Tailored Hydrothermal Liquefaction Strategies Based on Sludge Structure: The Role of Biochemical Wastewater Treatment in Shaping Sludge Composition

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From Waste to Valuable Resources

Algae

Municipal Sludge

Industrial Hemp

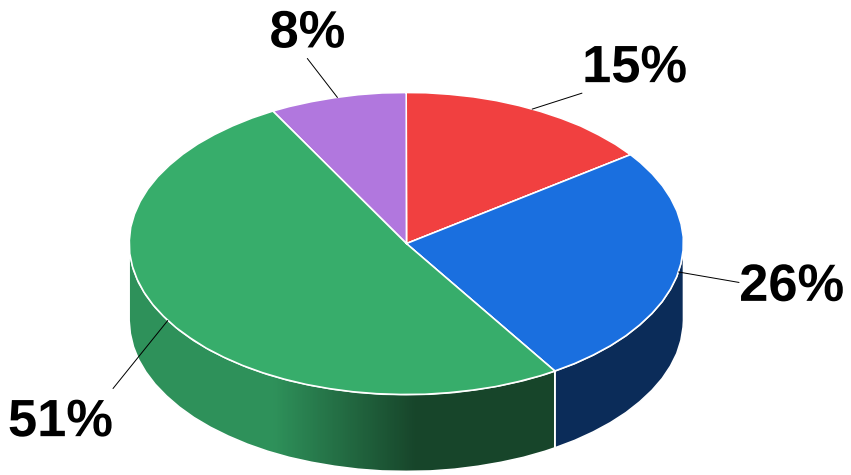
Crude oil

Pistachio Shells

Fertilizer

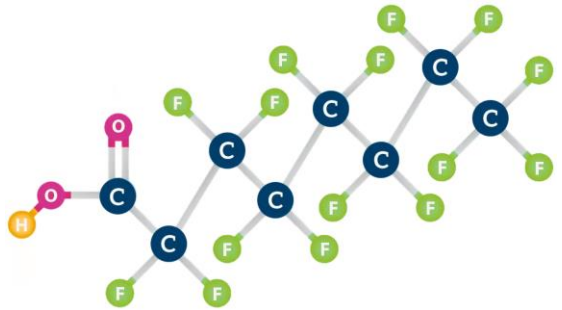
Sludge as a Potential Feedstock

- **Availability** 34 billion gallons of wastewater processed daily in the US [1].
- **Financial Importance** Sludge handling and disposal accounts for **1/3** of a wastewater treatment plant energy capital cost [2].
- **Conventional Practices for Disposal** [3]



- Land Application
- Landfill
- Incineration
- Other

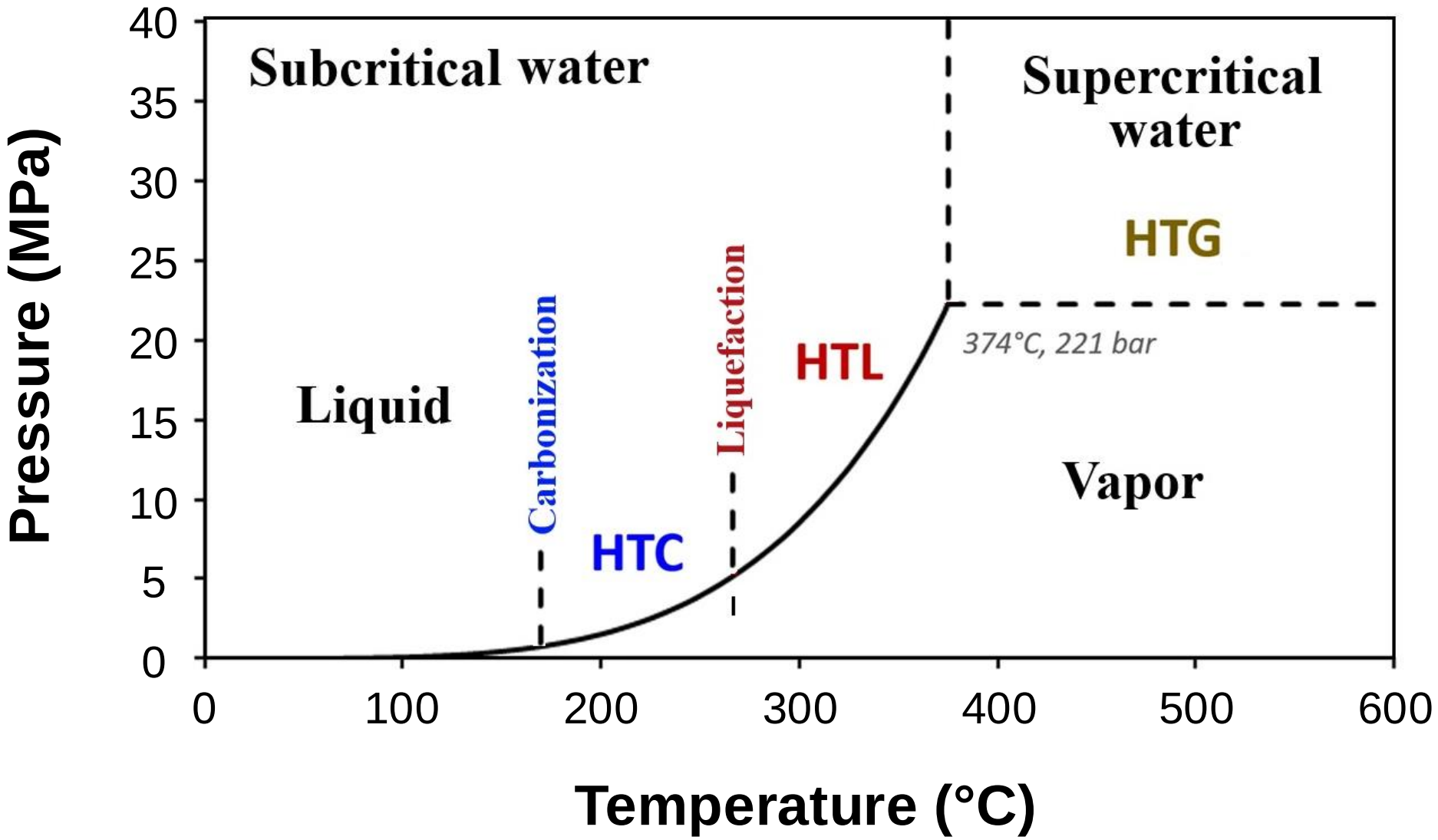
Toxicity Concerns



PFAS

1. US Environmental Protection Agency. *Sources and Solutions: Wastewater*. EPA, 7 Mar. **2024**, https://www.epa.gov/nutrientpollution/sources-and-solutions-wastewater. Accessed 11 Apr. 2025.
2. Örmeci, Banu, and Hansruedi Siegrist. "Cost Evaluation of Sludge Treatment Options and Energy Recovery from Wastewater Treatment Plant Sludge." *IULTCS Congress Proceedings*, 2013.
3. Beecher, Ned, et al. *National Biosolids Data Project: Biosolids Management in the U.S.* **2022**, https://www.biosolidsdata.org/national-summary. Accessed 11 Apr. 2025.

