# High Efficacy Two-Stage Metal Treatment Incorporating Basic Oxygen Furnace Slag and Microbiological Sulfate Reduction

Evelyn M. Miranda, Caleb McLaughlin, Leonard Santisteban, Anca G. Delgado

Assistant Professor of Environmental Engineering, Arizona State University, Tempe, AZ

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Biodesign Swette Center for Environmental Biotechnology

## Delgado Lab Spring 2024

https://biodesign.asu.edu/environmental-biotechnology/

Graduate students:

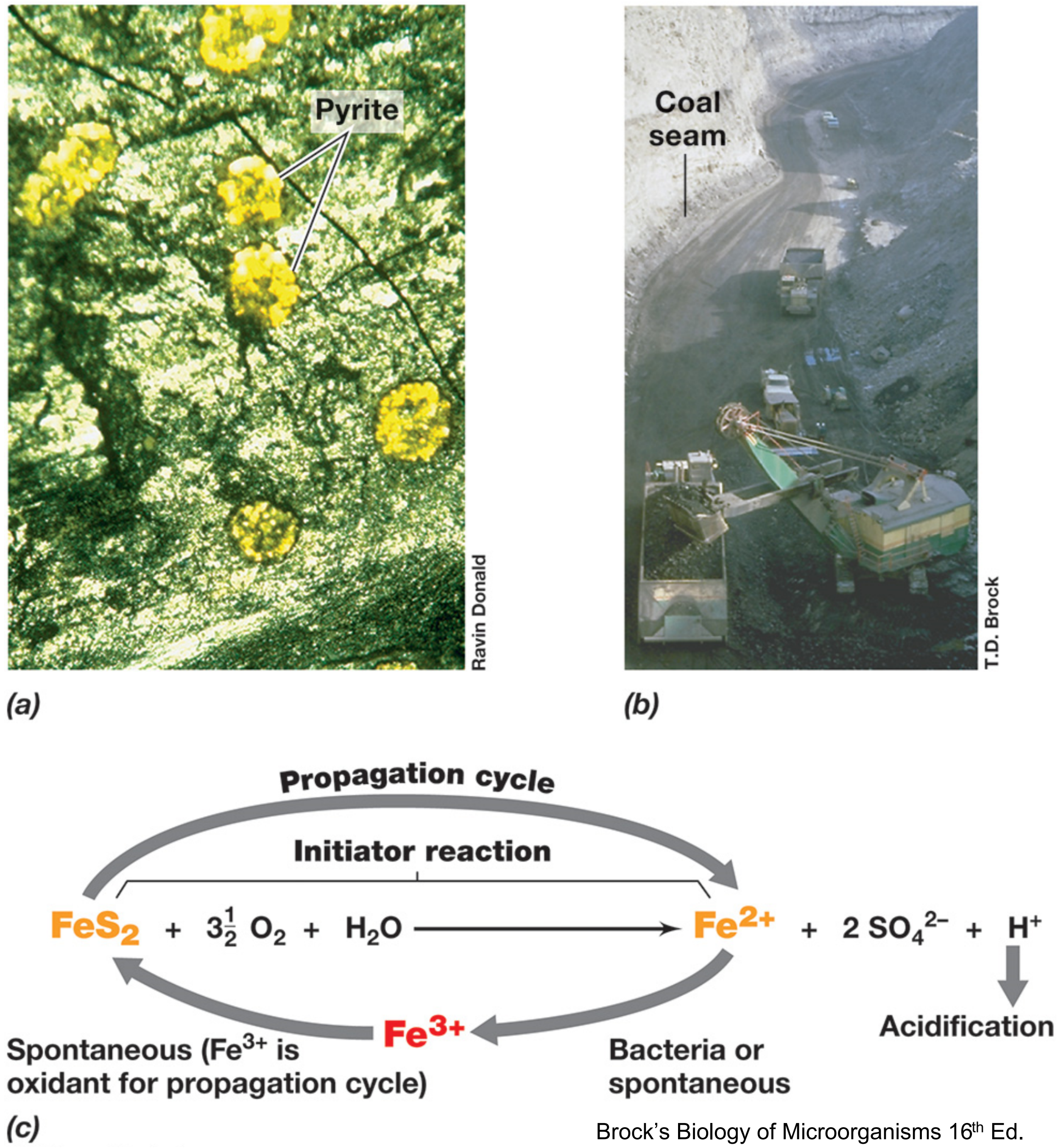
Evelyn Miranda, Ph.D.
Caleb McLaughlin, Michael Edgar

Undergraduate students:
Kyle Reep, Carli Severson, Colton Landrum

Collaborators:
Leonard Santisteban, Shane Hansen (Freeport-McMoRan)
Nasser Hamdan, Dennis Grubb (Jacobs Engineering)

# Mining is globally essential


https://mrdata.usgs.gov/general/map-global.html




Brock's Biology of Microorganisms 16th Ed.

**Environmental challenge**
**- mining-influenced water (MIW)** (rock/mine drainage) contains high concentrations of sulfate and heavy metals, e.g., iron, arsenic, aluminum, cadmium, copper, lead, zinc, nickel, mercury.

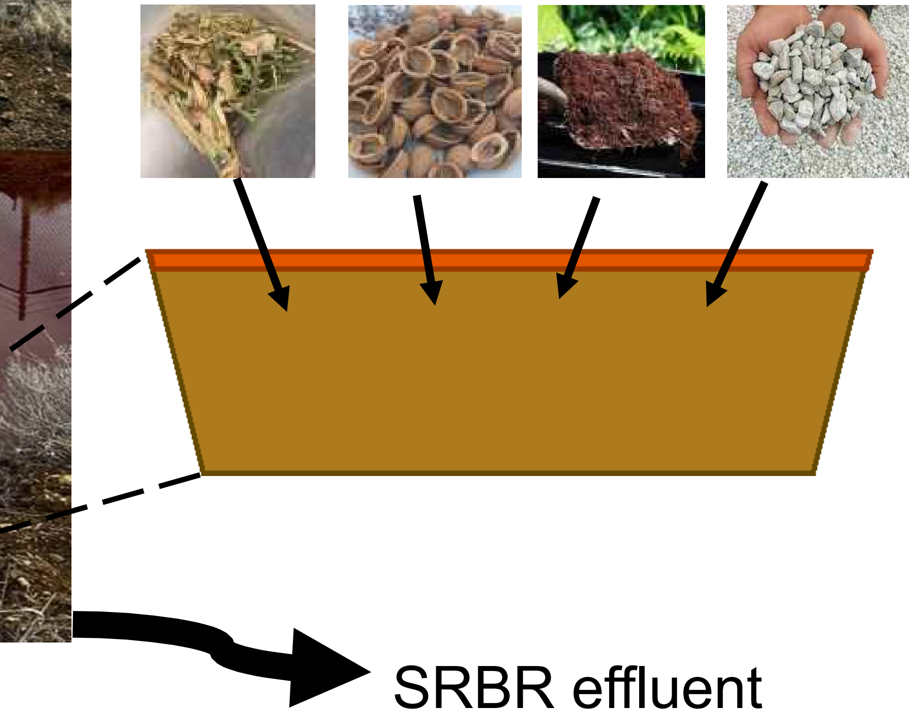
- pH is commonly acidic (e.g., 2.5)
- MIW requires treatment to prevent metal mobility in the environment.

