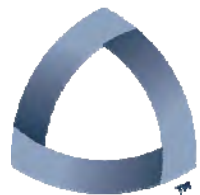


Comprehensive Investigation of Factors Enhancing Microbially Generated Coal Bed Methane

RPSEA 07122-14



COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

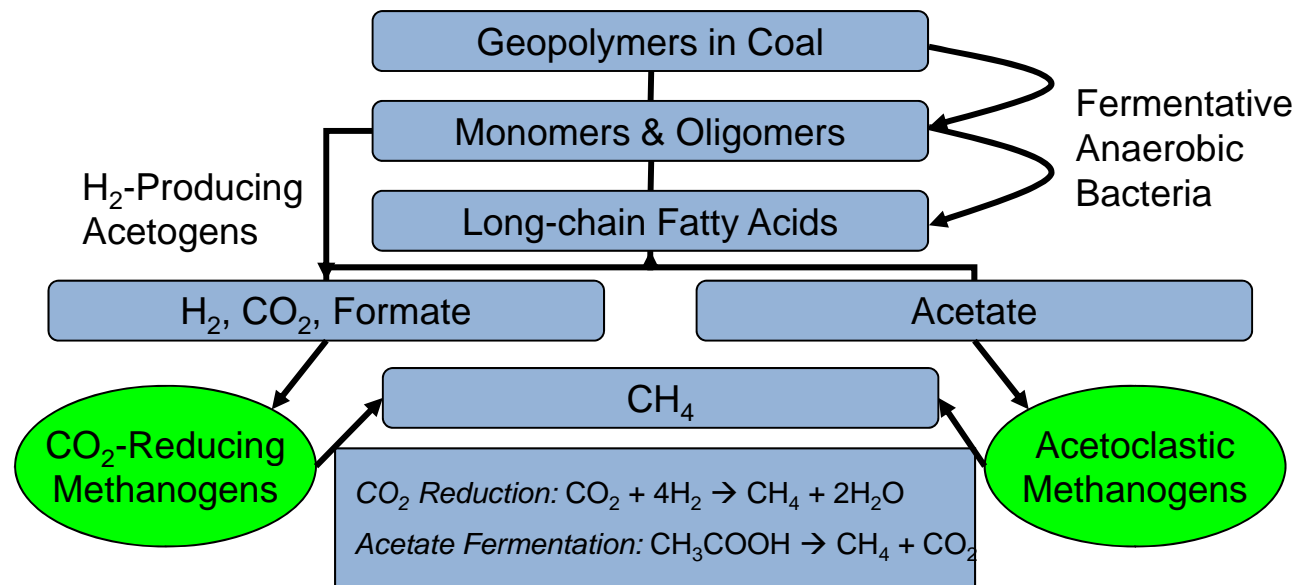
Participants

- Colorado School of Mines
 - J. Munakata Marr, L. Landkamer, L. Figueroa, K. Mandernack
 - L. Gallagher, A. Glossner
- University of Wyoming
 - D. Bagley, F. Basile, M. Urynowicz
 - Y. Liu, W. Rodgers, Z. Huang, R. Mahat
- U.S. Geological Survey
 - S. Harris
- Industrial partners
 - Coleman Oil and Gas
 - Pinnacle Gas Resources
 - Pioneer Natural Resources



Overview

- Much coal bed methane is microbial in origin.
- Enhancement of microbial methane production from coal has shown promise.
- Fundamental factors influencing methane generation from coal are not well understood.



Adapted from Flores R. M., et al., 2008. *Int. J. Coal Geol.* **76**, 52-75.



Potential Impact

- Previous laboratory experiments showed that methane associated with coal can be increased from 60 SCF/ton to over 300 SCF/ton.
- Example: if 1% of the coal in the Powder River Basin could be converted to methane, approximately 30 TCF of gas would be produced.
- Gas could be produced without dewatering the coals.
⇒ Substantial energy reserve with a relatively minor environmental impact



Project Objectives and Goals

- Identify chemical constituents of coal that are bioconverted
- Identify organisms associated with biogas generation from coal
- Characterize the influence of culture growth amendments and conditions on biogas generation
- Determine impacts of coal pre-treatment on levels of biogas precursor compounds, microbial communities, and ultimate methane generation
- Determine the rate limiting step(s) of microbial methane generation from coal
- Capture chemical and microbial dynamics observed in a computer model, to allow comparisons of different incubation scenarios

