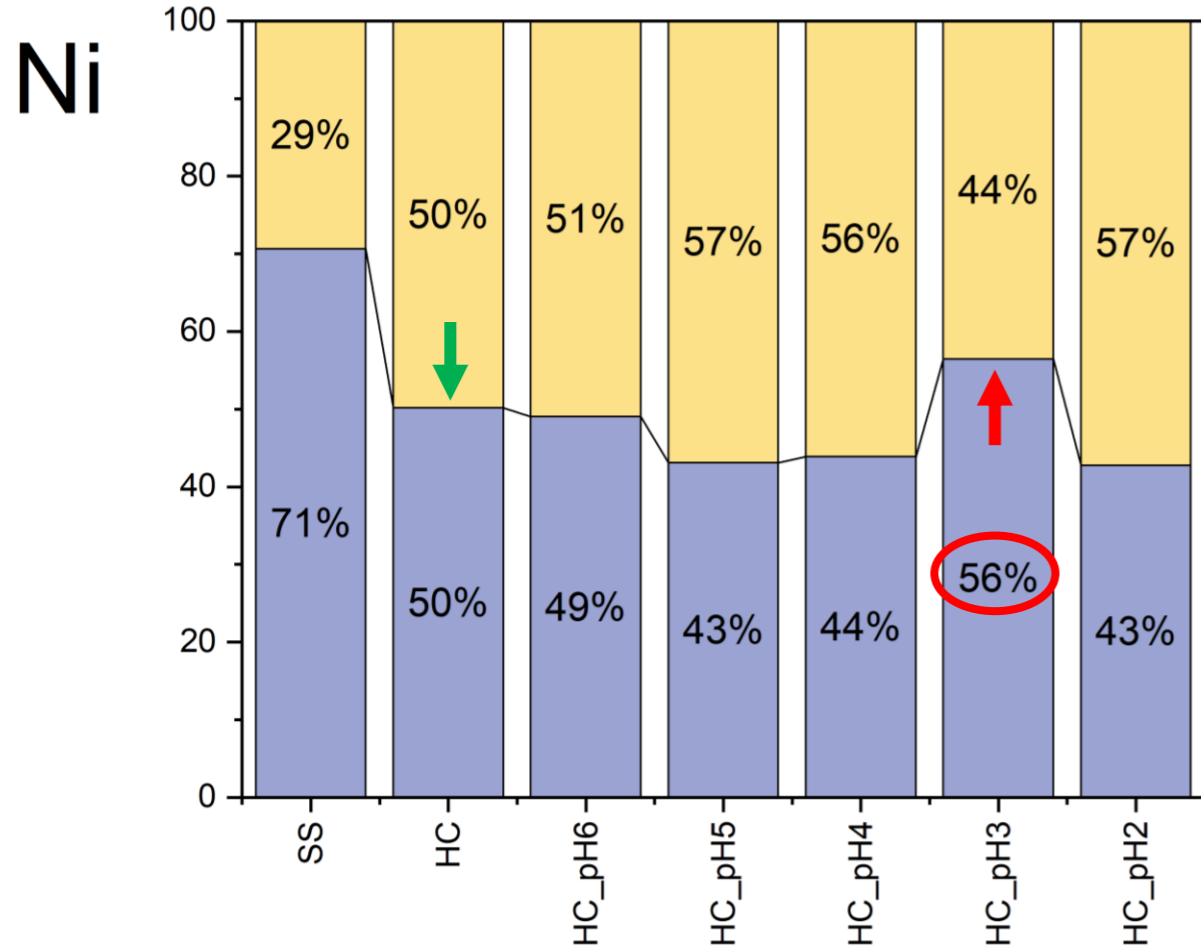


$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	66.49	100.00	108.11	102.21	101.46	83.46	96.16

HIGHER →

Heavy metals in hydrochar by Tessier and the Community Bureau of Reference (BCR)

F3+F4 (non-mobile fraction, %) F1+F2 (mobile fraction, %)