# Passive treatment at remote locations: lignocellulosic sulfate-reducing biochemical reactors (SRBRs)

Mine adit

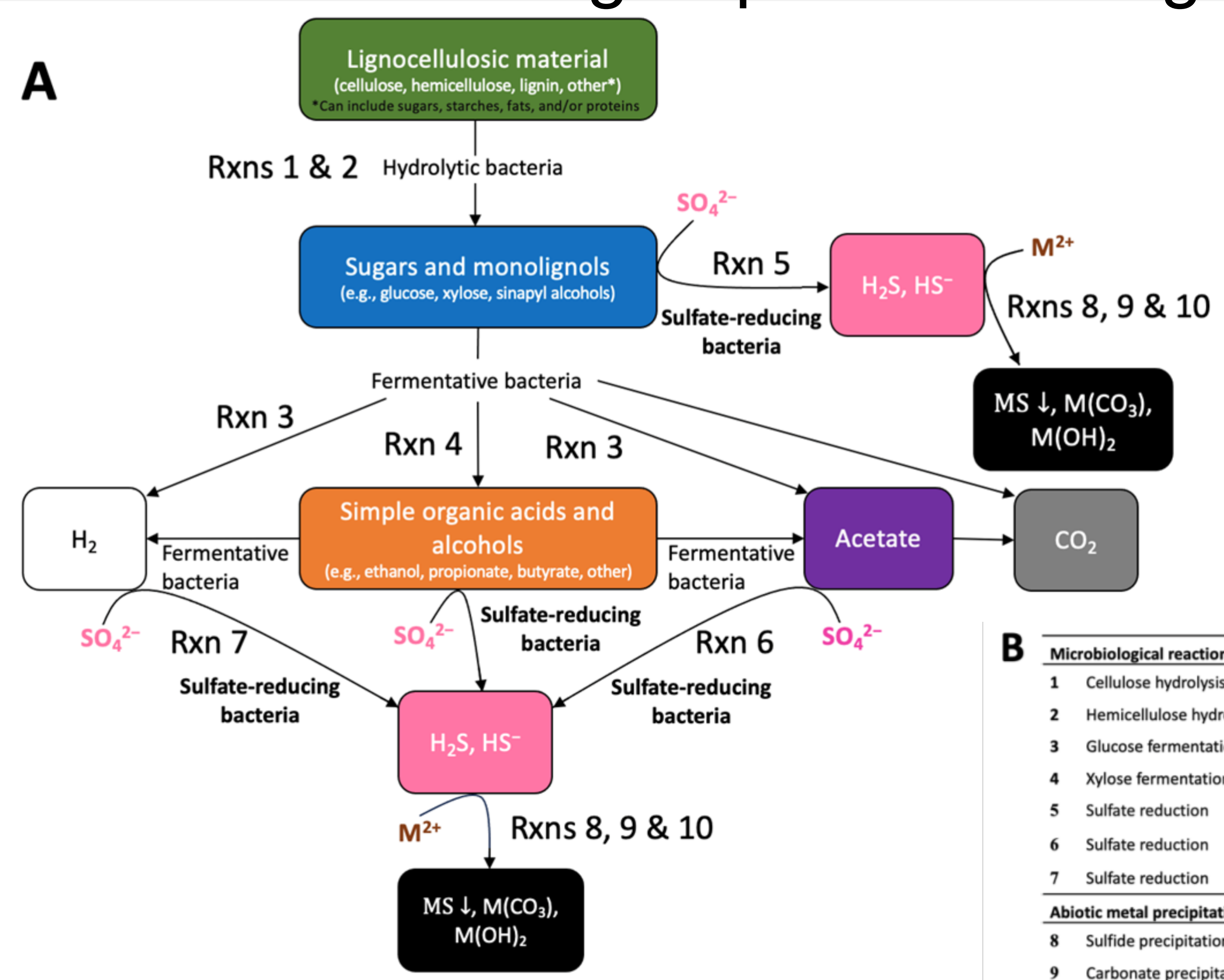
SRBR

Lignocellulose: woodchips, alfalfa hay, nut shells, compost
Alkalinizing material: limestone



SRBR effluent

# Metal (M) treatment in a lignocellulosic SRBR and involved groups of microorganisms




**B**

| | Microbiological reaction | Equation |
|---|---|---|
| 1 | Cellulose hydrolysis | $(C_6H_{10}O_6)_n + H_2O \rightarrow n\ C_6H_{12}O_6$ (glucose) |
| 2 | Hemicellulose hydrolysis | $(C_5H_8O_4)_n + H_2O \rightarrow n\ C_5H_{10}O_5$ (xylose) |
| 3 | Glucose fermentation | $C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COO^-$ (acetate) $+ 2\ CO_2 + 4\ H_2 + 2\ H^+$ |
| 4 | Xylose fermentation | $C_5H_{10}O_5 \rightarrow 2\ C_2H_5O$ (ethanol) $+ CO_2$ |
| 5 | Sulfate reduction | $2\ C_6H_{12}O_6$ (glucose) $+ 6\ SO_4^{2-} + 9\ H^+ \rightarrow 12\ CO_2 + 12\ H_2O + 3\ H_2S + 3\ HS^-$ |
| 6 | Sulfate reduction | $SO_4^{2-} + CH_3COO^-$ (acetate) $\rightarrow HS^- + 2\ HCO_3^-$ |
| 7 | Sulfate reduction | $SO_4^{2-} + 4\ H_2 + H^+ \rightarrow HS^- + 4\ H_2O$ |
| | **Abiotic metal precipitation reaction** | **Equation** |
| 8 | Sulfide precipitation | $HS^- + M^{2+} \rightarrow MS \downarrow + H^+$ |
| 9 | Carbonate precipitation | $HCO_3^- + M^{2+} \rightarrow M(CO_3) \downarrow + H^+$ |
| 10 | Hydroxide precipitation | $2\ H_2O + M^{2+} \rightarrow M(OH)_2 \downarrow + 2\ H^+$ |

Miranda et a. in preparation

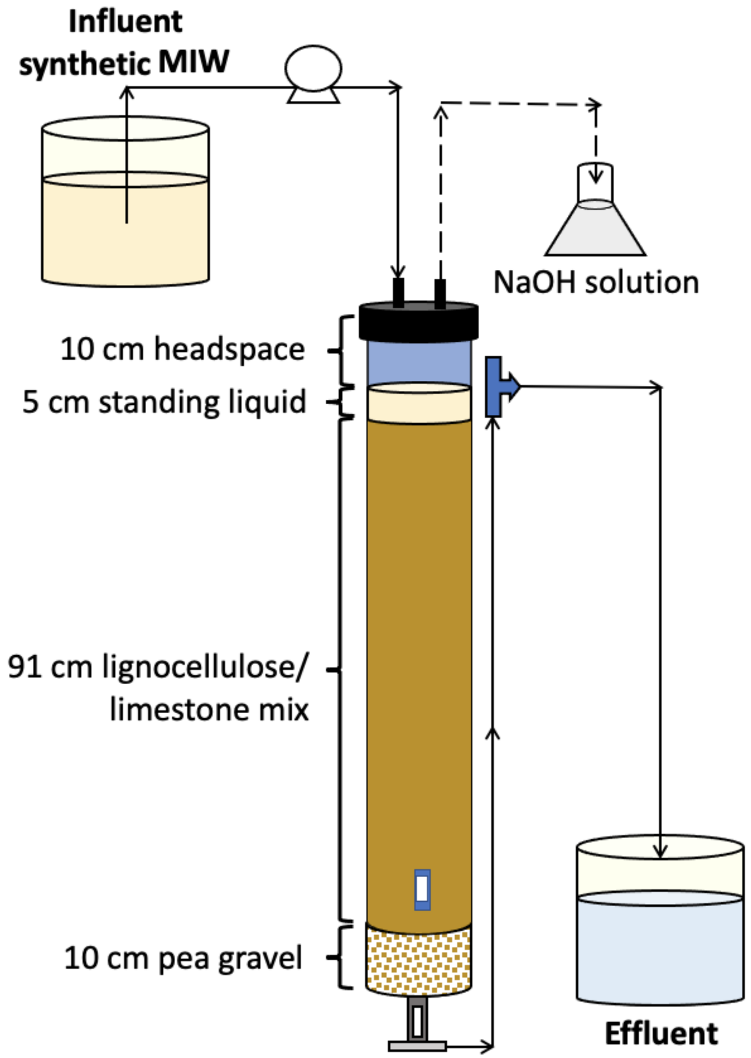
# Enhancing SRBR longevity and treatment efficacy: Novel lignocellulosic materials to support sulfate reduction