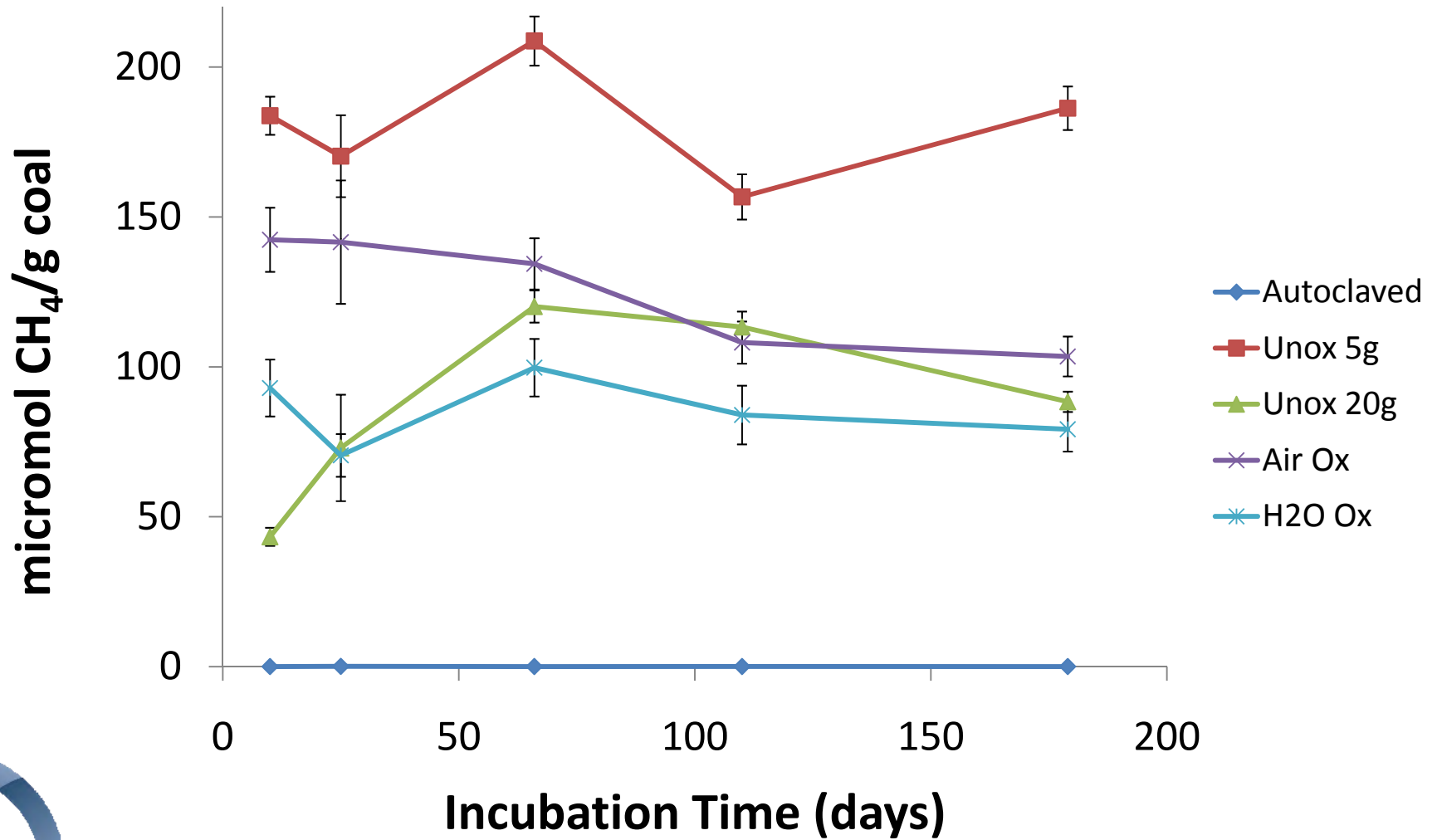


Progress to Date

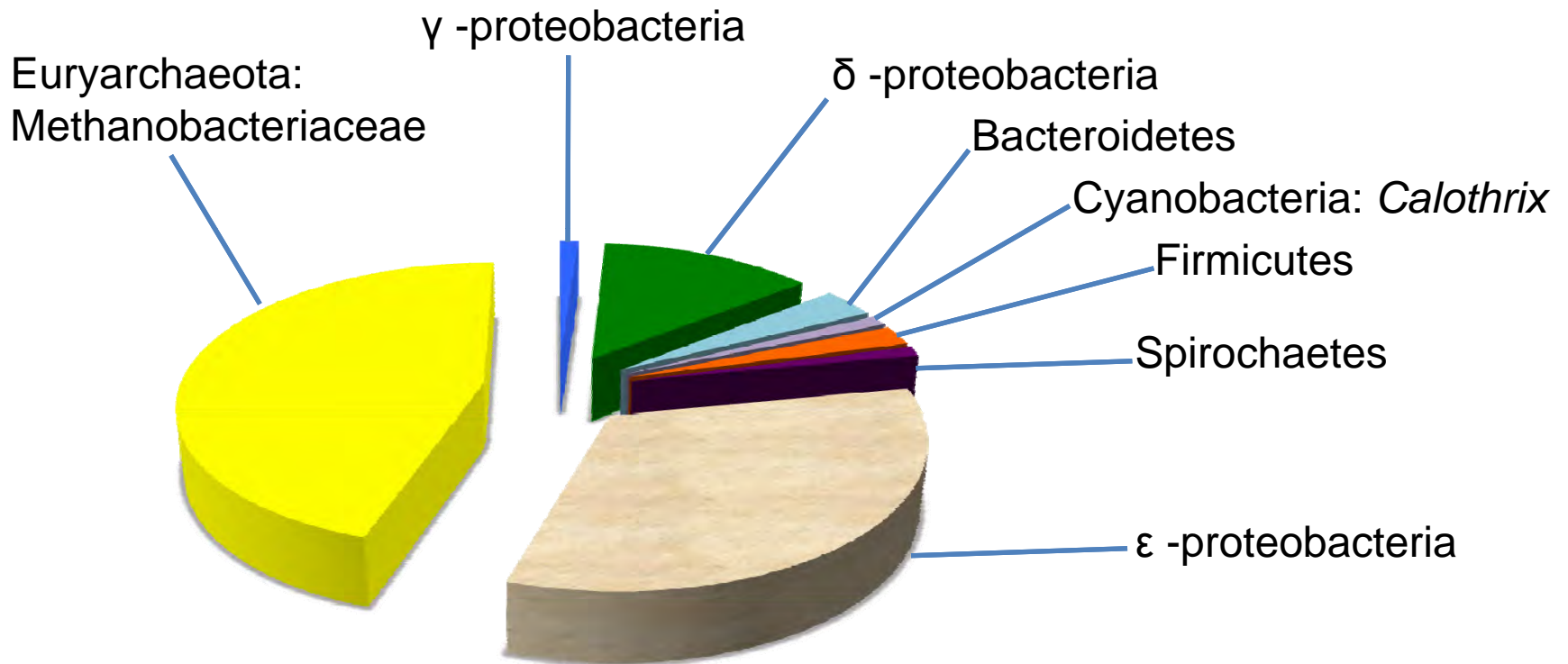
- Coal samples collected
- Incubations established, methane generated
- Microbial analyses initiated
- Analyses of soluble coal constituents, coal solvents conducted



Methane Production: oxidized vs. unoxidized coal

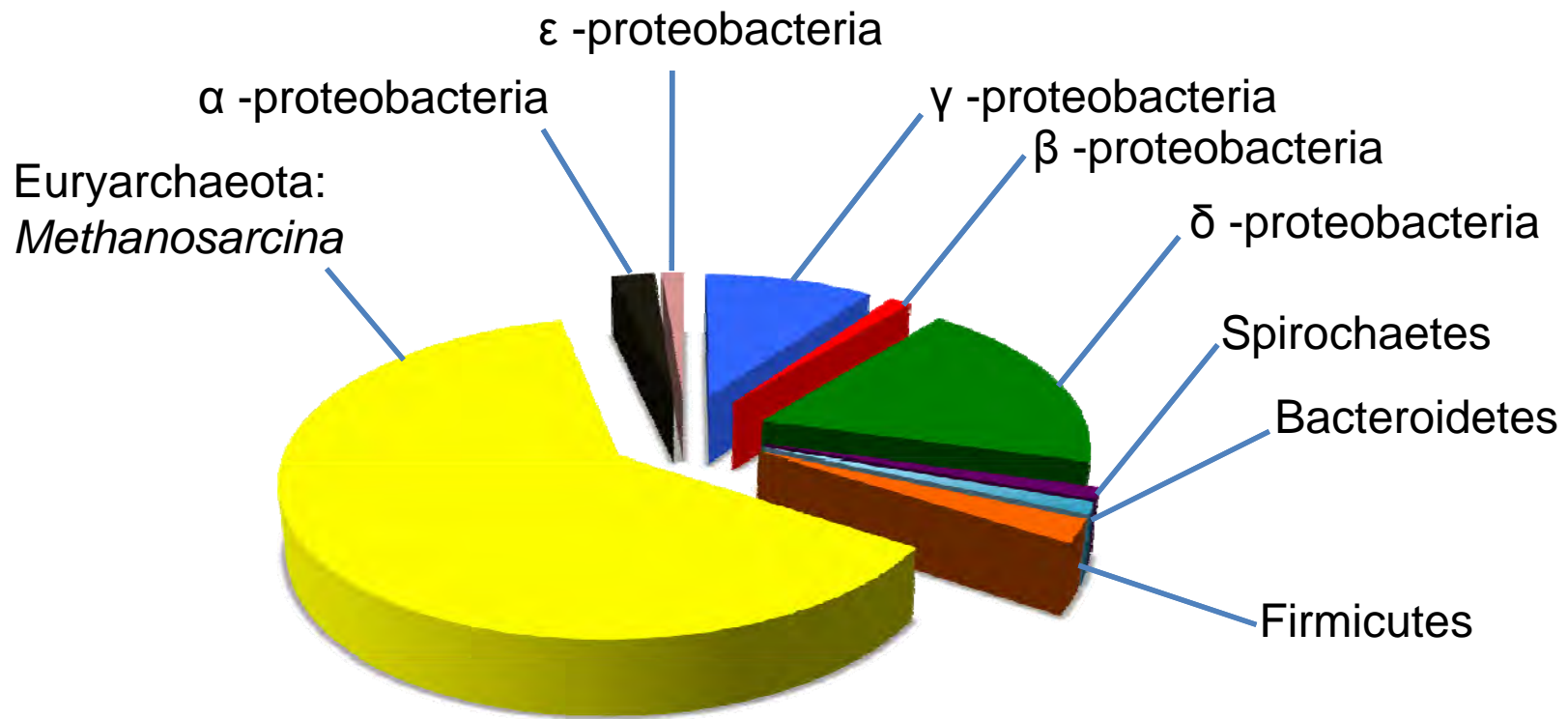


Microbial Community: enrichment



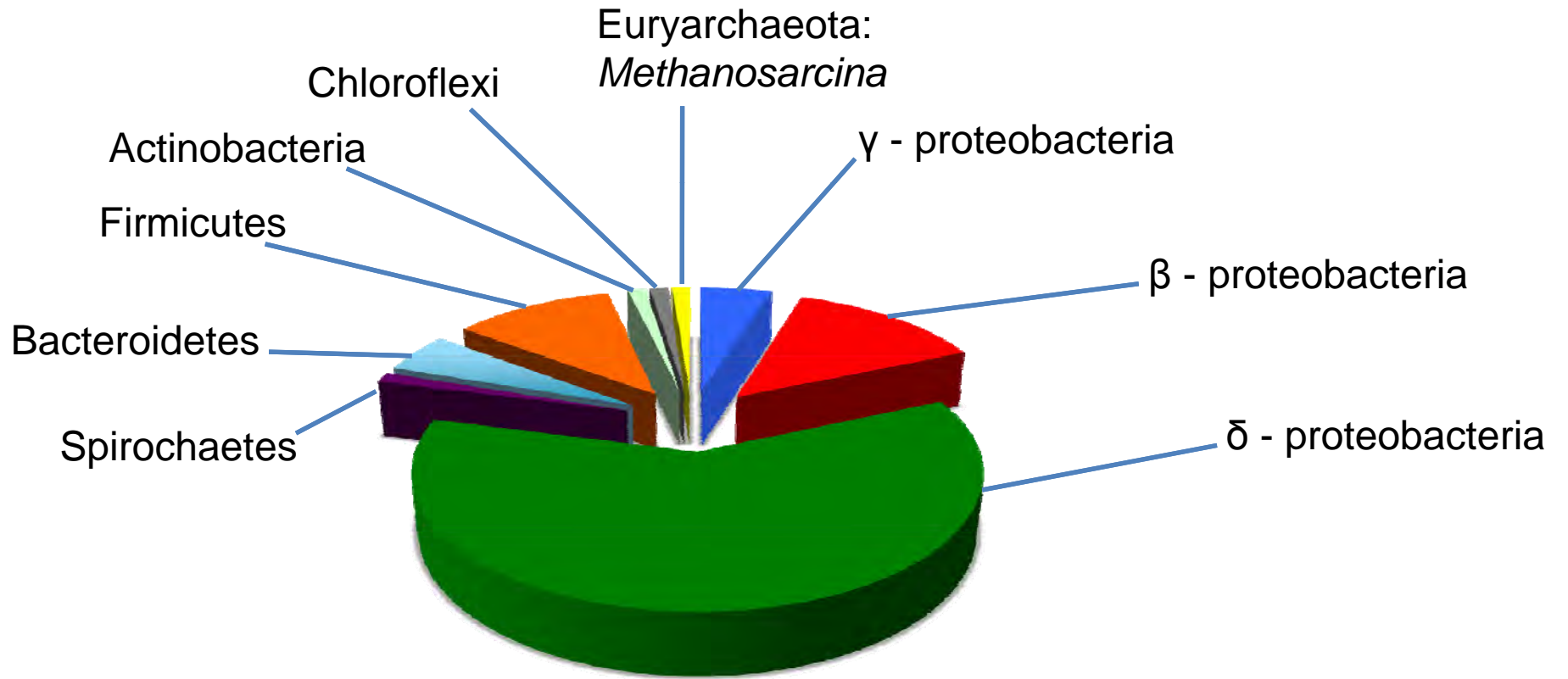
Acetobacterium, Desulfovibrio, Pelobacter, Sulfospirillum, Pseudomonadaceae

