Use of Biotechnology for Air Pollution Control at Produced Water Evaporation Facilities

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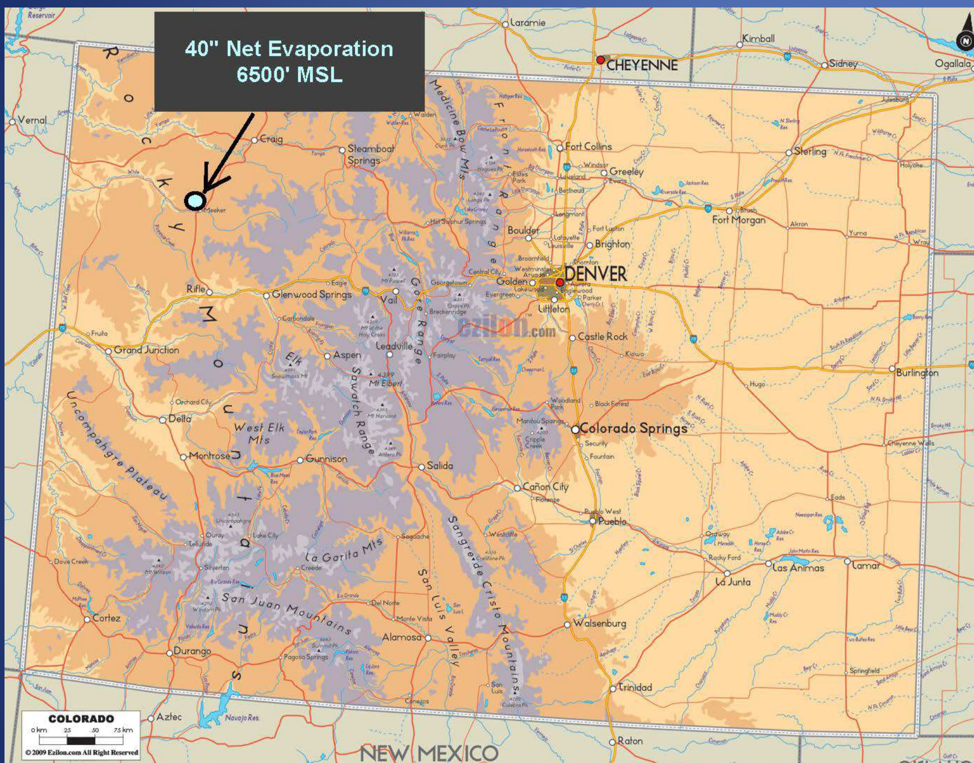
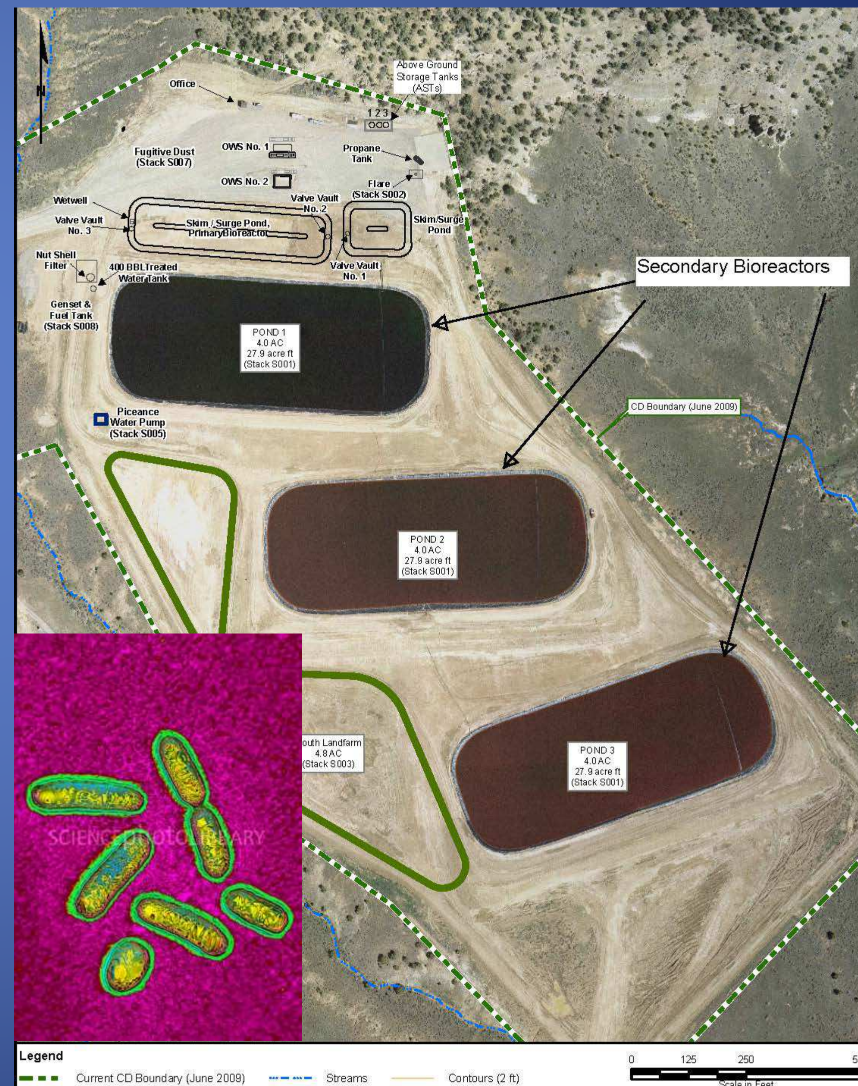
Piceance Disposal Facility