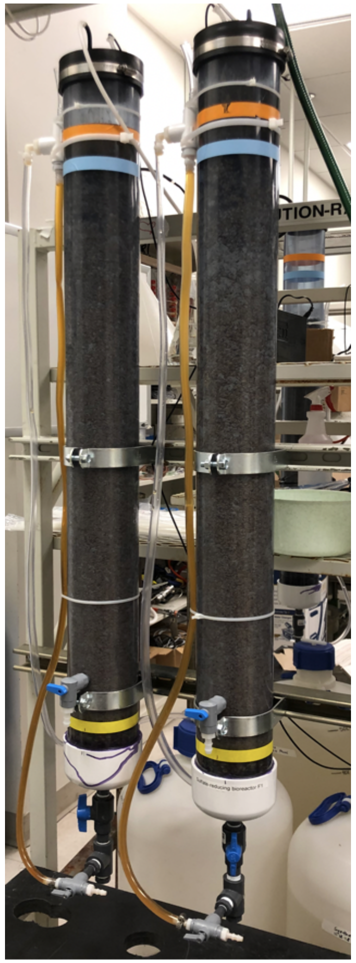
Spent brewing grains – 2.7% residual starch*

Sugarcane bagasse – 5% residual sugars**

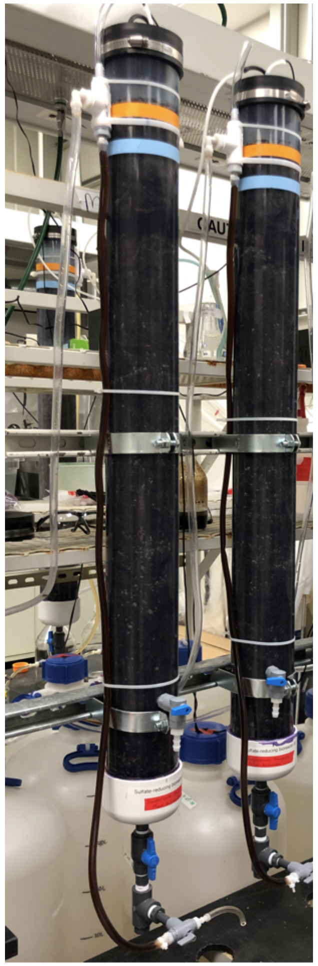
*Xiros et al. 2008. *Bioresource Technology*, **99**(13), 5427-5435.
**Nikodinovic-Runic et a. 2013. *Advances in Applied Microbiology*, **84**, 139-200.