Microbial Community: high methane

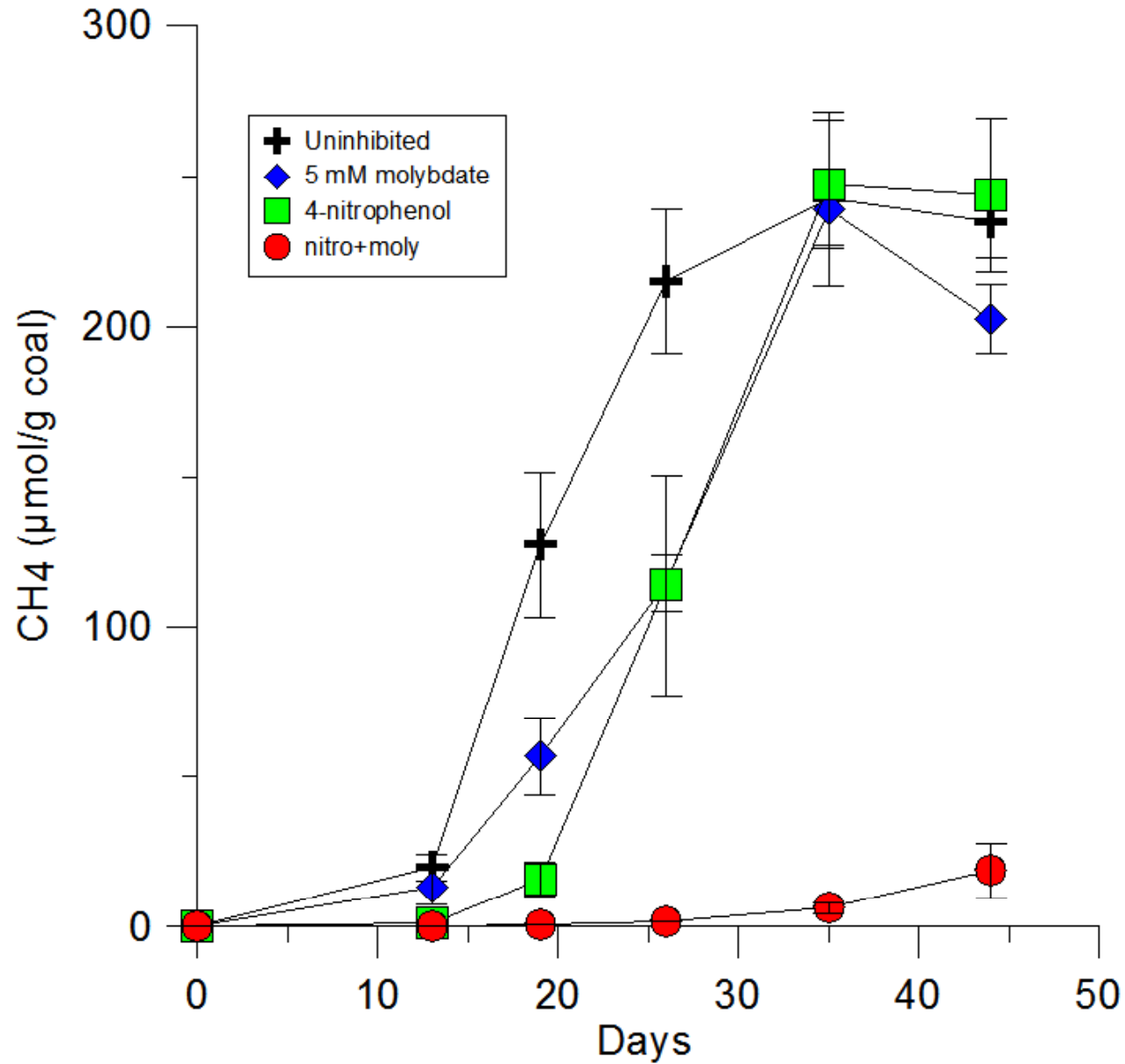


Acetobacterium, Bradyrhizobiaceae, Delftia, Desulfovibrio, Desulfuromonas, Pelobacter, Sulfurospirillum, Psychrobacter, Pseudomonas, Acidaminobacter