Hydrothermal Processing



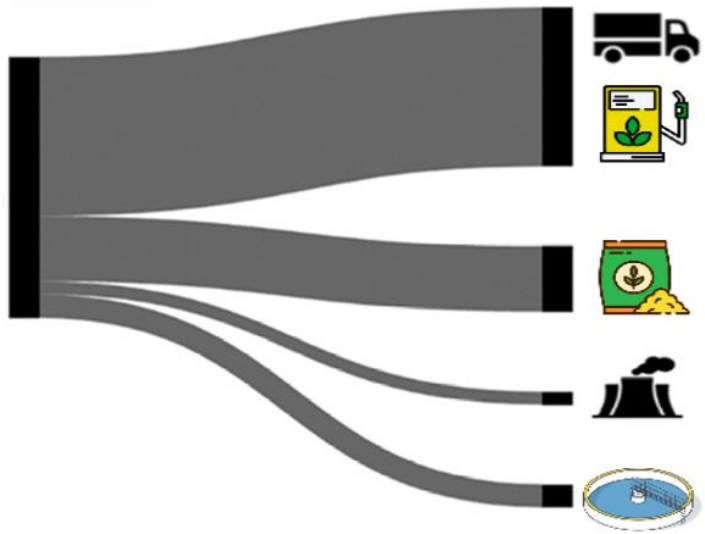
Hydrothermal Liquefaction (HTL)

Uses temperatures and pressures to convert **wet biomass** into four products [4].

Wastewater Treatment Plant

Sludge

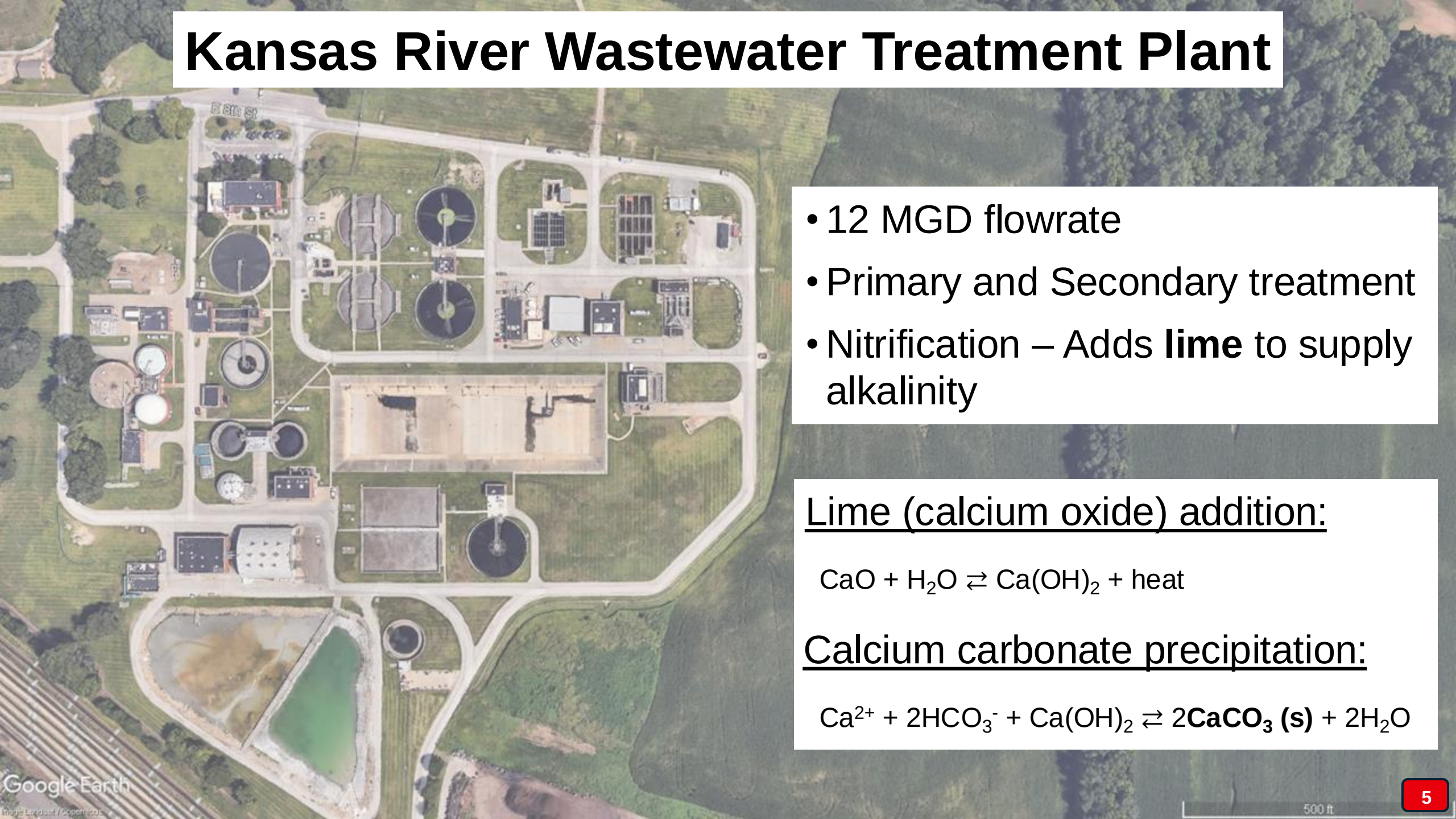
HTL Reactor



What is the impact of the WWTP process on the sludge properties?

4. **Ahmed, J., Rehman, S., Sultan, S. H., et al. (2022).** *Hydrothermal Liquefaction of Lignocellulosic and Protein-Containing Biomass: A Comprehensive Review.* MDPI.

Kansas River Wastewater Treatment Plant



- 12 MGD flowrate
- Primary and Secondary treatment
- Nitrification – Adds **lime** to supply alkalinity

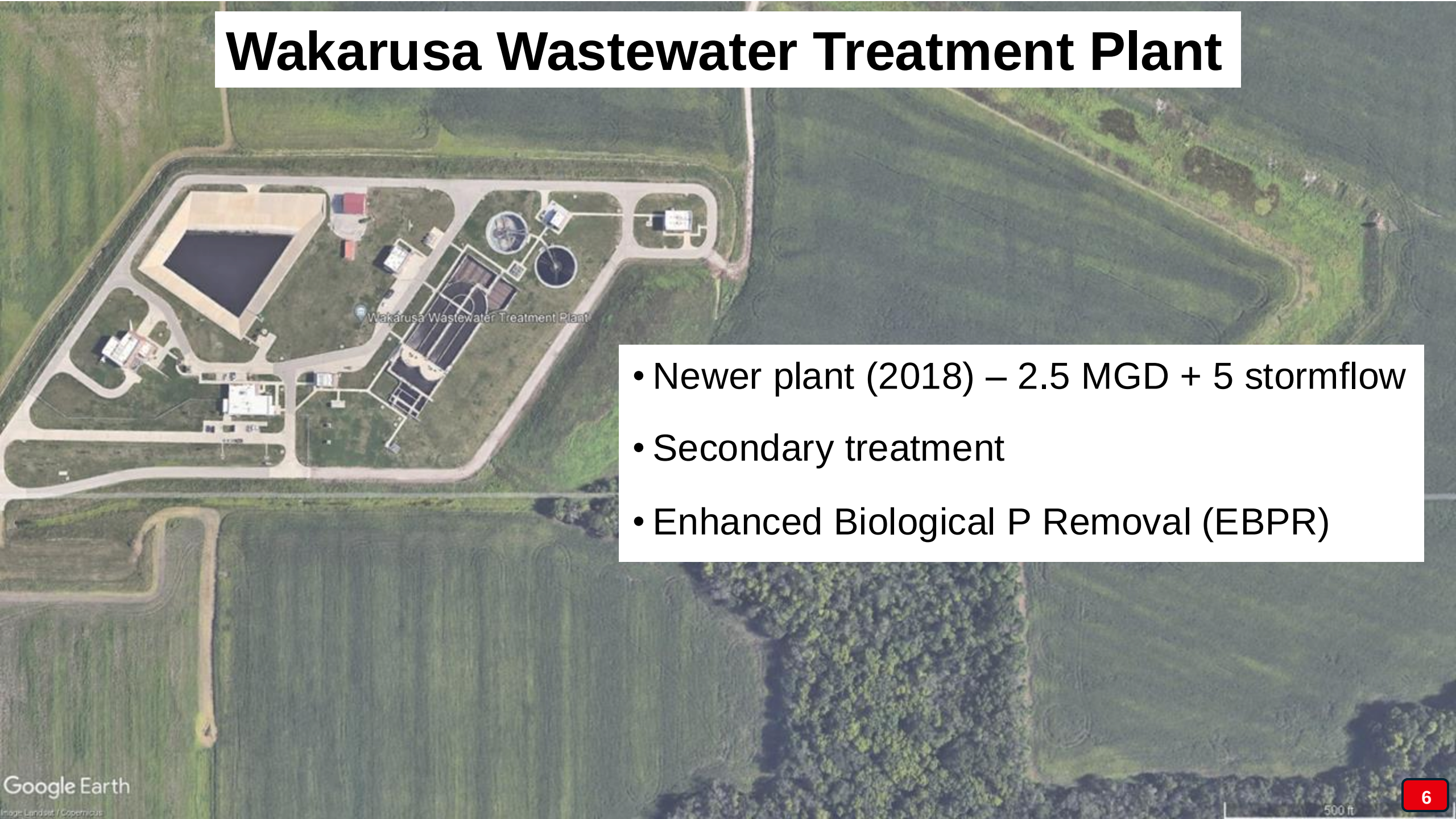
Lime (calcium oxide) addition:

$$CaO + H_2O \rightleftarrows Ca(OH)_2 + heat$$

Calcium carbonate precipitation:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightleftarrows 2\mathbf{CaCO_3\ (s)} + 2H_2O$$

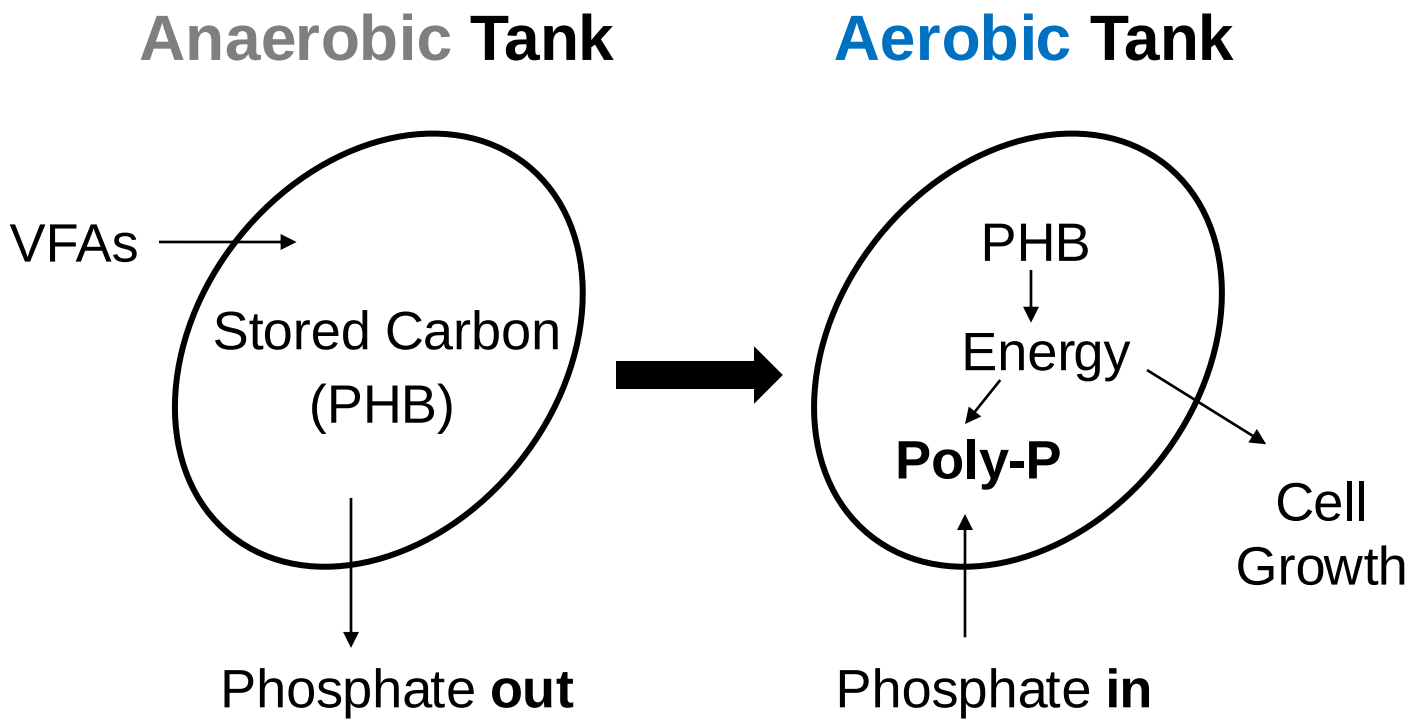
Wakarusa Wastewater Treatment Plant

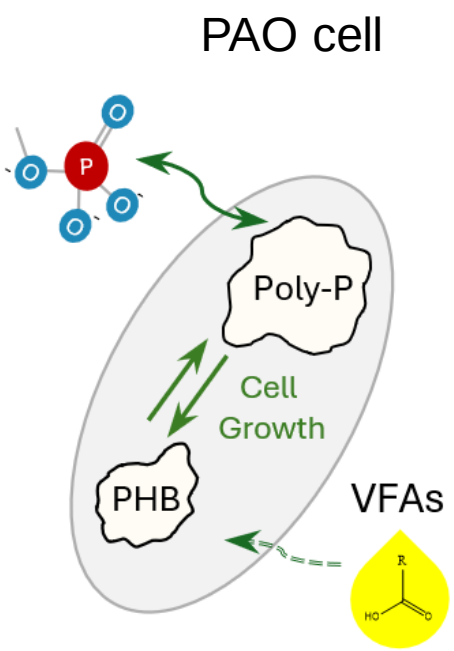


- Newer plant (2018) – 2.5 MGD + 5 stormflow
- Secondary treatment
- Enhanced Biological P Removal (EBPR)

Enhanced Biological Phosphorus Removal

Phosphorus Accumulating Organisms (PAOs) are microorganisms that, under certain conditions, promote P removal from wastewater.





Research Study: Methodology

Sludge: Kansas WWTP
- Stored Aerobically
- Lime added
- No EBPR

Sludge: Wakarusa WWTP
- Stored Anaerobically
- No Lime added
- EBPR

Sludge: Wakarusa WWTP
- Stored Aerobically
- No Lime added
- EBPR

1. WWTP Processes

2.Storage Methodology

Understand if these different processes and storage conditions impact sludge composition

Results: Sludge Composition

WWTP Collected	Kansas	Wakarusa	Wakarusa
Storage Method	Aerobic	Anaerobic	Aerobic
Carbon (%)	32.6	46.4	42.6
Hydrogen (%)	4.7	6.9	6.2
Nitrogen (%)	5.3	8.2	7.5
Oxygen (%)	30.3	29.7	31.3
Ash (%)	30.3	10.7	15.3
Phosphorus (%)*	7.6	11.0	15.9
Calcium (%)*	30.7	13.5	8.7

*Percentage corresponding to the ash fraction

- Values shown in %dw
- Standard deviation ± 1.2%
- Highest ash % from Kansas WWTP

Lime addition

Results: Sludge Composition

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- Values shown in %dw
- Standard deviation ± 1.2%
- Highest ash % from Kansas WWTP
  - **Lime addition**
- 10% higher Carbon at Wakarusa WWTP
  - **Only final clarifier**