# SRBR configuration and operation



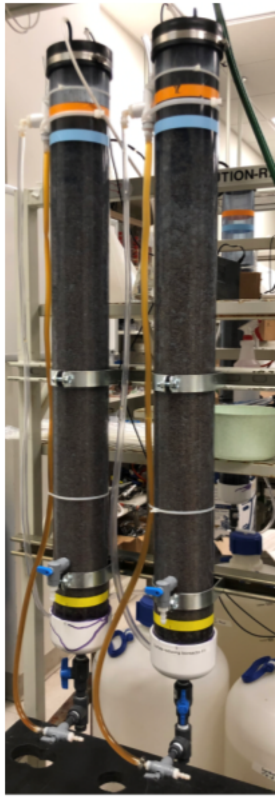
Spent brewing grains SRBRs

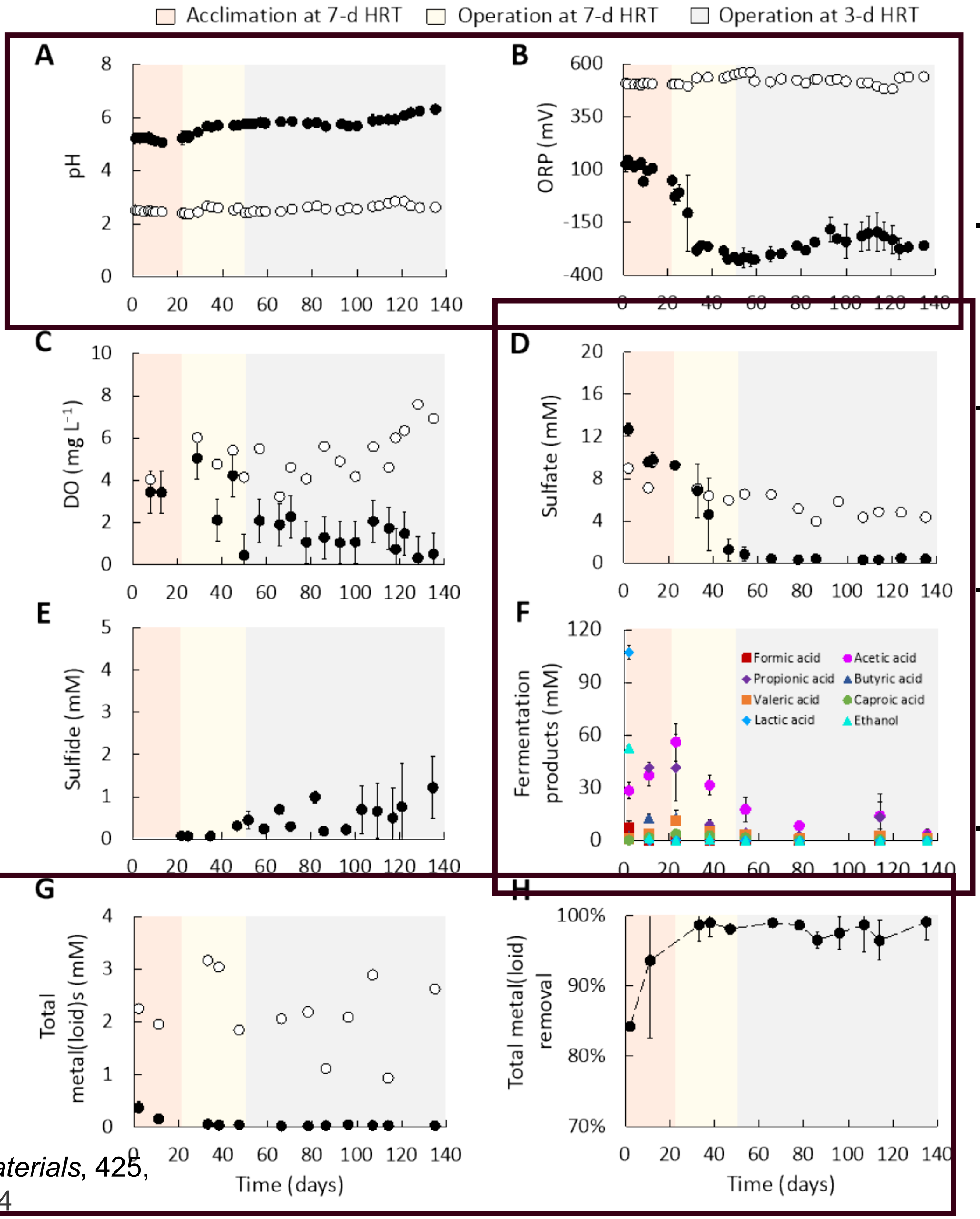


Sugarcane bagasse SRBRs

- SRBR total vol: 10 L
- Packed with 70% lignocellulosic material and 30% limestone
- Inocula: anaerobic digestor sludge and a sulfate-reducing enrichment
- Full flow operation: 1-2 L/d to achieve a 3-d hydraulic retention time (HRT))
- Mining-influenced water (MIW): pH 2.5, 750 mg/L sulfate, 18 metals at μg/L to mg/L concentration.

# Spent brewing grains SRBRs






○ = influent ● = effluent

- SRBRs were acclimated during continuous-flow operation.
- Sulfate reduction was fueled by a variety of fermentation products.
- Metal removal at high rates was sustained during entire period of SRBR operation (135 days).
- Similar outcomes achieved in sugarcane bagasse SRBRs.

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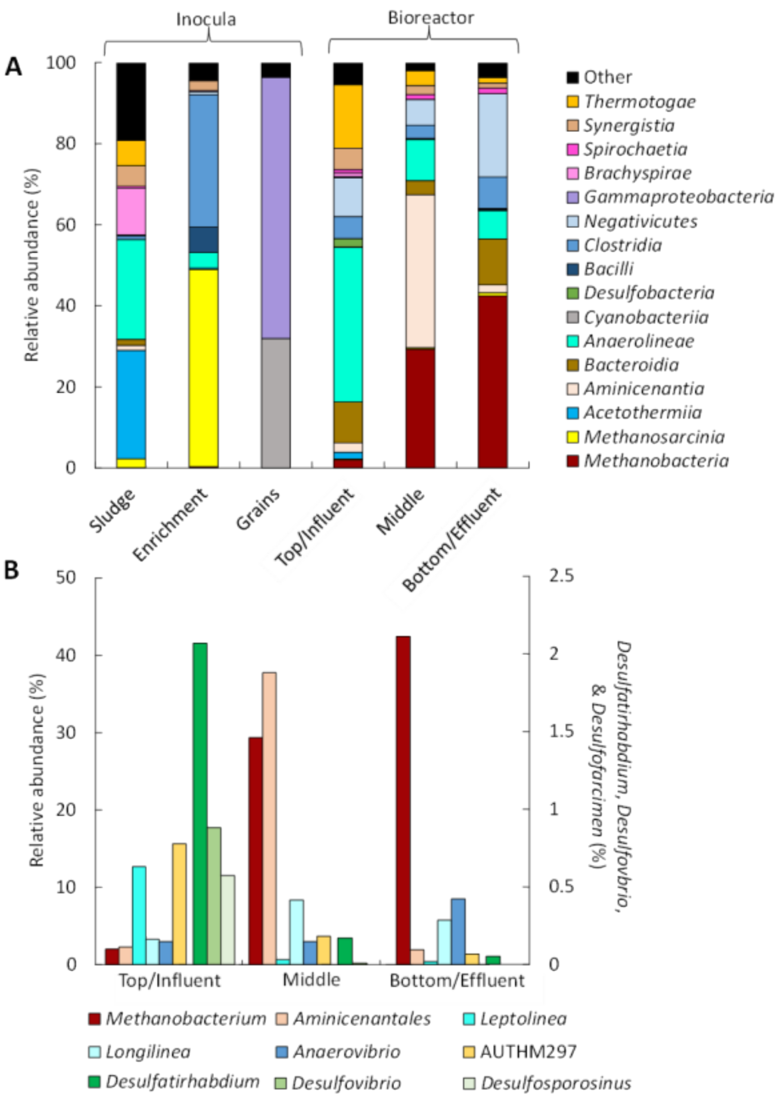
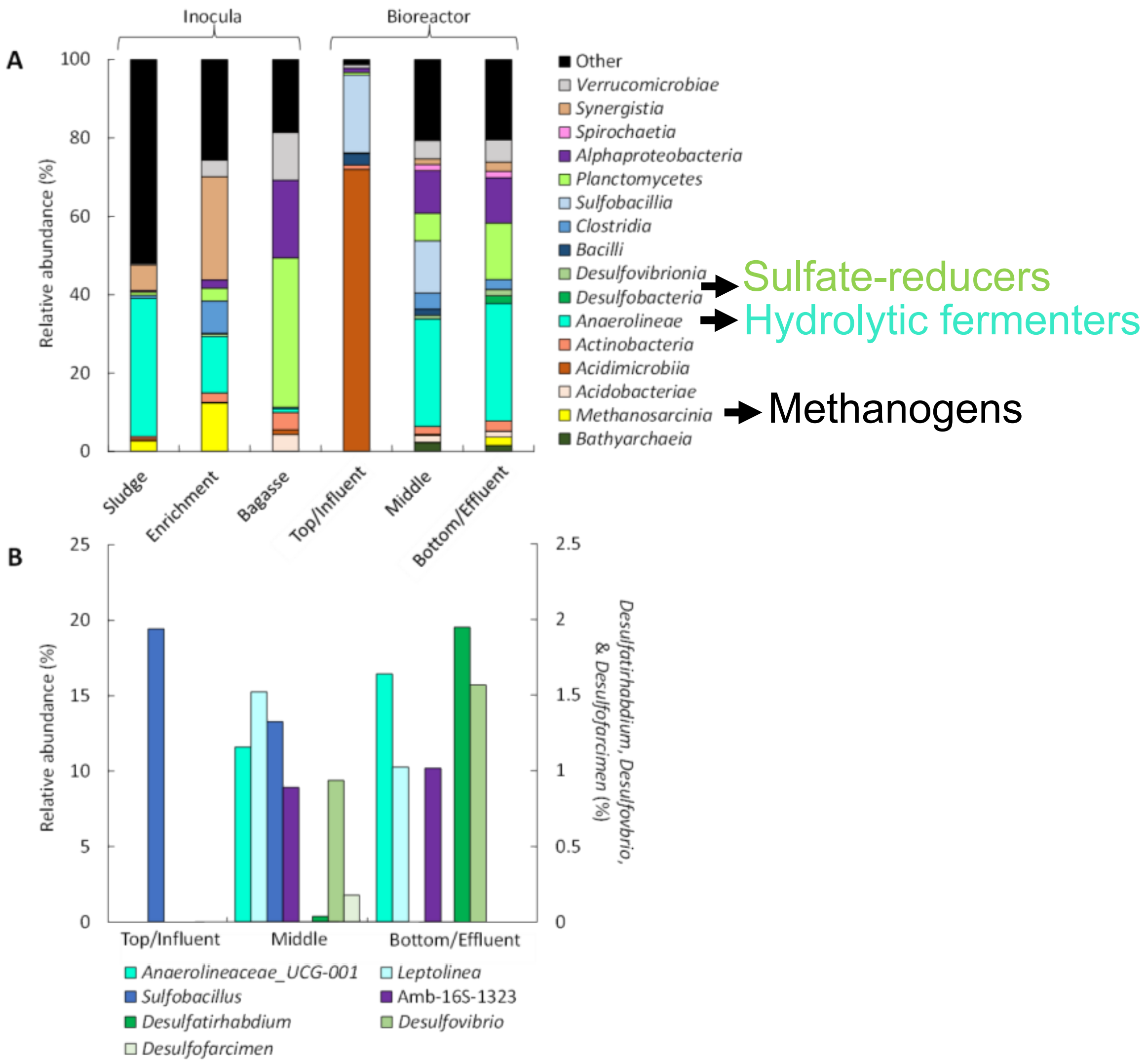
# Microbial community analyses identified key taxa involved in treatment and their location in SRBRs.