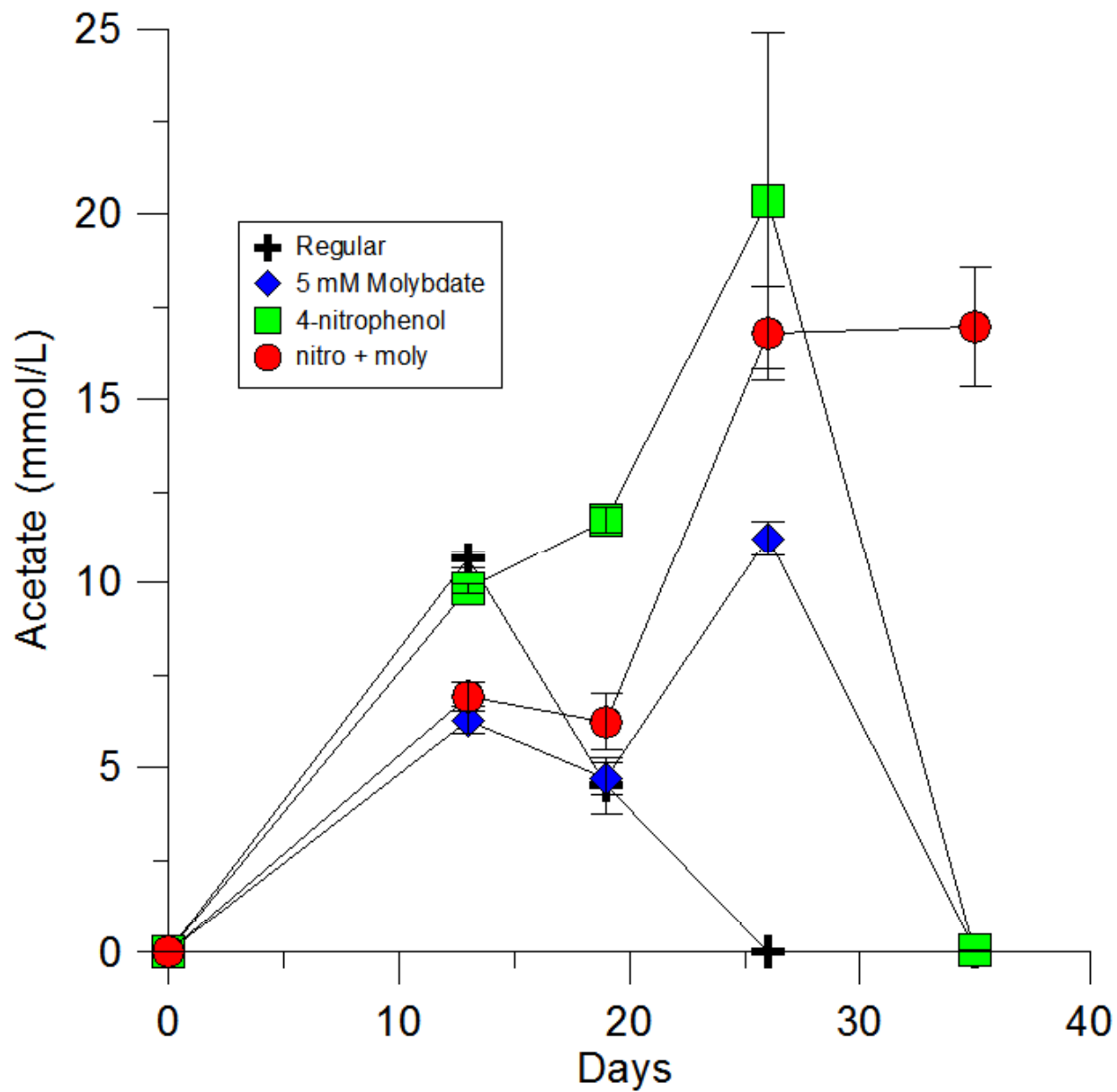
Microbial Community: low methane



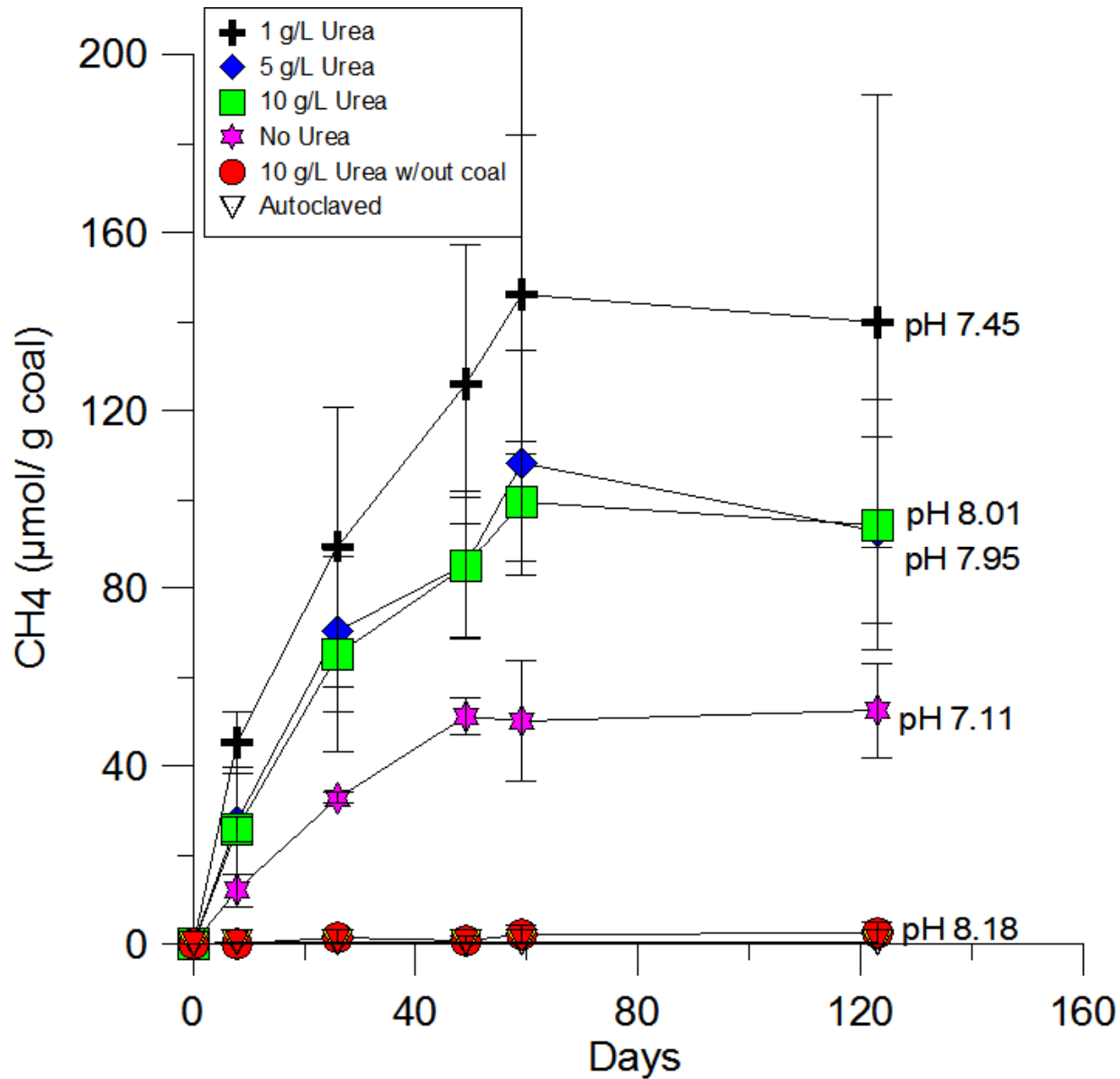
Inhibition Experiments: methane



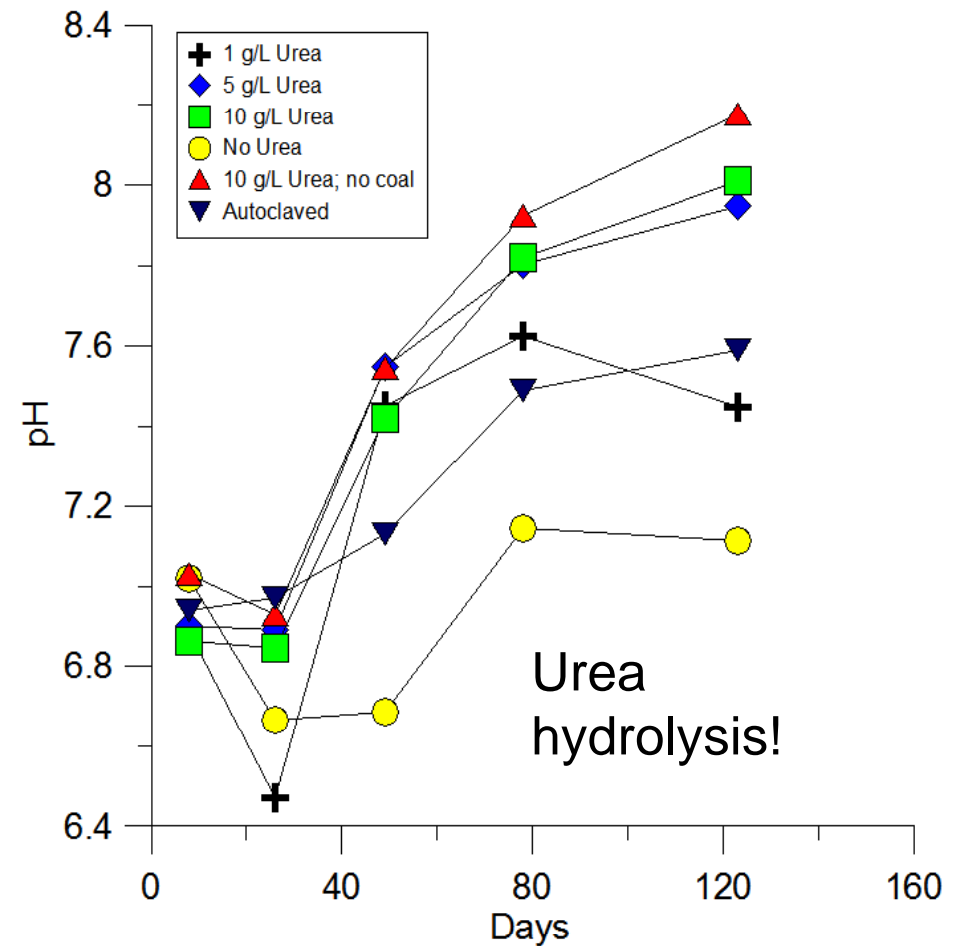
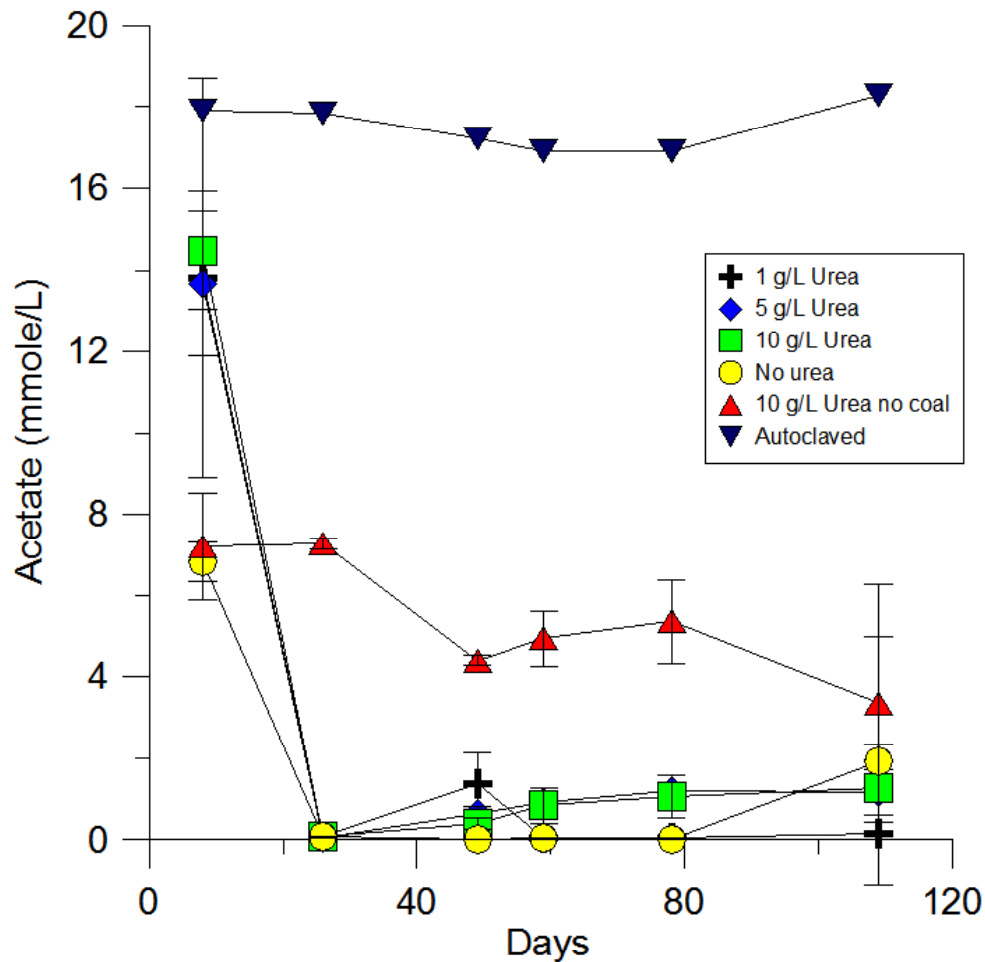
Inhibition Experiments: acetate