Use of Biotechnology Colorado

- July 2014 Permit - 1^{st} time biotechnology has been proposed as an air pollution control technology in Colorado.

- Previously had to assume that 100 % of VOCs dissolved in the evaporation pond water ends up in the atmosphere.

- Our permit quantified mass of VOCs removed by metabolism at the facility.

Developed Predictive Model

- For each month it calculates:
  - mass removal by metabolism.
  - mass emitted to the atmosphere.

  - For the covered bioreactor and uncovered evaporation ponds.

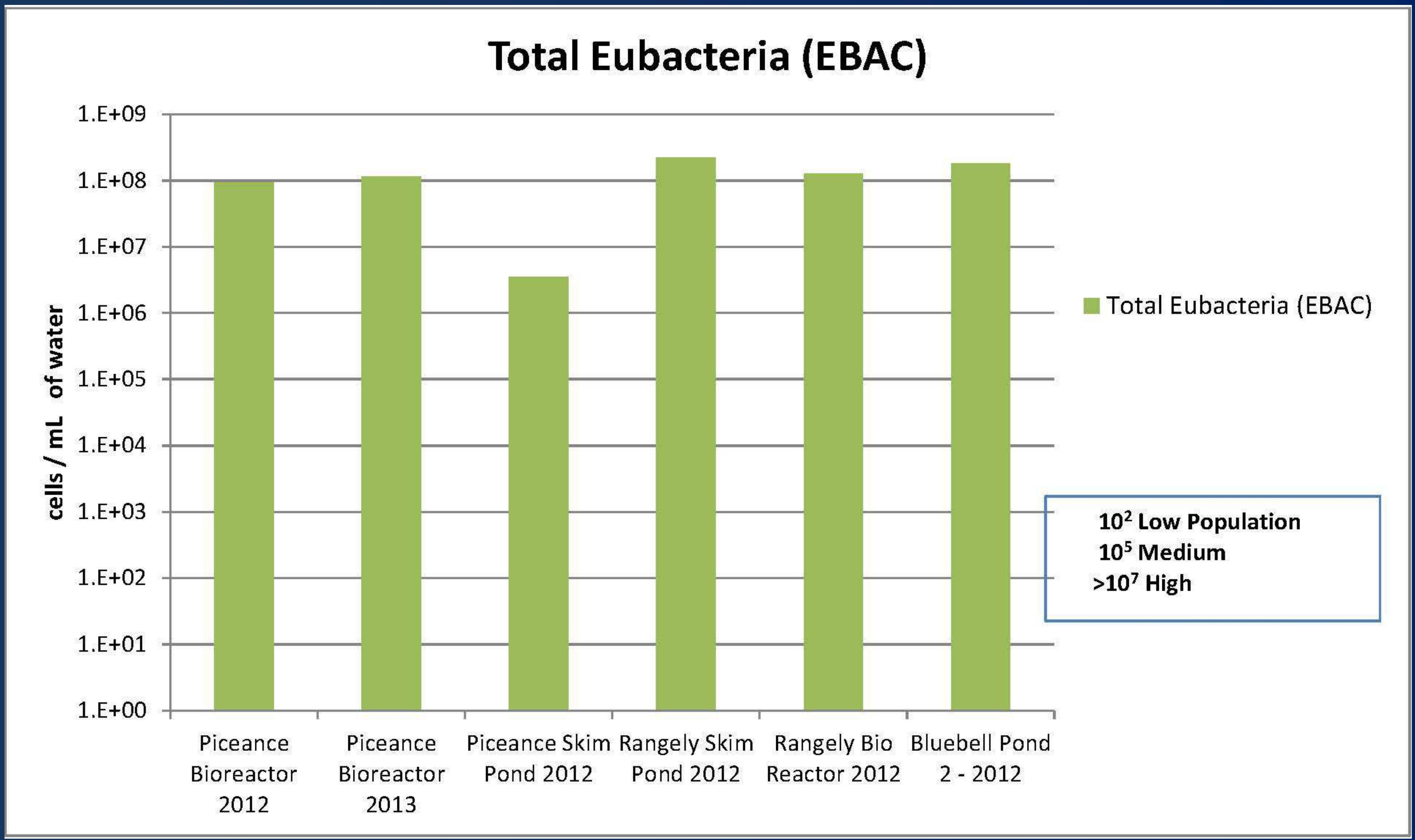
Overall Mass Balance Summary