## Spent brewing grains SRBRs




## Sugarcane bagasse SRBRs

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# Alternative alkalinizing agent for metal treatment and sulfate reduction: basic oxygen furnace (BOF) slag



- By-product of the steel industry
- 10–20% $SiO_2$, 40–50% CaO, 10% MgO, 15–20% iron (mixed oxides), 2–5% $Al_2O_3$, 10% manganese oxide (MnO), and other oxides
- BOF slag: 500-2000 mg $L^{-1}$ $CaCO_3$ equivalents; limestone: 60-80 mg $L^{-1}$ $CaCO_3$**
- BOF slag is also effective at precipitating metals.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

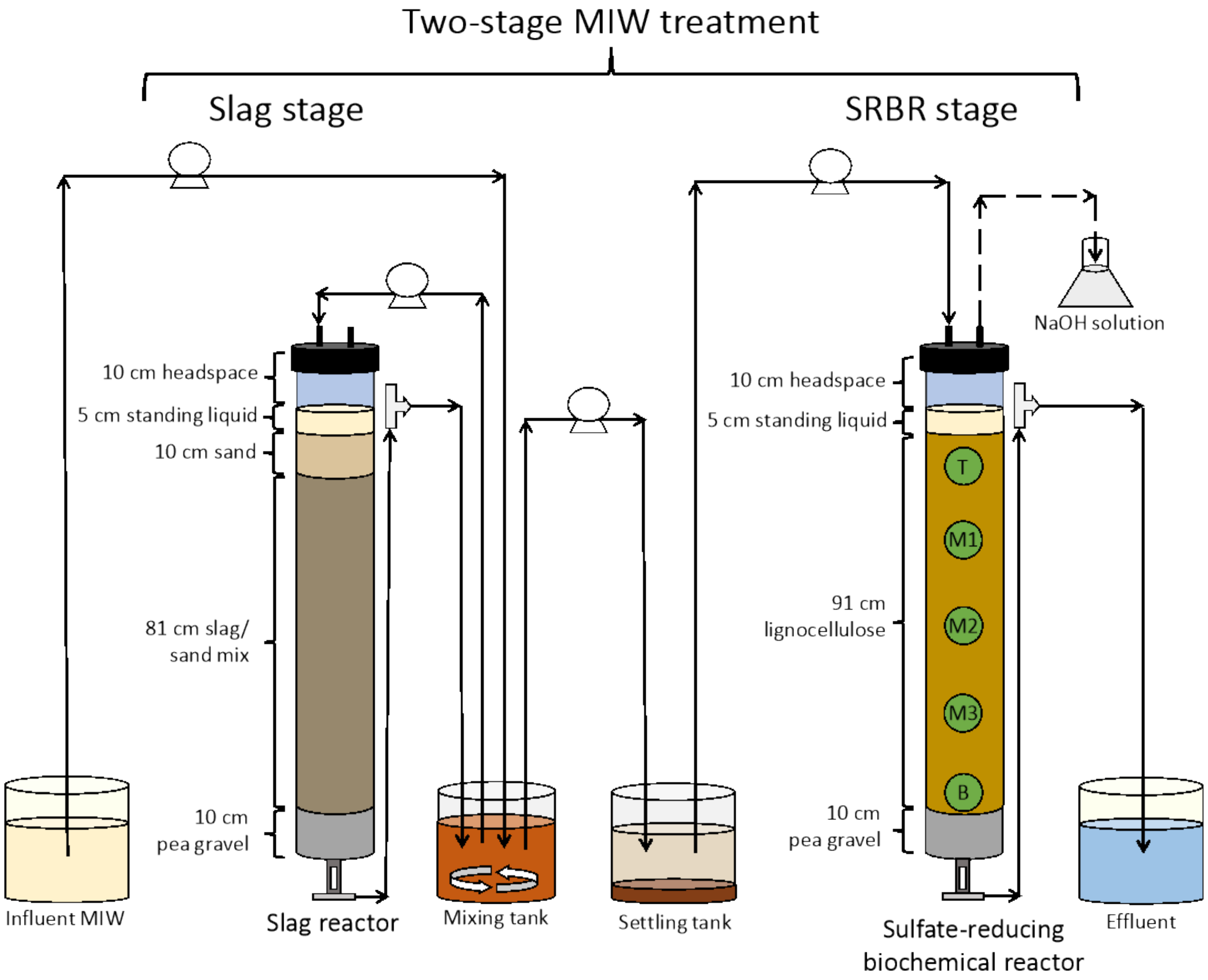
$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^- \quad (2)$$

$$M^{x+} + xOH^- \rightarrow M(OH)_x \quad (3)$$

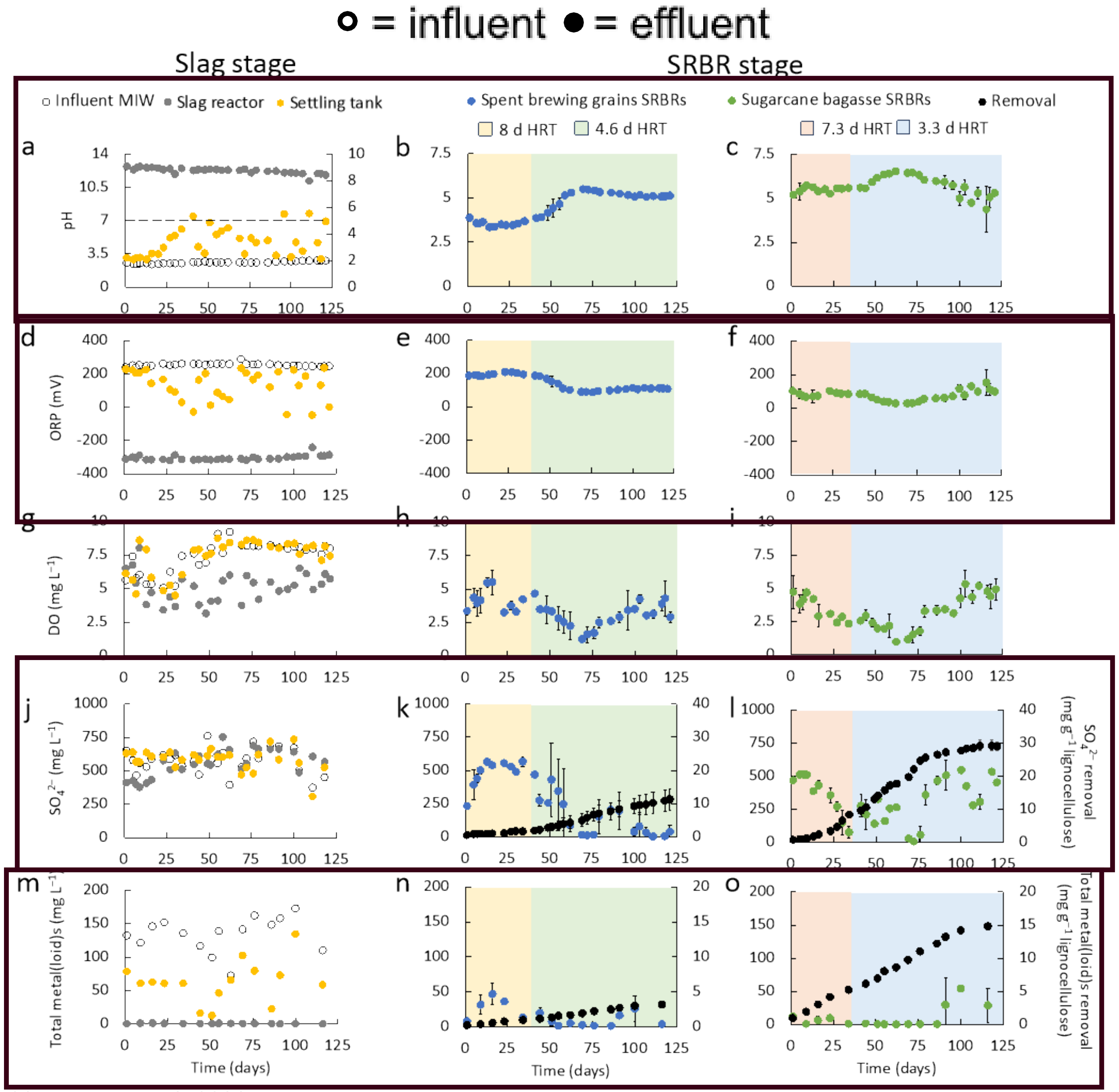
*www.usgs.gov/centers/national-minerals-information-center/iron-and-steel-slag-statistics-and-information