Results: Sludge Composition

WWTP Collected Storage Method	Kansas Aerobic	Wakarusa Anaerobic	Wakarusa Aerobic
Carbon (%)	32.6	46.4	42.6
Hydrogen (%)	4.7	6.9	6.2
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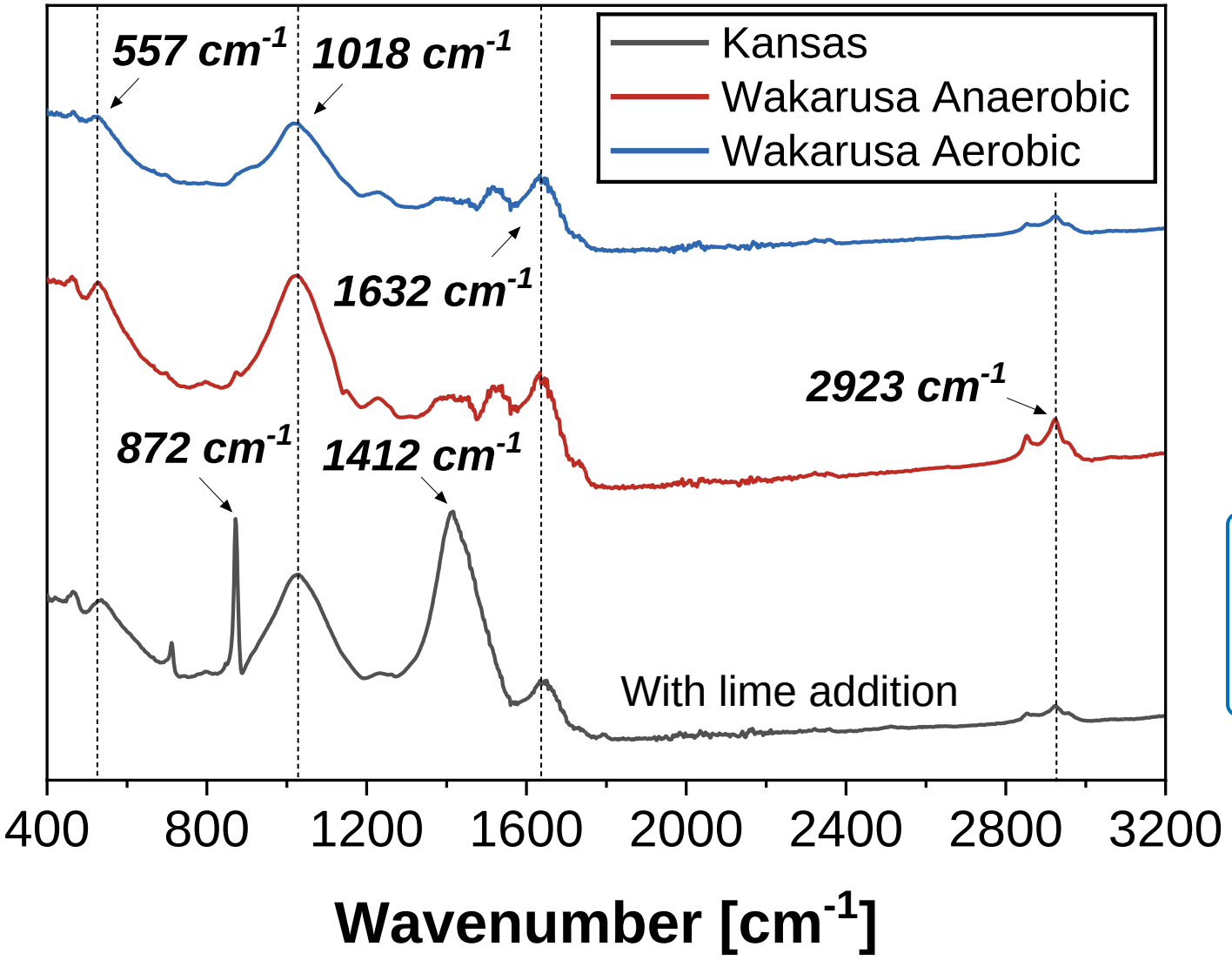
*Percentage corresponding to the ash fraction

- Values shown in %dw
- Standard deviation ± 1.2%
- P higher with EBPR
- Aerobically stored sludge retains more P

EBPR

Results: Sludge Structure FTIR



557 and 1018 cm^{-1} **phosphate** peaks

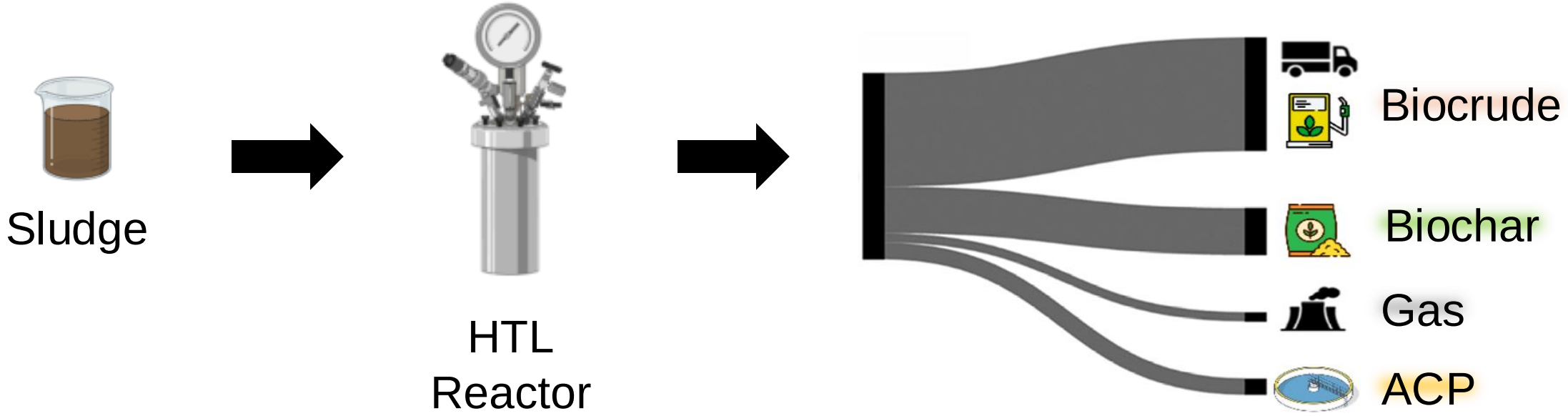
872 and 1412 cm^{-1} **carbonate** peaks

Lime addition

$CaO + H_2O \rightleftarrows Ca(OH)_2 + heat$

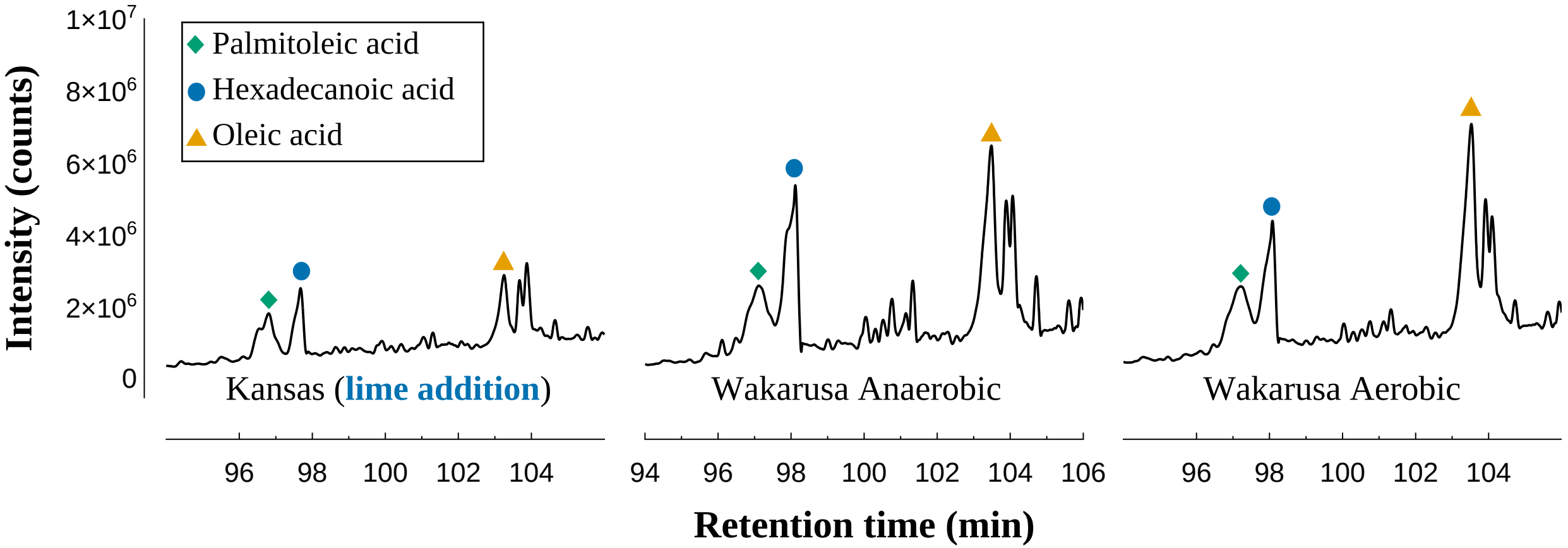
$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightleftarrows 2\mathbf{CaCO_3\ (s)} + 2H_2O$