26.3%	of Methanol gets biodegraded in Primary Bioreactor.
59.6%	of Methanol gets biodegraded in Secondary Bioreactors (Evaporation Ponds).
14.1%	of Methanol gets discharged to the atmosphere.
100.0%	**Mass Balance**
86%	of Methanol will be biologically metabolized..

Successful Anaerobic Treatment Requires 10 Things

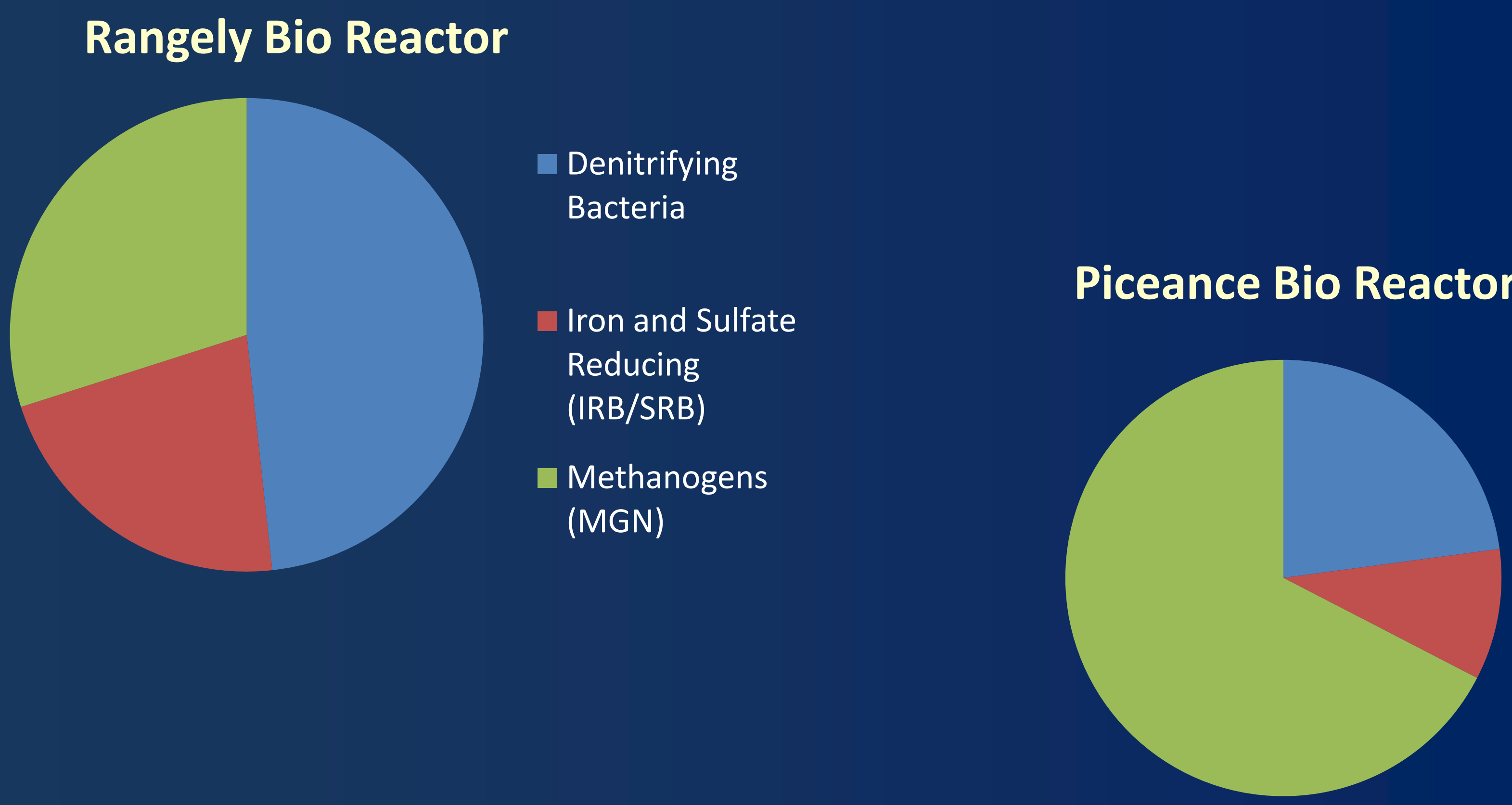
1. Right Microorganisms
2. Substrate (Food)
3. Water
4. Proper Temperature
5. Proper pH / Alkalinity
6. Macronutrients
7. Micronutrients
8. Control of Toxicity
9. Contact between Microbe and Substrate
10. Reaction Time