**Ziemkiewicz, P. and Skousen, J. *16th Annual Meeting of the American Society for Surface Mining and Reclamation*, Scottsdale, Arizona, 651-656.

# Incorporating basic oxygen furnace slag and SRBRs for treatment of mining-influenced water




- Slag and SRBR total vol:10 L
- Slag and SRBR stages in series
- SRBRs packed with 100% lignocellulosic material (spent brewing grains or sugarcane bagasse)
- Full flow operation: 1.1-1.8 L/d (to achieve an HRT of 3.3-4.6 d)
- Mining-influenced water (MIW): pH 2.5, 750 mg/L sulfate, 18 metals at µg/L to mg/L concentration.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| metal(loid) | MIW influent (mg $L^{-1}$) | slag reactor removal (%) | SRBR influent (settling tank) (mg $L^{-1}$) | spent brewing grains SRBR stage removal (%) | spent brewing grains two-stage treatment removal (%) | sugarcane bagasse SRBR stage removal (%) | sugarcane bagasse two-stage treatment removal (%) |
|---|---|---|---|---|---|---|---|
| Al | 2.8 ± 0.9 | >99 | 1 ± 2 | 95 ± 3 | 98 ± 2 | 70 ± 42 | 89 ± 29 |
| As | 0.05 ± 0.04 | >99 | 0.0 | N/A | 96 ± 11 | N/A | ≥99 |
| Cd | 0.08 ± 0.04 | >99 | 0.08 ± 0.03 | >99 | 99 ± 3 | 99.6 ± 0.9 | 98 ± 23 |
| Co | 0.008 ± 0.008 | >99 | 0.006 ± 0.006 | 70 ± 50 | 80 ± 42 | 88 ± 35 | 88 ± 40 |
| Cr | 0.03 ± 0.02 | >99 | 0.01 ± 0.01 | 67 ± 38 | 90 ± 15 | 65 ± 39 | 89 ± 24 |
| Cu | 0.6 ± 0.2 | >99 | 0.5 ± 0.4 | 97 ± 8 | 99 ± 3 | 98 ± 6 | 99 ± 24 |
| Fe | 60 ± 20 | >99 | 10 ± 20 | 20 ± 36 | 88 ± 14 | 43 ± 48 | 77 ± 33 |
| Ni | 0.02 ± 0.02 | >99 | 0.01 ± 0.01 | 96 ± 11 | 88 ± 32 | 89 ± 40 | 92 ± 34 |
| Pb | 0.01 ± 0.01 | >99 | 0.003 ± 0.005 | 23 ± 44 | 58 ± 45 | 37 ± 49 | 74 ± 32 |
| V | 0.06 ± 0.04 | >99 | 0.02 ± 0.02 | 9 ± 19 | 41 ± 46 | 12 ± 20 | 55 ± 41 |
| Zn | 70 ± 20 | >99 | 60 ± 20 | >99 | >99 | 99.4 ± 0.9 | 99 ± 24 |
| Total | 130 ± 40 | >99 | 80 ± 40 | 91 ± 9 | 95 ± 6 | 86 ± 30 | 89 ± 16 |

- The slag stage provided appropriate conditions for downstream sulfate reduction and served as the major mechanism for metal removal from mining-influenced water
- The extensive metal removal of the slag could be advantageous to reduce the metal loading in the SRBRs and increase overall SRBR longevity in the field.

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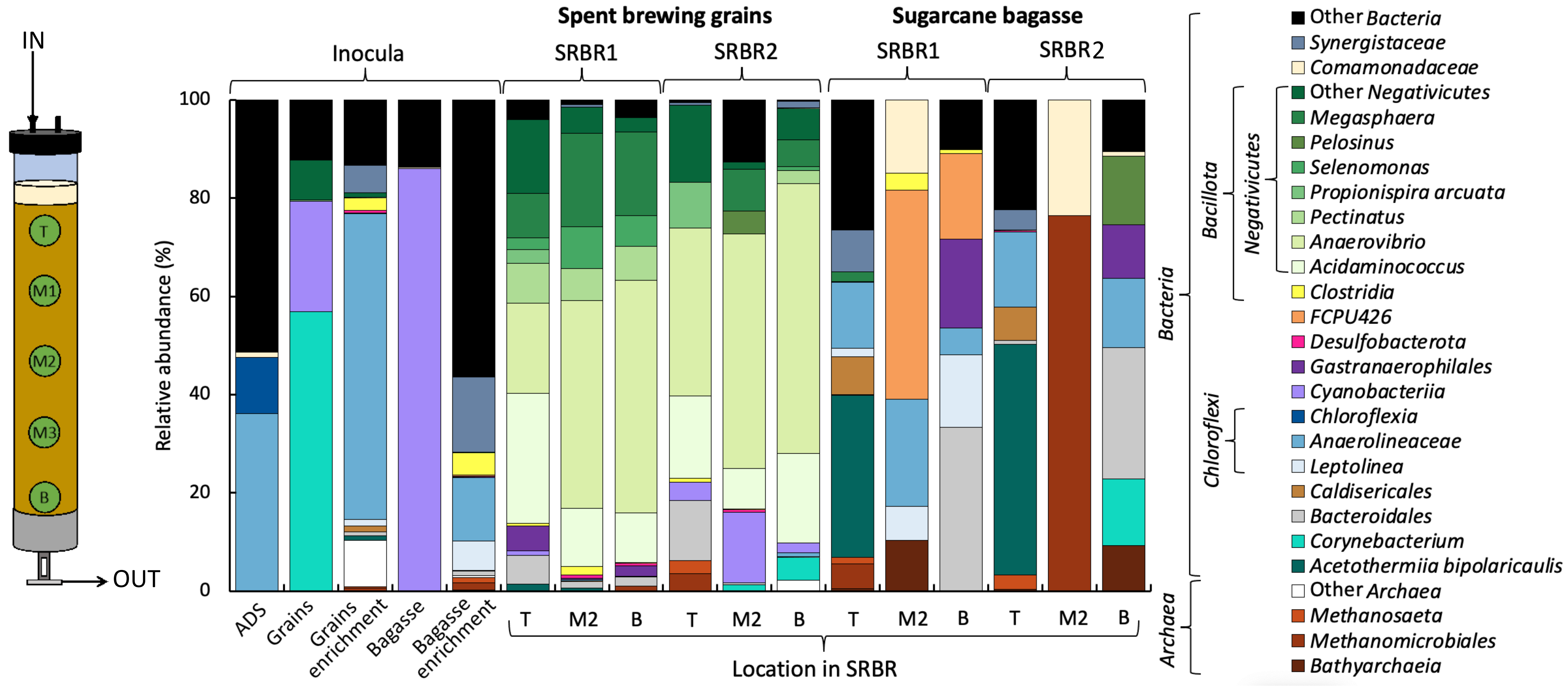
# Two-stage treatment enriched lignocellulolytic, fermentative, and sulfate-reducing microorganisms