Hydrothermal Liquefaction (HTL)



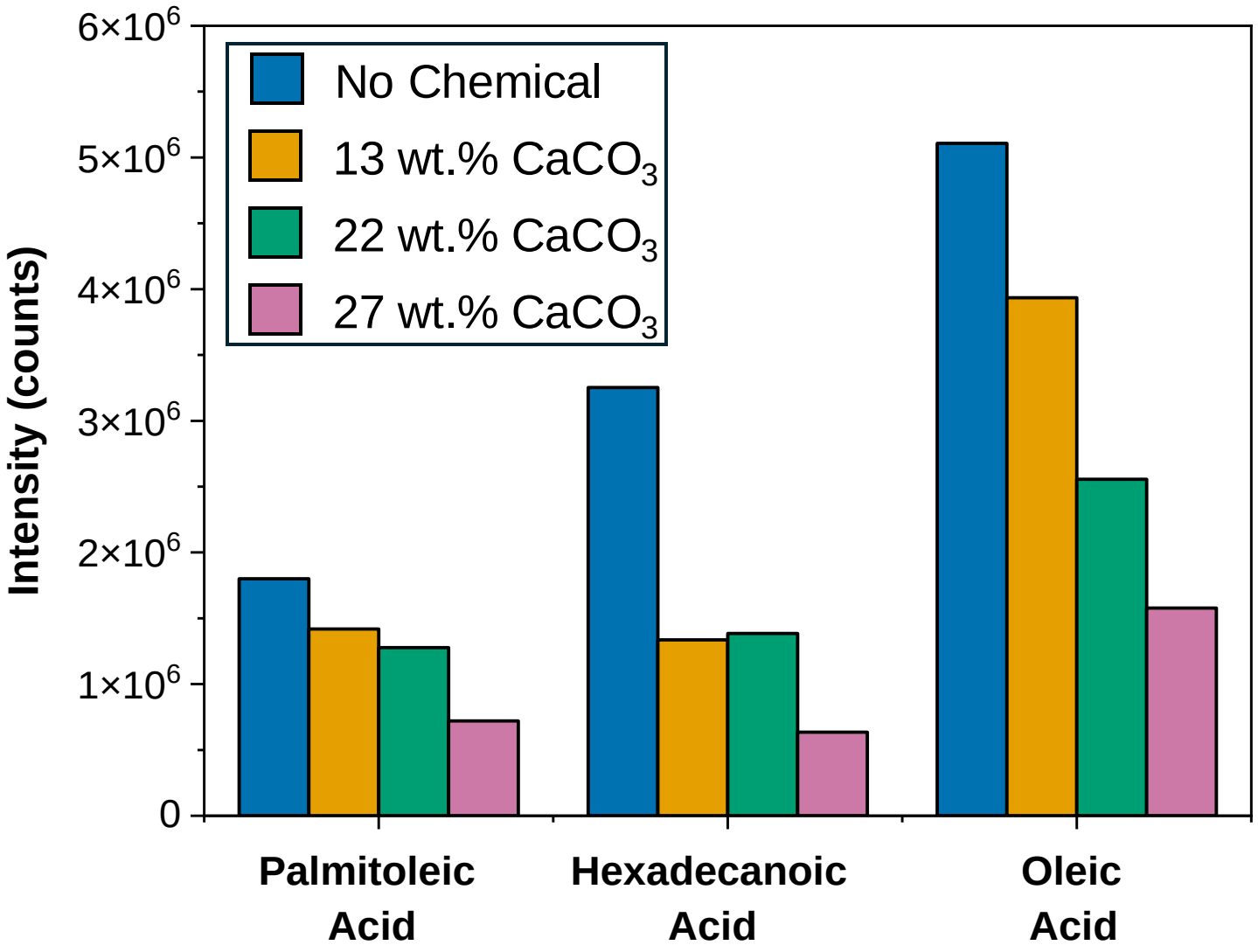
Reaction conditions: 10 wt.% solids at 350 °C for one hour

Biocrude Characterization: GC-MS



Lime addition in wastewater treatment **hinders the formation of carboxylic acids** in the crude

Biocrude Characterization: GC-MS



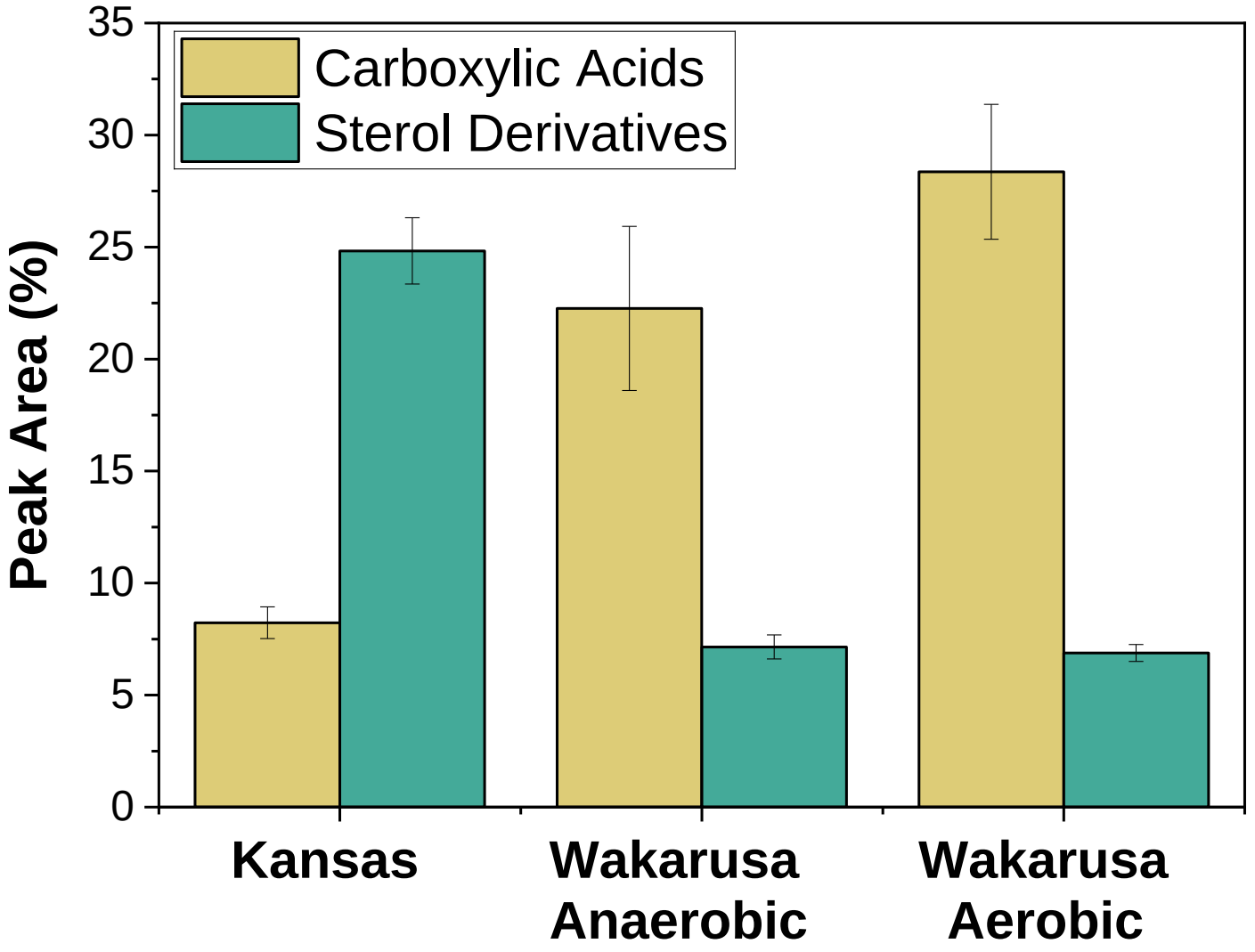
Complementary Study:

Sludge from Wakarusa WWTP (no lime addition) and added $CaCO_3$.

Confirmed carboxylic acids decrease

Are there any other changes?

Biocrude Characterization: GC-MS



- What are we forming?

Sterol derivatives

Decarboxylation Reaction

$$C_nH_{2n+2}COO \rightarrow C_nH_{2n+2} + CO_2$$

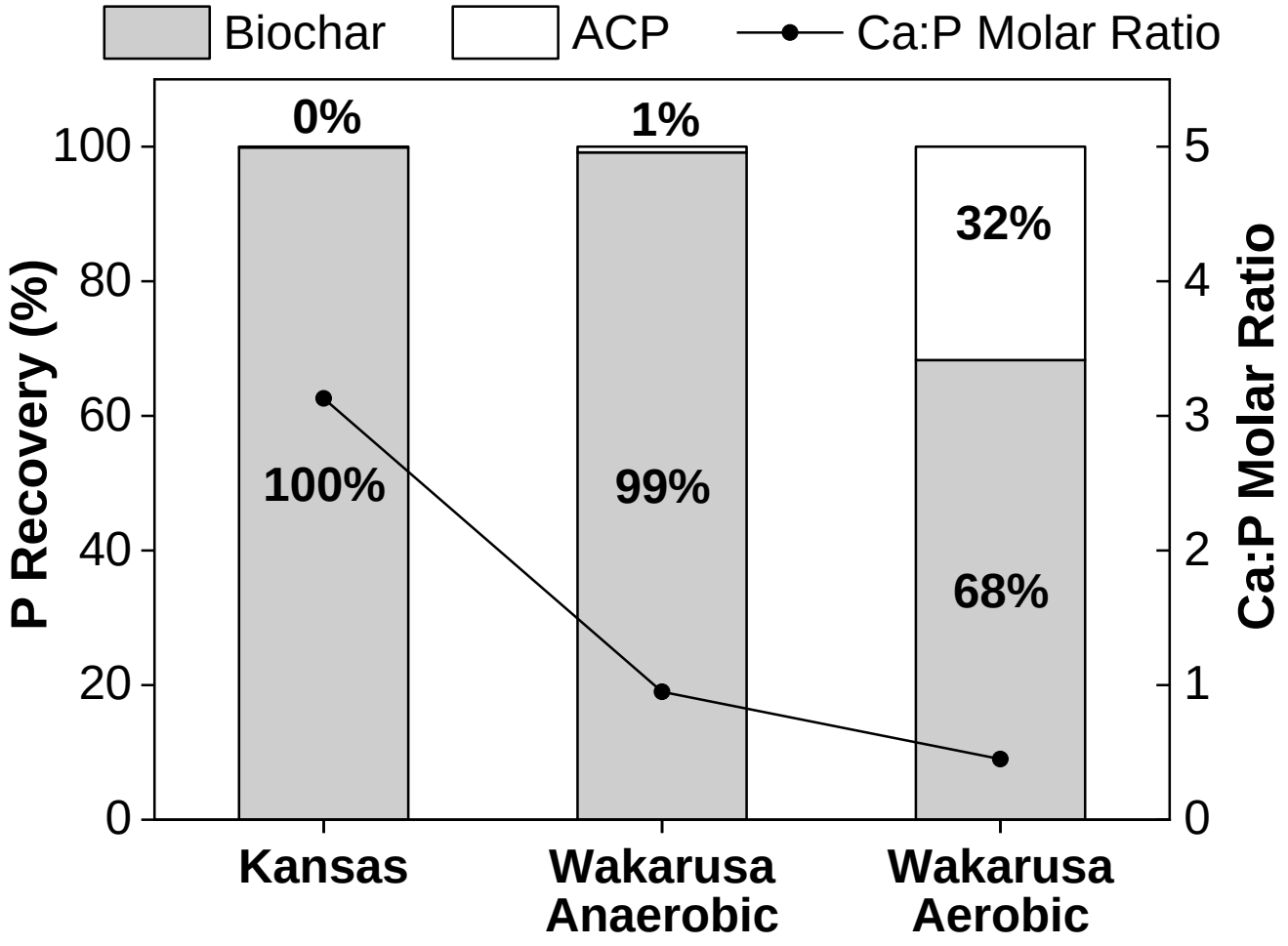
Carboxylic acid — Alkane

$CaCO_3$ in HTL promotes recombination reactions, forming more **complex** and **stable** hydrocarbon structures, such as sterol derivatives [4, 5]