RNI Bacteria Populations

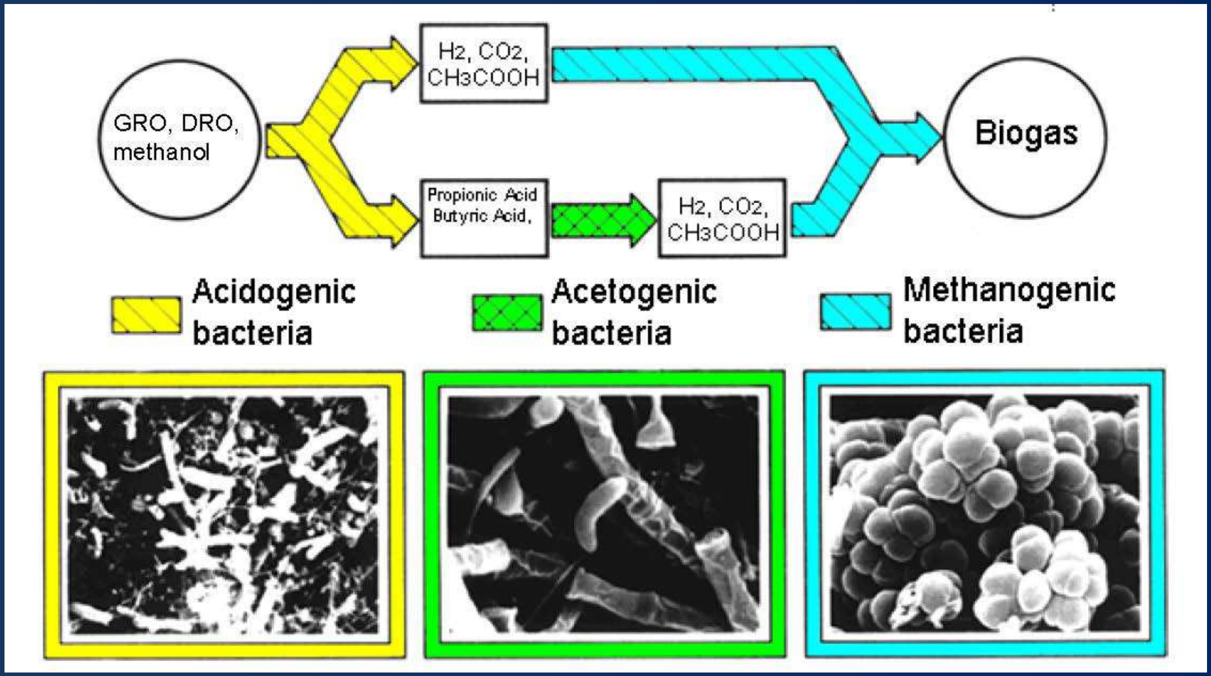


Microbial Insights - CENSUS Method DNA/RNA Extraction - ID gene sequences

Bacteria


Rangely Bio Reactor
Denitrifying Bacteria
Iron and Sulfate Reducing (IRB/SRB)
Methanogens (MGN)
Piceance Bio Reactor

Anaerobic Digestion



$CH_3CO\ OH$ = Acetic Acid

Acidogens metabolize hydrocarbons faster than methanogens.