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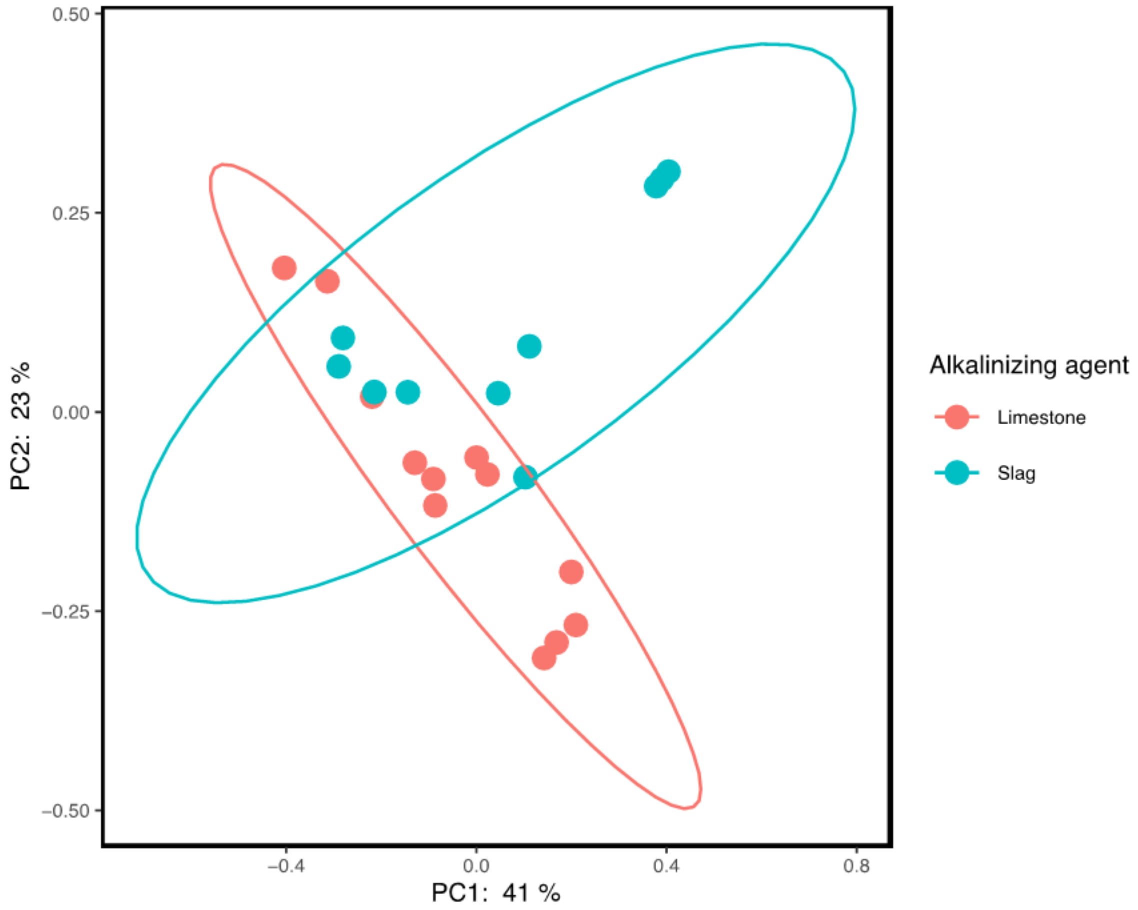
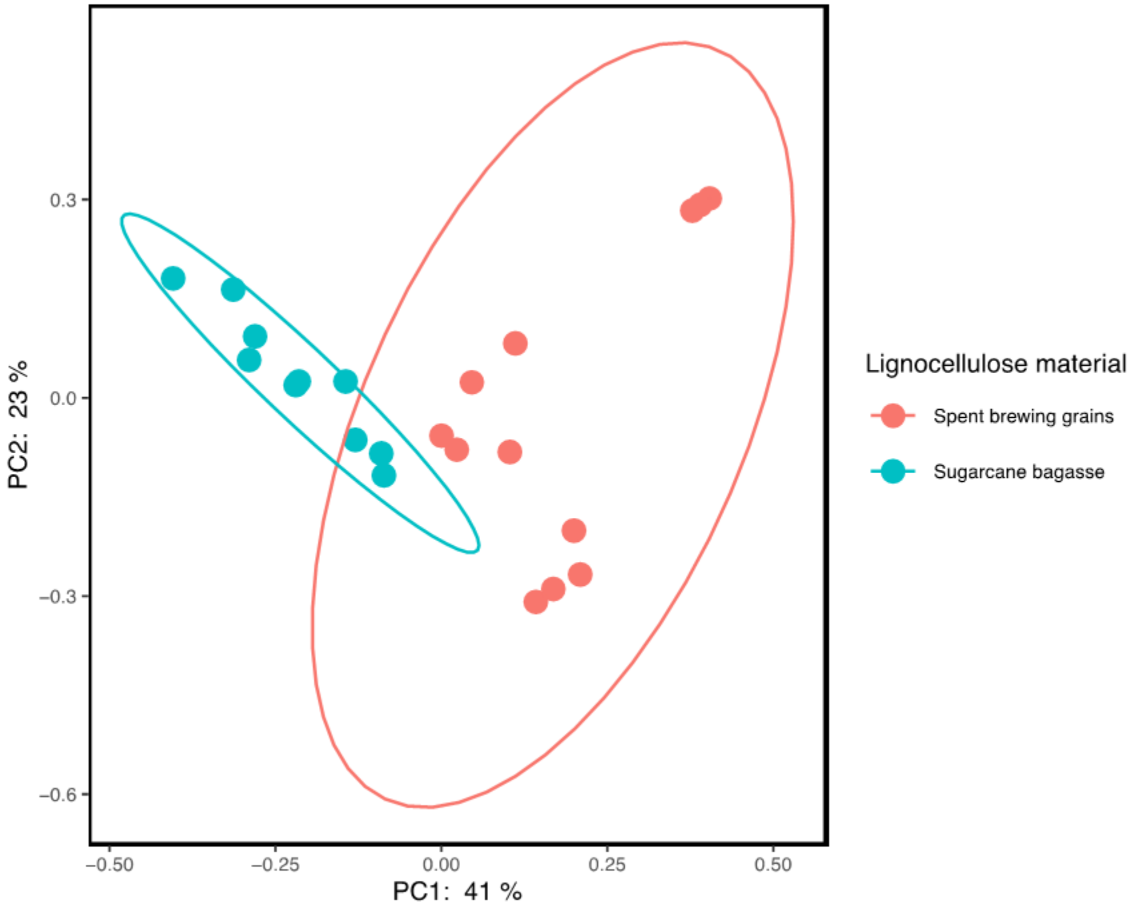
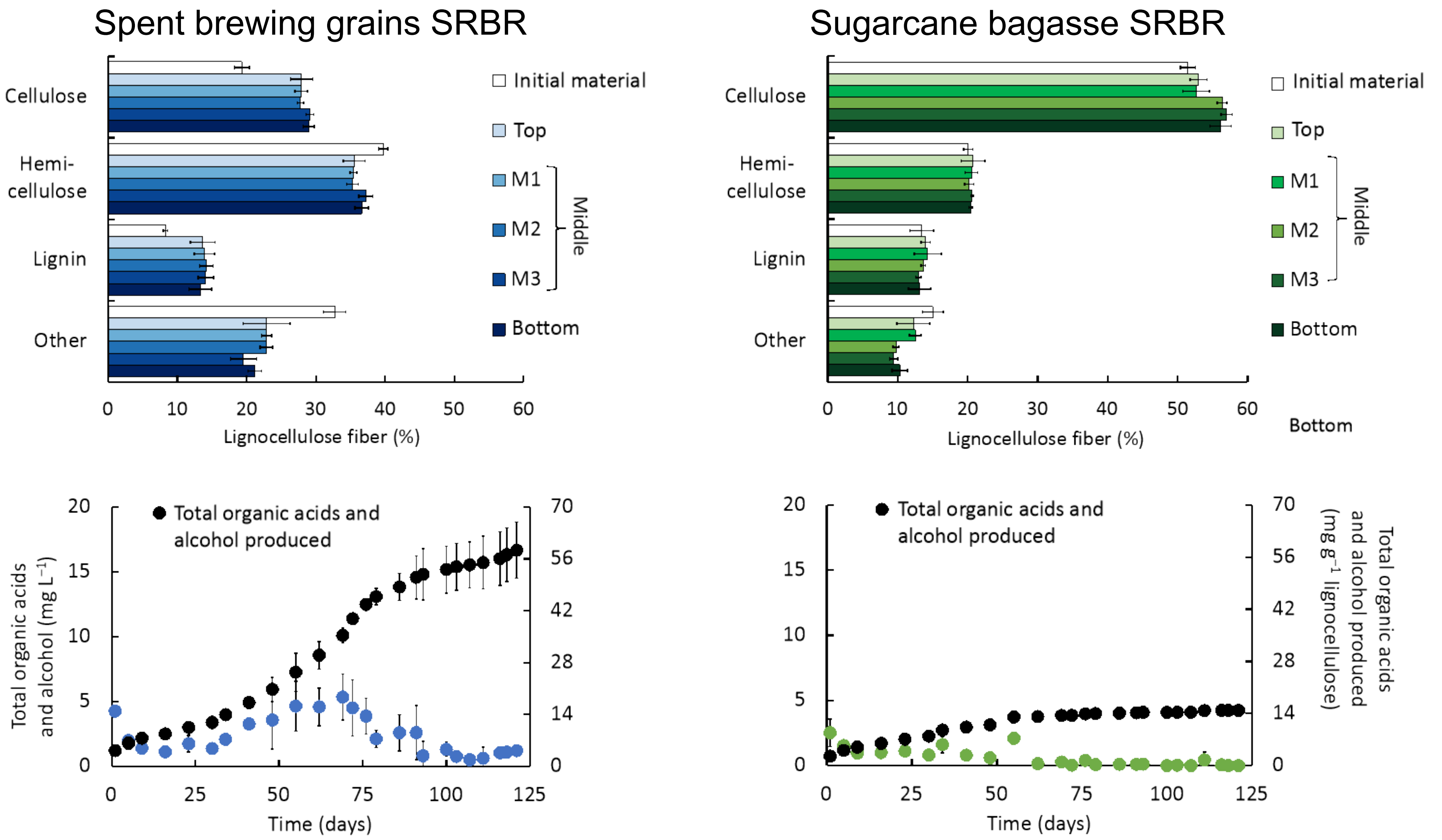
# The microbial community composition in SRBRs was most heavily influenced by the type of lignocellulosic material