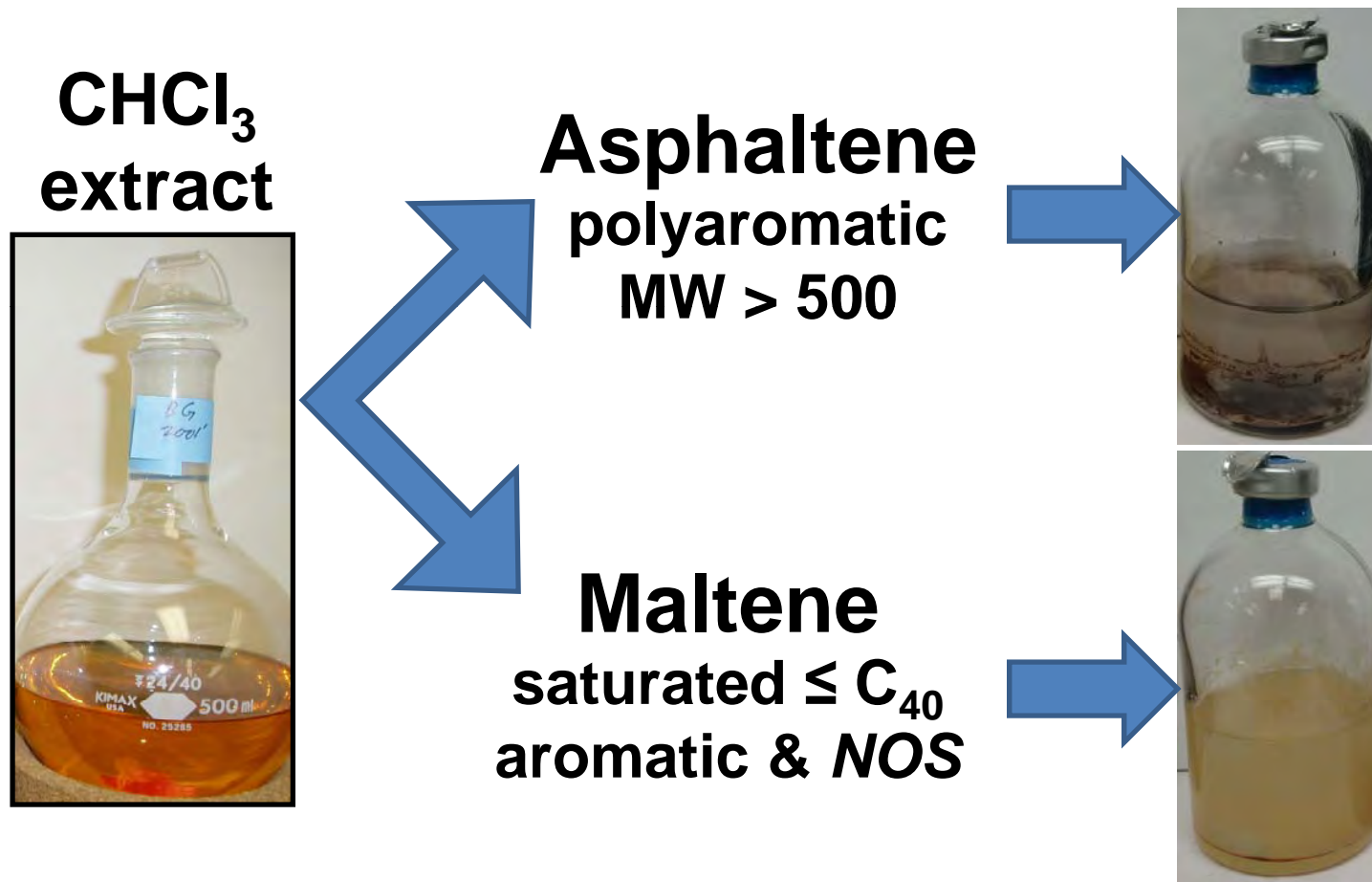
Urea Amendment: methane



Urea Amendment: acetate

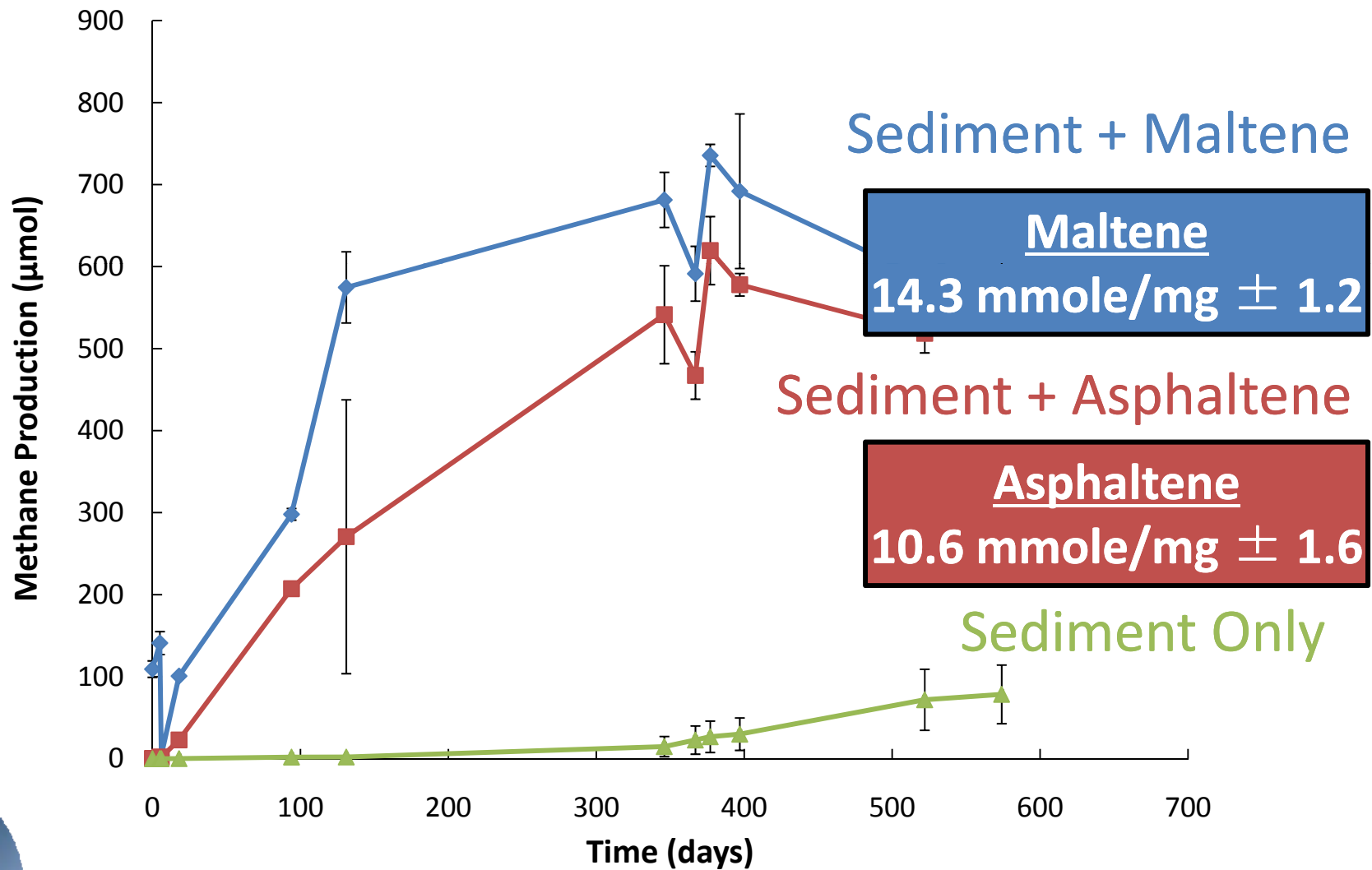


Coal Characterization: asphaltene and maltene extracts

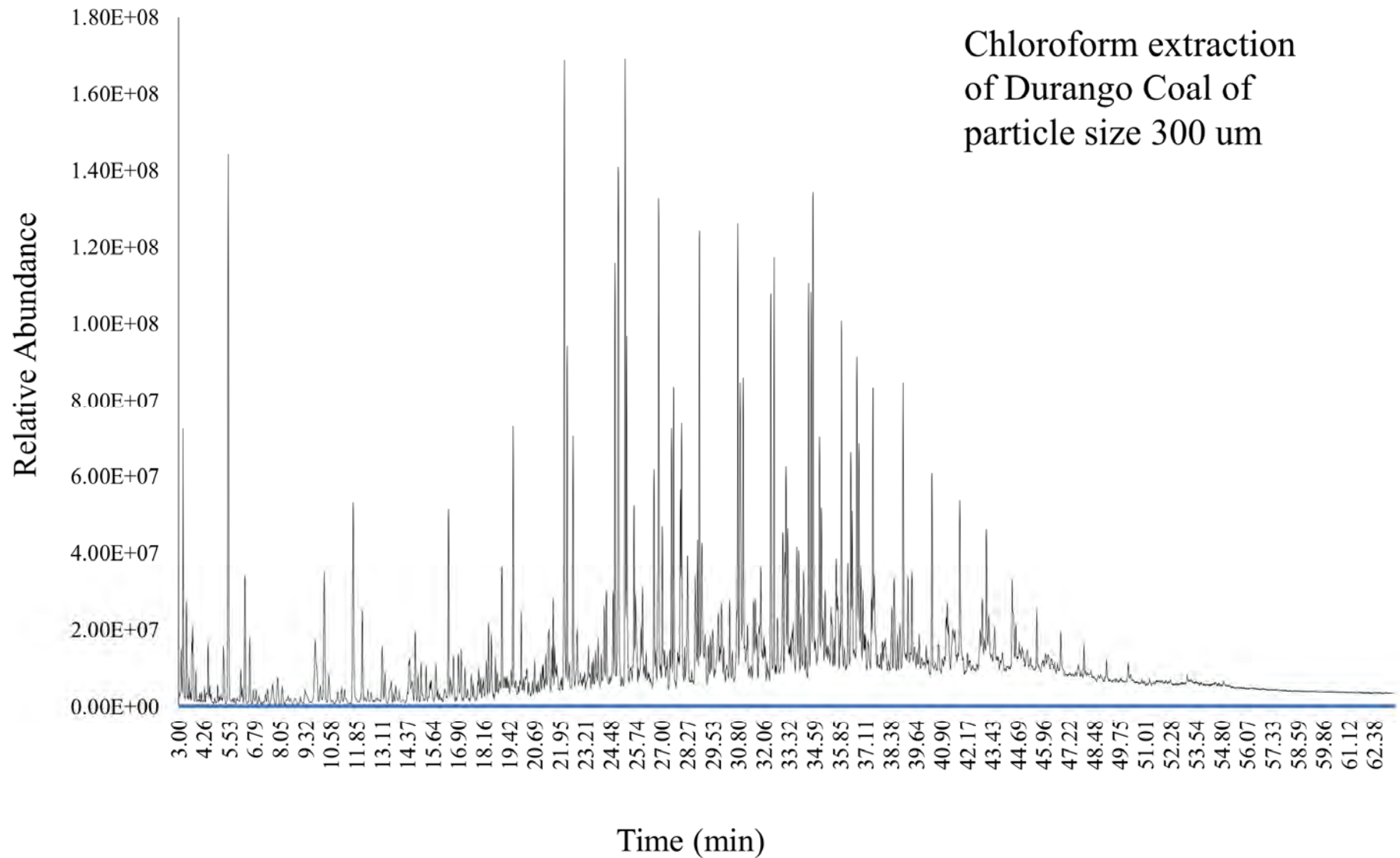


Anoxic creek sediment added to bottles

Methane Production



GCMS Characterization



Compounds Identified (tentative)

RT	Aliphatic Compound	RT	Aromatic Compounds	RT	Heteroatomic Compound
6.52	Nonane	5.46	o-xylene	29.96	Benzidine
12.11	Decane	6.29	m-xylene	31.03	N-2-Fluorenylacetamide
12.12	3 Ethyl-3 methylheptane	9.78	1-ethyl-2-methyl-benzene	33.7	4,4'-methylene bis - Benzamine
15.03	2-Methyl-Decane	10.22	1,2,3-Trimethyl-benzene	34.5	Bitoscante
16.40	Undecane	19.05	Naphthalene	36.37	2,4-bis (1,1-dimethylethyl) Phenol