Biochar: Nutrient Distribution Results

- **Fertilizer**

Biochar can be used as a fertilizer depending on its **P** content

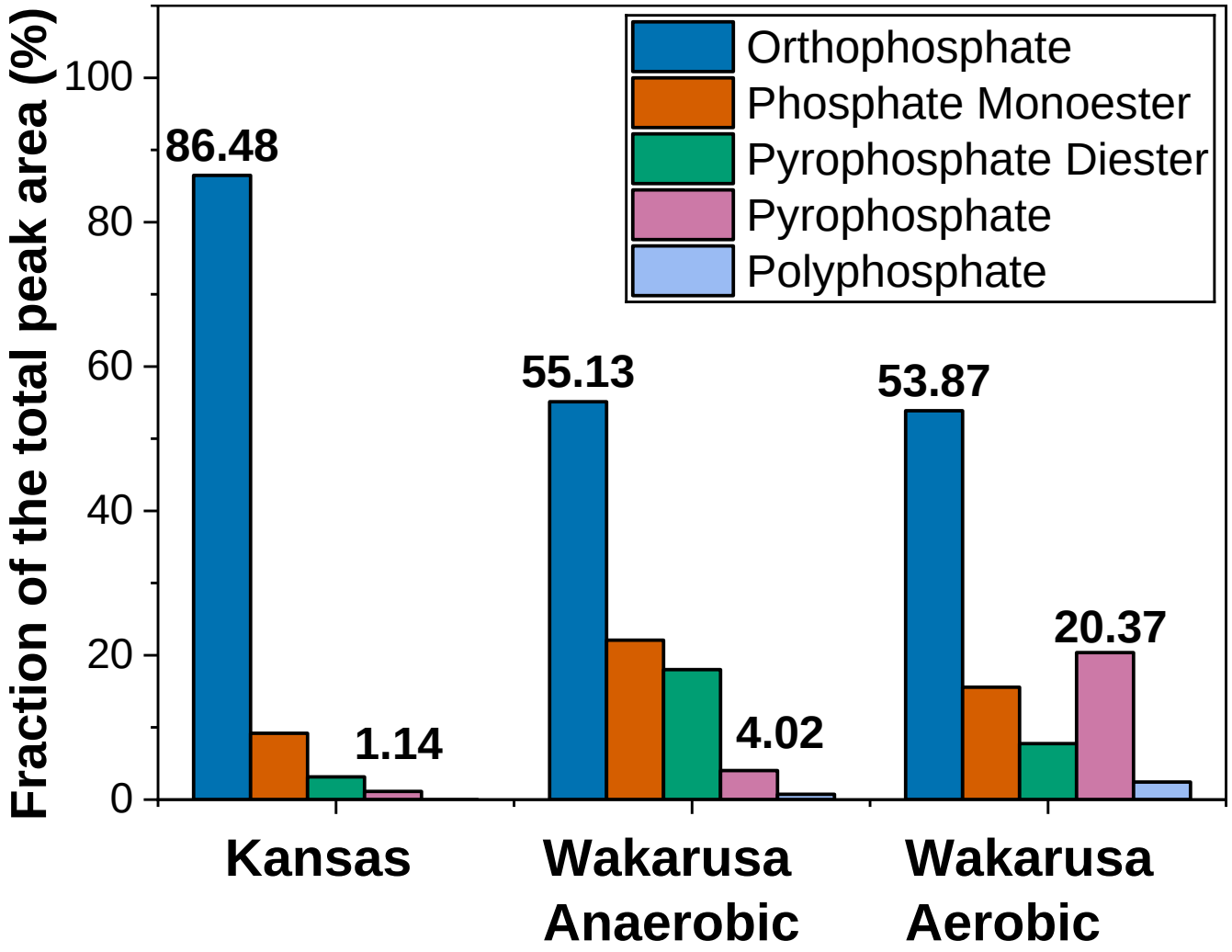


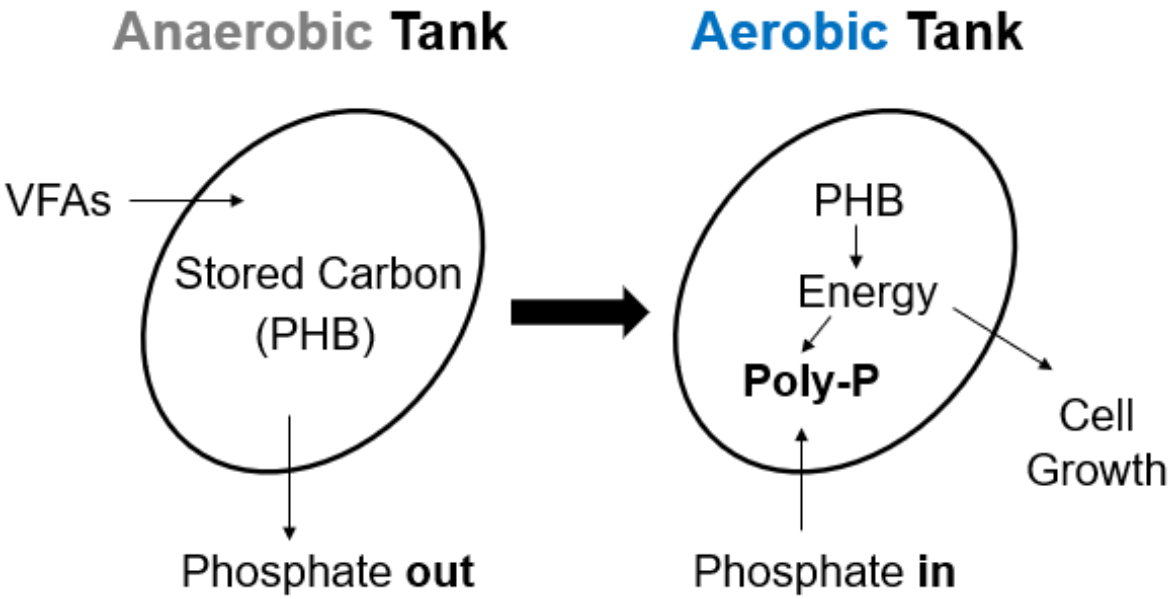
During HTL, inorganics such as P goes through a series of transformations and can end up either in the biochar or ACP.

Why do storage conditions play a role in P distribution?

Remember EBPR?

Biochar: Nutrient Distribution Results

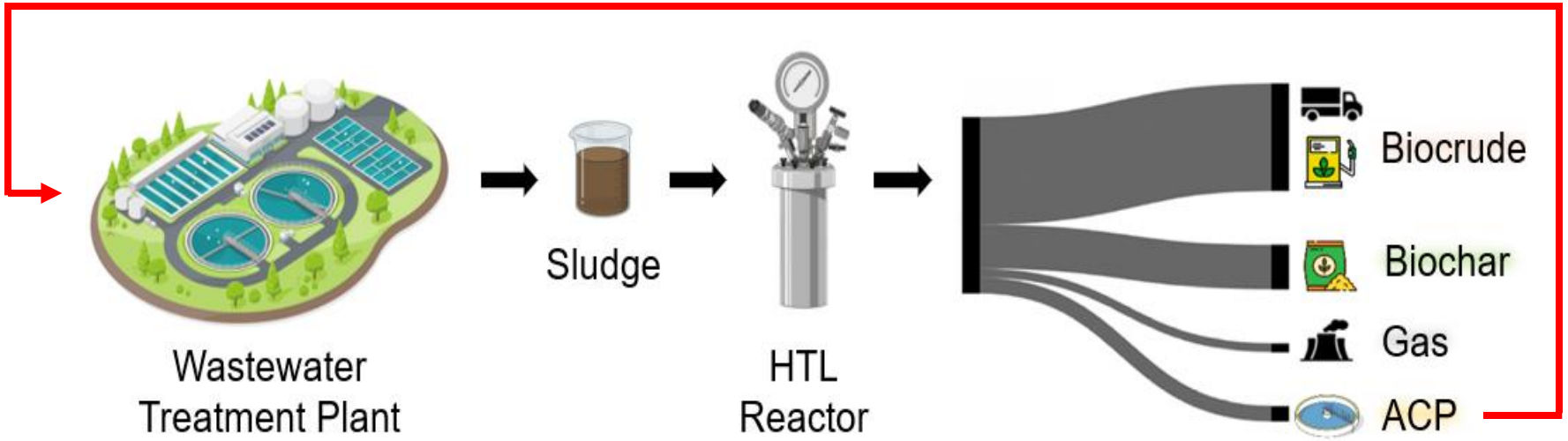




Pyro-P and **Poly-P** may not fully precipitate during HTL, leading to their accumulation in the ACP.