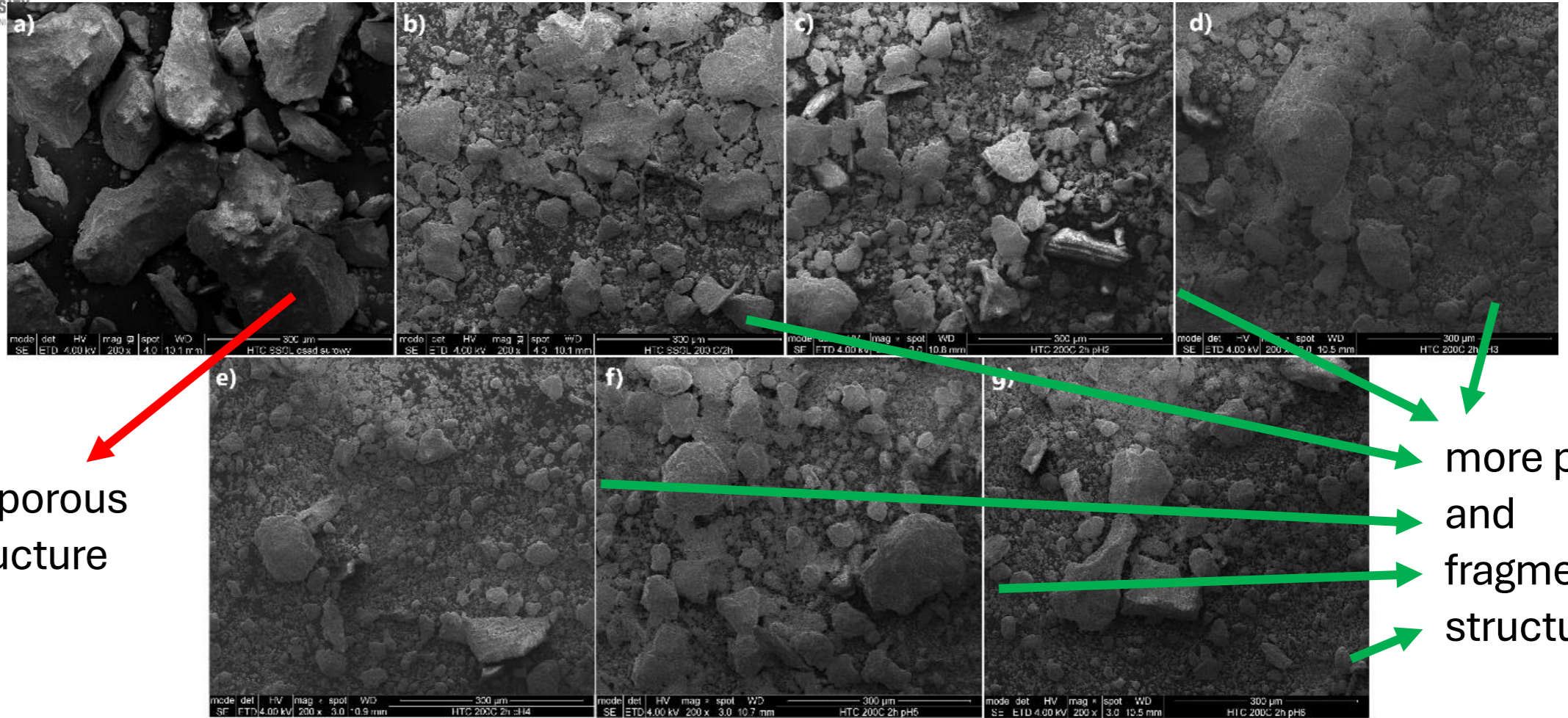
$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	144.29	223.84	219.52	212.22	199.59	150.31	176.02

HIGHER →

$\Sigma F1...F4$	SS	HC	pH6	pH5	pH4	pH3	pH2
(mg/kg)	53.61	80.19	89.34	69.46	76.69	69.87	75.68

HIGHER →

SEM analysis of hydorchar



non porous structure

more porous and fragmentated structure

a) SS, b) HC, c) HC_pH2, d) HC_pH3, e) HC_pH4, f) HC_pH5, g) HC_pH6

	HC	HC_pH6	HC_pH5	HC_pH4	HC_pH3	HC_pH2
SSA, m ² /g	10.28	12.28	13.54	12.12	11.28	7.65
		HIGHER	HIGHER	LOWER	LOWER	LOWER

Conclusions

1

The value of pH during the HTC affects the properties of the resulting products.

2

Extremely decreasing pH causes an increasing in the phosphorus content.

3

Heavy metals content in hydrochar increase after HTC process.

4

HTC process resulted in a decrease in the content of mobile phases of heavy metals after the HTC process.



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Thank you for your attention!

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