18.52	2-Methyl-Undecane	22.14	2-methyl-Naphthalene		
19.60	Dodecane	24.23	Biphenyl		
20.00	2,6-Dimethyl-Undecane	25.17	2-methyethyl-Naphthalene		
21.36	2-Methyl-Dodecane	26.6	Diphenylmethane		
21.59	2,3,7-Trimethyl-Octane	28.65	Fluorene		
22.28	Tridecane	35.65	Fluoranthene		
24.66	Tetradecane	41.16	Chrysene		
26.83	Pentadecane	42.91	Benz(a)anthracene		
28.86	Hexadecane				
30.76	Heptadecane				
40.40	Tricosane				
41.78	Tetracosane				



Chemical Pre-treatment

Chemicals	C0	C1 (M)	C2 (M)	C3 (M)
NaOH (SH)	0	0.13	0.67	1.33
HNO ₃ (NA)	0	0.33	1.67	3.33
H ₂ O ₂ (HP)*	0	0.032	1.62	3.24
KMnO ₄ (PP)	0	0.01	0.05	0.1

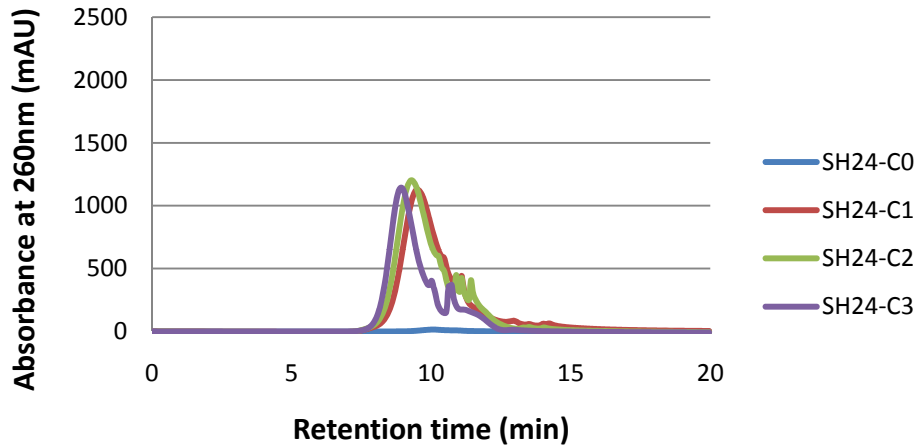
*Fe(II) at a final concentration of 0.027M was added as catalyst