ACP Recycling within Acceptable Limits

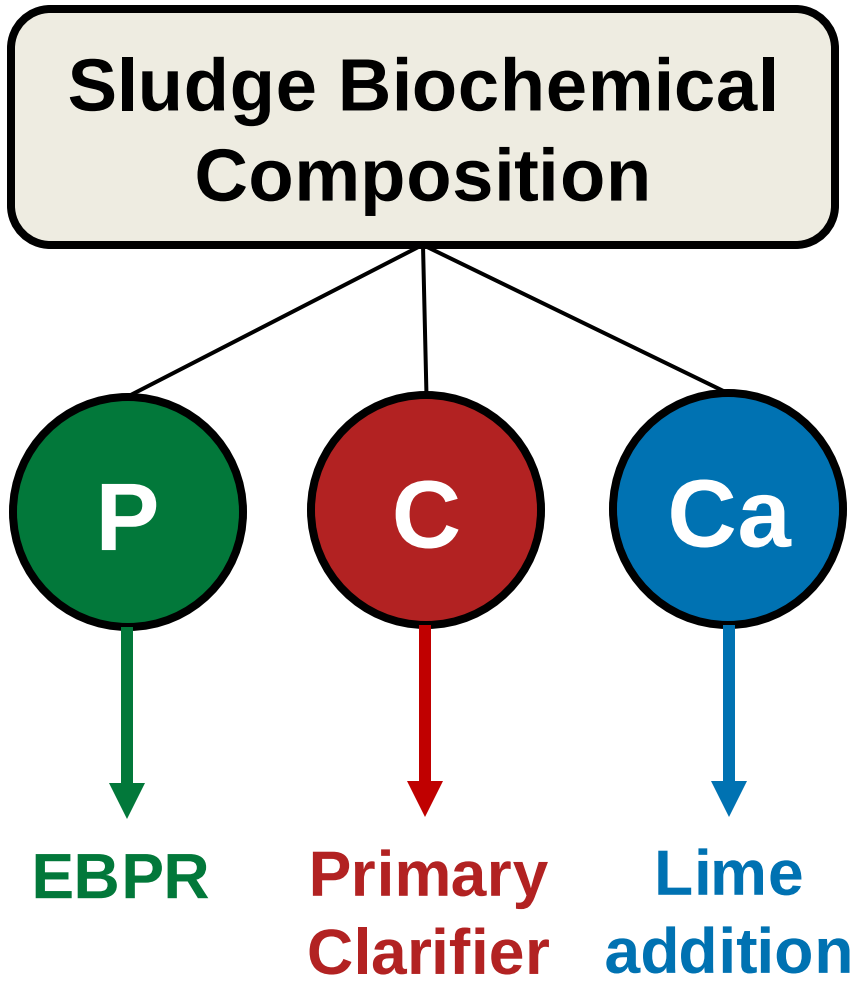
How does recycling ACP back to aeration basins affect the microbes?

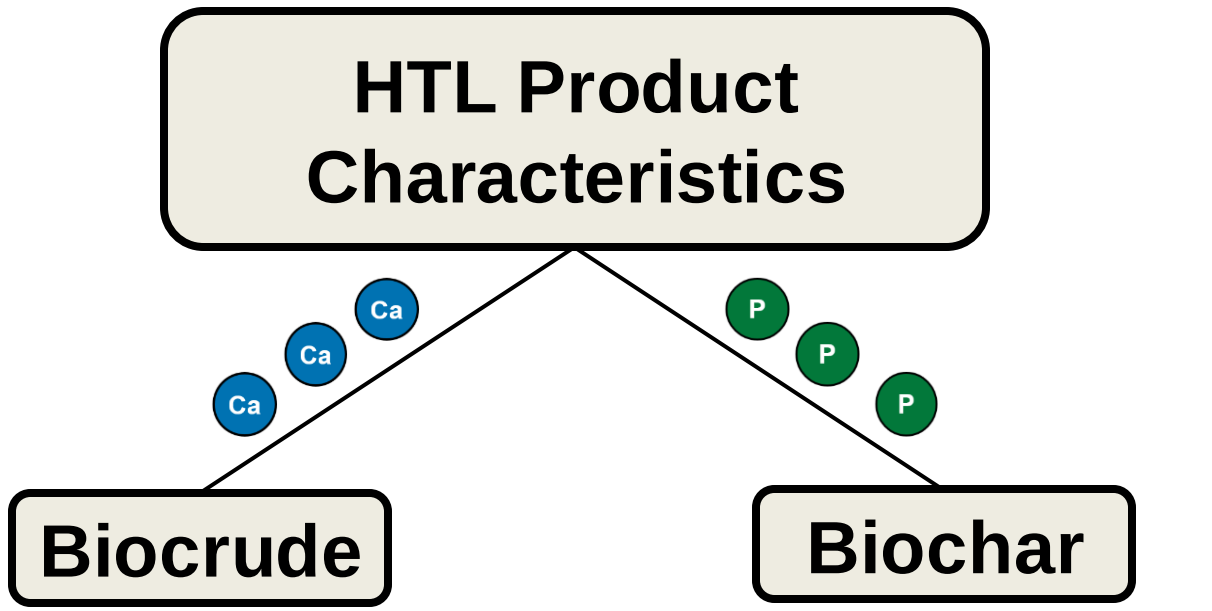


Link to Publication

- Toxicity is due to presence of primarily **pyrrolidinone**, **pyrazine**, and **piperidinone**.
- Storing the ACP over time can significantly reduce its toxicity.
- Completely recycle the ACP – still within range of acceptable limits.

Variations in WWTP processes influence:





- Carboxylic acids
- Carbon Recovery
- Oxygen Composition

- P distribution
- Quality

Acknowledgements

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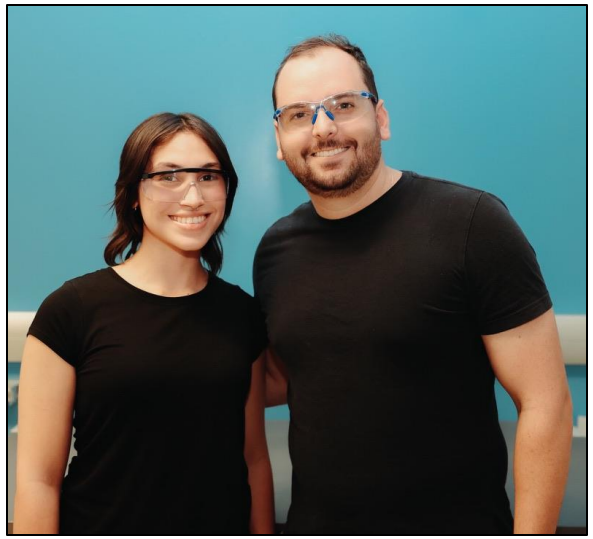

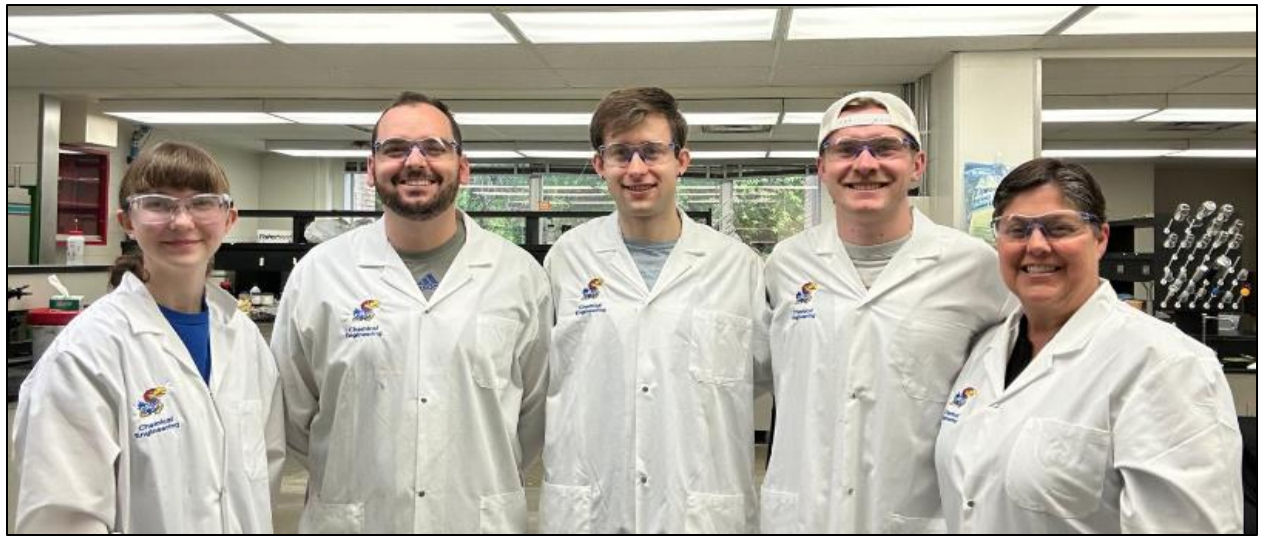

Thank you!

Happy to answer any questions.

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