- Other = non-lignocellulosic components (e.g., sugars, starches, proteins).
- Measurable decreases between 4-10% in hemicellulose and the non-lignocellulosic category ‘other’ in the SRBRs after 121 days of operation.

# Key outcomes and implications

i. The slag stage was exceptional at removing metals (as hydroxides and oxides), increasing MIW pH, and decreasing ORP and DO.

ii. The SRBR stage was focused on removing sulfate and immobilizing remaining metals as more stable sulfide precipitates.

iii. Spent brewing grains and sugarcane bagasse had distinct advantages when treating mining-influenced water and enriched compositionally different functionally redundant microbial communities.

# Thank you!

anca.delgado@asu.edu

| | Spent brewing grains | | | Sugarcane bagasse | | |
|---|---|---|---|---|---|---|
| Metal(loid) | Avg. MIW (μM) | Avg. effluent (μM) | Removal (%) | Avg. MIW (μM) | Avg. effluent (μM) | Removal (%) |
| Al | 140 ± 60 | 12 ± 3 | 91 ± 2 | 150 ± 60 | 15 ± 4 | 90 ± 1 |
| As | 0.8 ± 0.4 | BDL | > 99 | 0.8 ± 0.4 | BDL | > 99 |
| Cd | 0.8 ± 0.3 | BDL | > 99 | 0.8 ± 0.3 | BDL | > 99 |
| Cr | 0.8 ± 0.2 | 0.1 ± 0.1 | 92 ± 6 | 0.8 ± 0.2 | 0.25 ± 0.01 | 83 ± 7 |
| Co | 0.6 ± 0.2 | BDL | > 99 | 0.7 ± 0.1 | 0.12 ± 0.05 | 69 ± 1 |
| Cu | 11 ± 4 | BDL | > 99 | 11 ± 3 | BDL | > 99 |
| Fe | 1000 ± 500 | 0.6 ± 0.7 | > 99 | 1000 ± 400 | 20 ± 4 | 98.1 ± 0.4 |
| Ni | 0.2 ± 0.1 | 0.03 ± 0.03 | 85 ± 11 | 0.18 ± 0.07 | 0.04 ± 0.05 | 80 ± 30 |
| Pb | 0.2 ±0.1 | 0.14 ± 0.02 | 30 ± 40 | 0.22 ± 0.05 | 0.056 ± 0.003 | 70 ± 40 |
| V | 1.7 ± 0.9 | 10 ± 10 | NR | 1.5 ± 0.9 | 1.29 ± 0.02 | 13 ± 1 |
| Zn | 800 ± 200 | 0.2 ± 0.3 | > 99 | 800 ± 200 | 13 ± 18 | 98 ± 3 |
| Total | 2000 ± 770 | 23 ± 17 | 98.8 ± 0.9 | 2000 ± 670 | 50 ± 26 | 97.5 ± 1.3 |

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