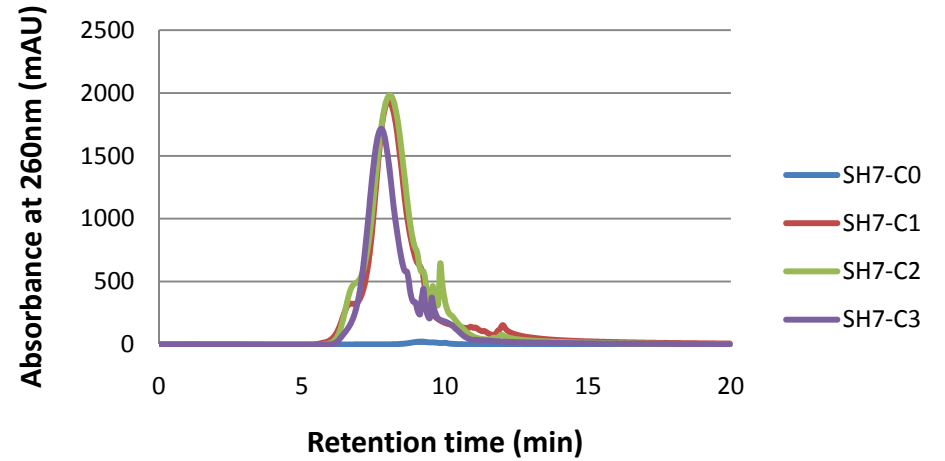
Sodium hydroxide

SEC

NaOH 24hr

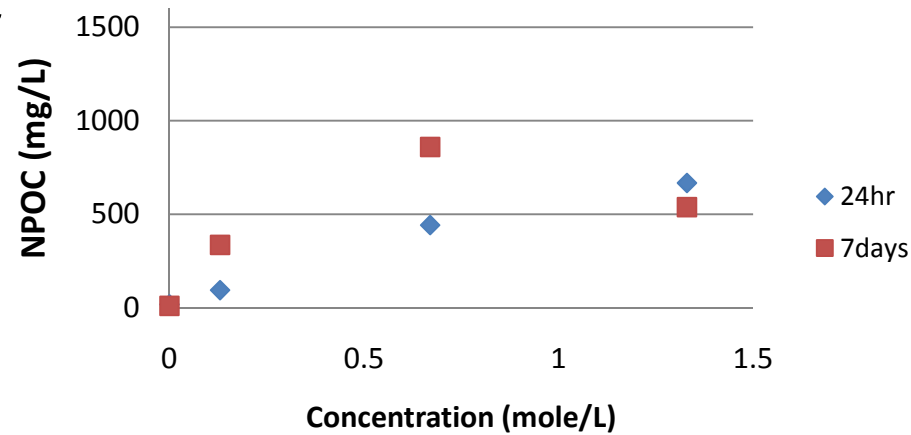


NaOH 7 days



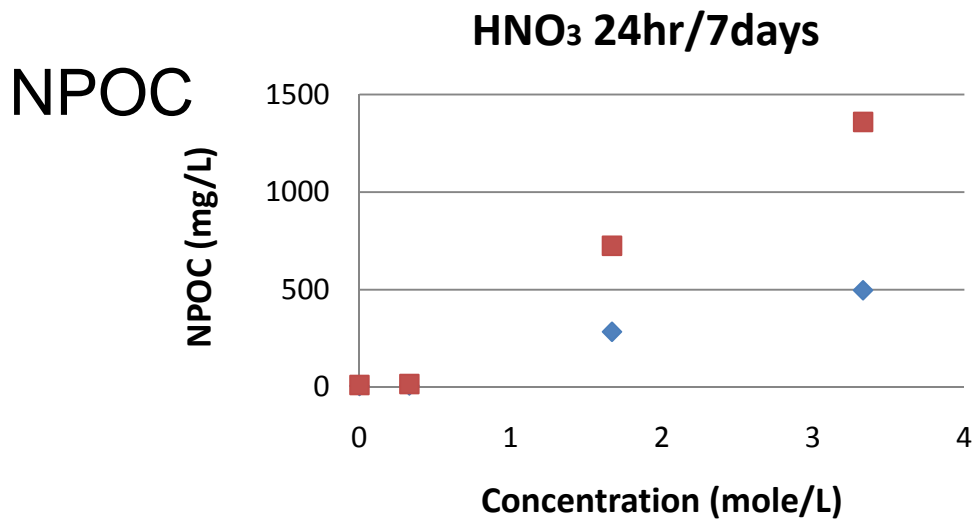
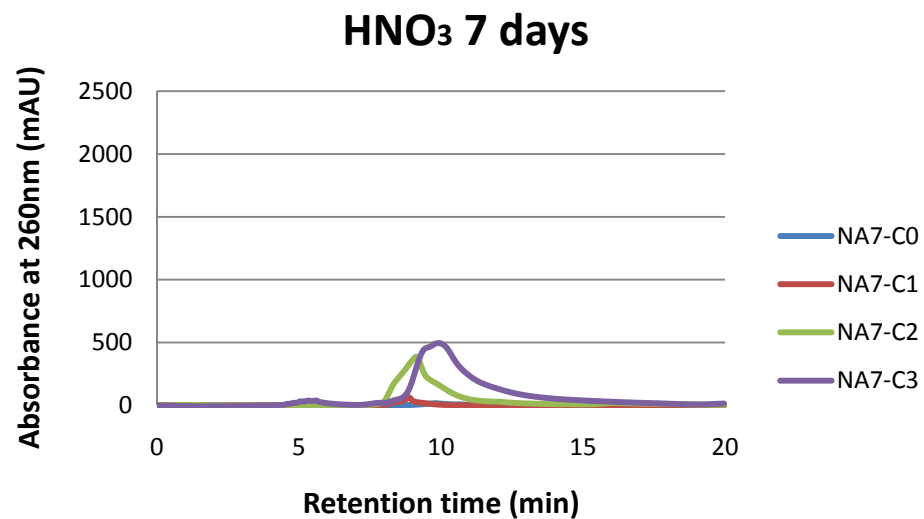
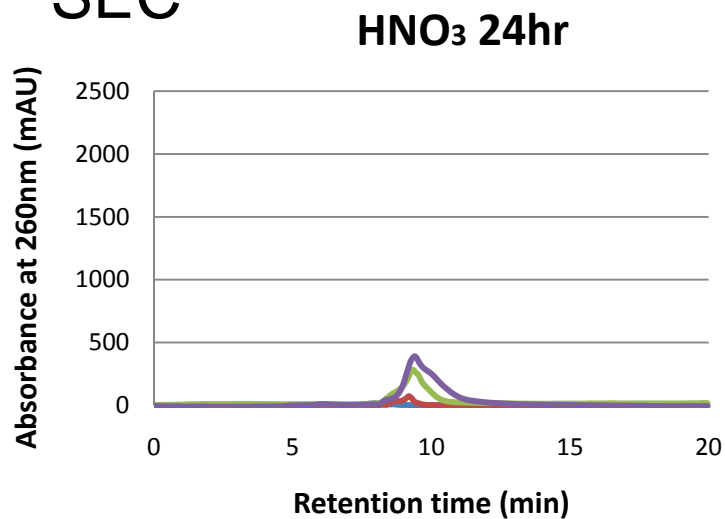
NaOH 24hr/7days

NPOC

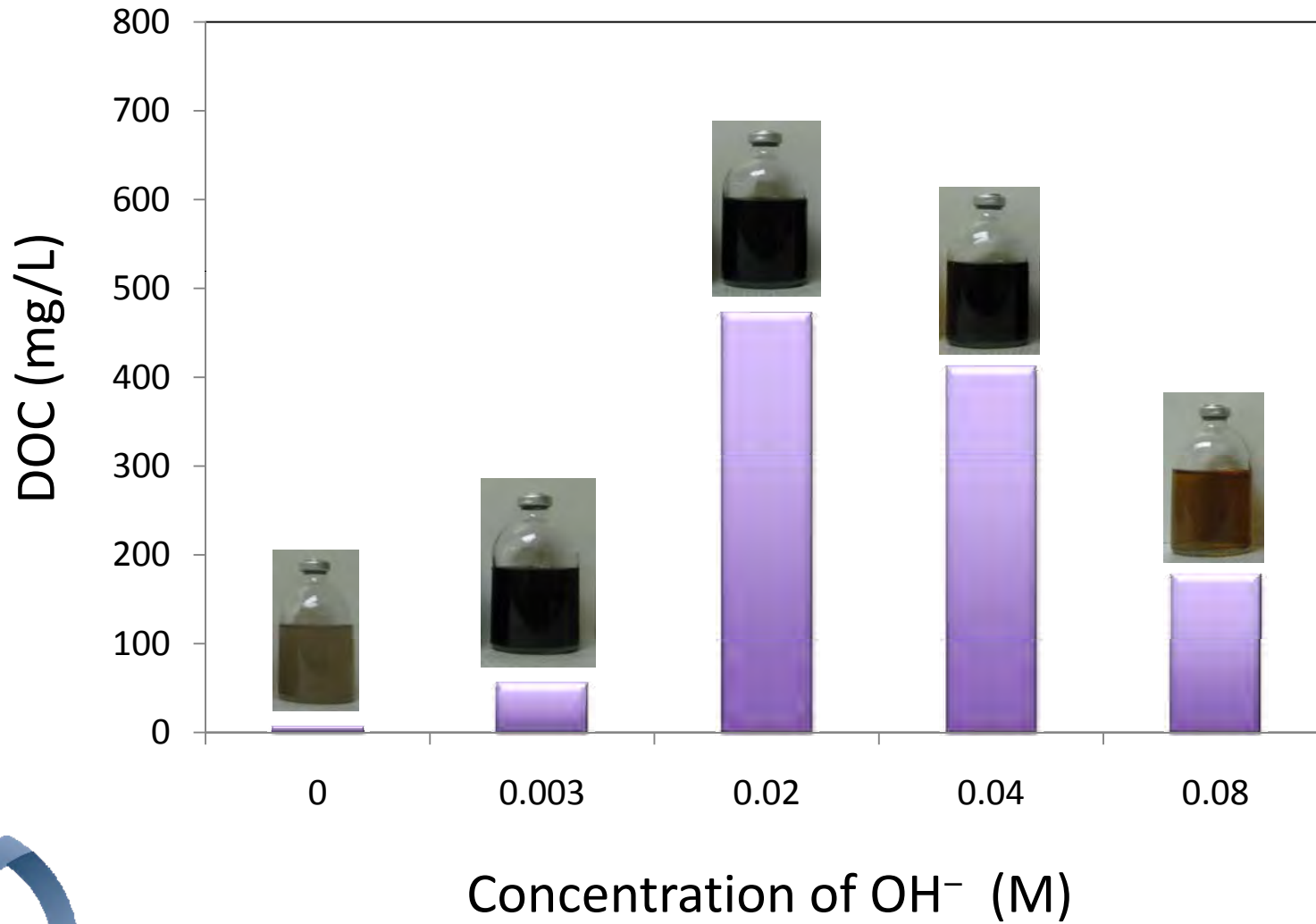


Nitric acid

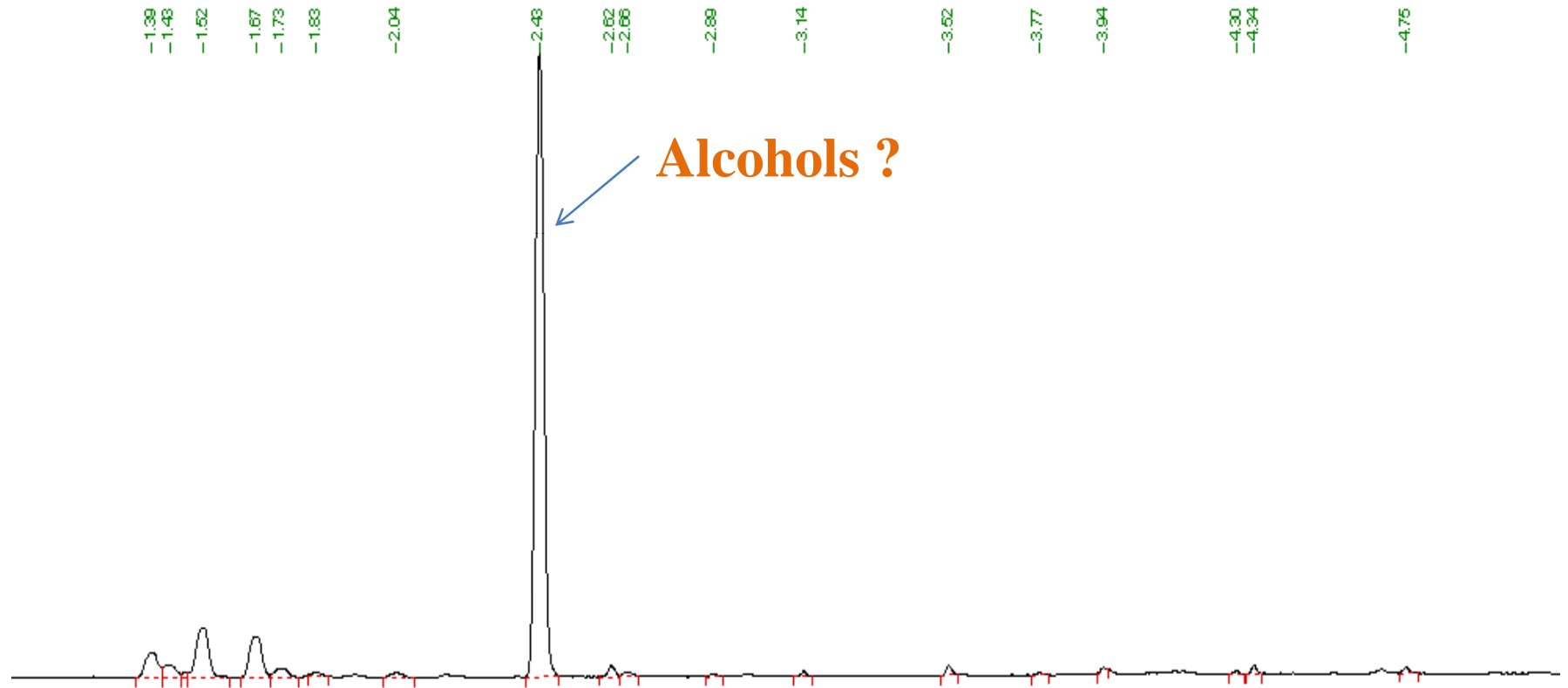
SEC



NaOH Extract from Anaerobic Coal



GC-FID Analysis of NaOH Extract



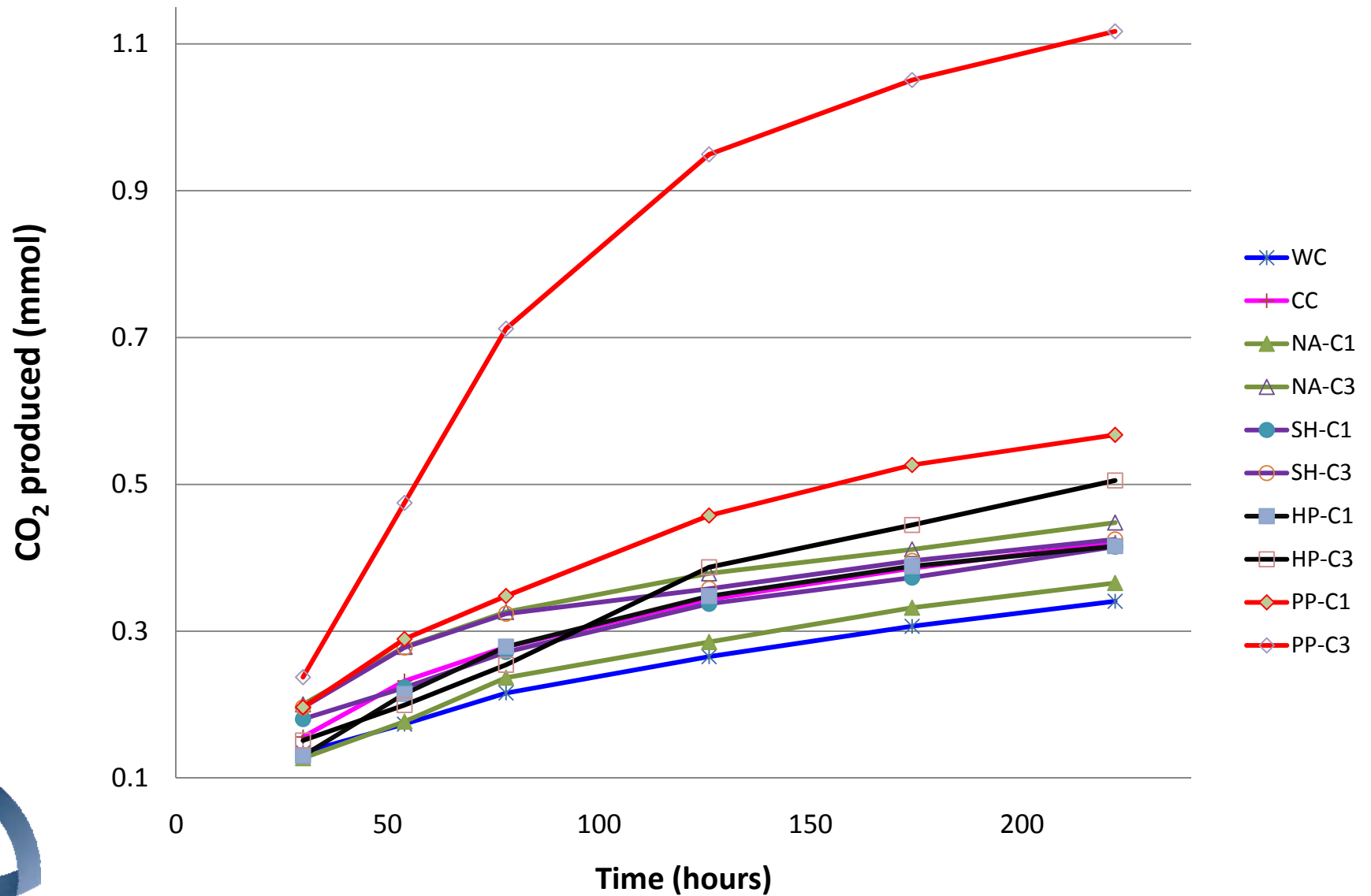
Bioavailability Experiment

	HNO ₃		NaOH		H ₂ O ₂		KMnO ₄		CC
	C1	C3	C1	C3	C1	C3	C1	C3	
Conc. (M)	0.33	3.3	0.13	1.3	0.32	3.2	0.01	0.1	
NPOC (mg/L)	8.8	170.1	239.6	1262.6	24.9	60.9	85.6	370.4	6.4

- *Pseudomonas putida* F1 (pH 7-8), 1mL
- Filtered water extraction sample, 15mL
- Sorensen's phosphate buffer, pH=7, 2mL
- KOH (0.05N) in side arm for CO₂ capture
- Titration to measure CO₂ production



Cumulative CO₂ Production



Conclusions

- *Methanosarcina* appears to be critical for methane generation in these systems; others?
- Urea may enhance methanogenesis
- Both low MW and polyaromatic hydrocarbons may support methanogenesis
- NaOH, HNO₃ or KMNO₄ are the most effective pre-treatment agents based on SEC, NPOC or aerobic CO₂ production, respectively