Sampling of Produced Water

- Sampled three evaporation facilities each quarter for one year.
- Elevated Methanol – Freeze protection
- BTEXH, methanol, GRO, DRO

Evaluation of Produced Water

Facility	Sample Date	Benzene (mg/l)	Ethylbenzene (mg/l)	Toluene (mg/l)	Xylene (mg/l)	Hexane (mg/l)	TVH 8260 (mg/l)	TEH-DRO (mg/l)	Methanol (mg/l)
Combined Averages		12	0.54	19	7	0.24	43	88	2619

Methanol = 95% of Total VOCs

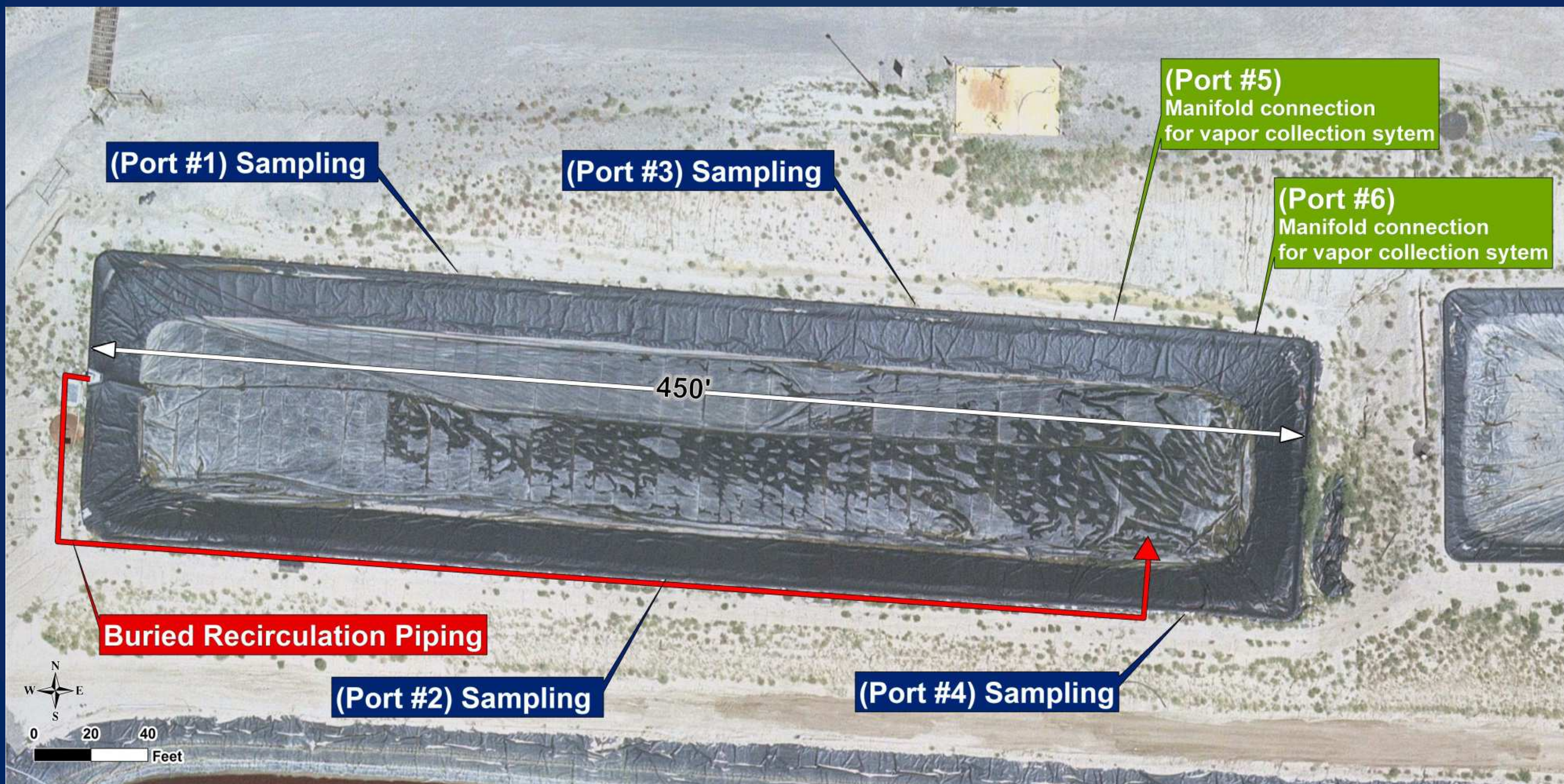
Methanol Is Readily Biodegradable

- Simplest form of alcohol.
- Used as an antifreeze throughout the winter months.
- Miscible
- Henry's Law Constant 4.55E-6 atm-m^3/mole

  Benzene 5.55E-3 atm-m^3/mole

- Readily metabolized by acidogens and 11 known species of methanogens.
- VOC and a HAP

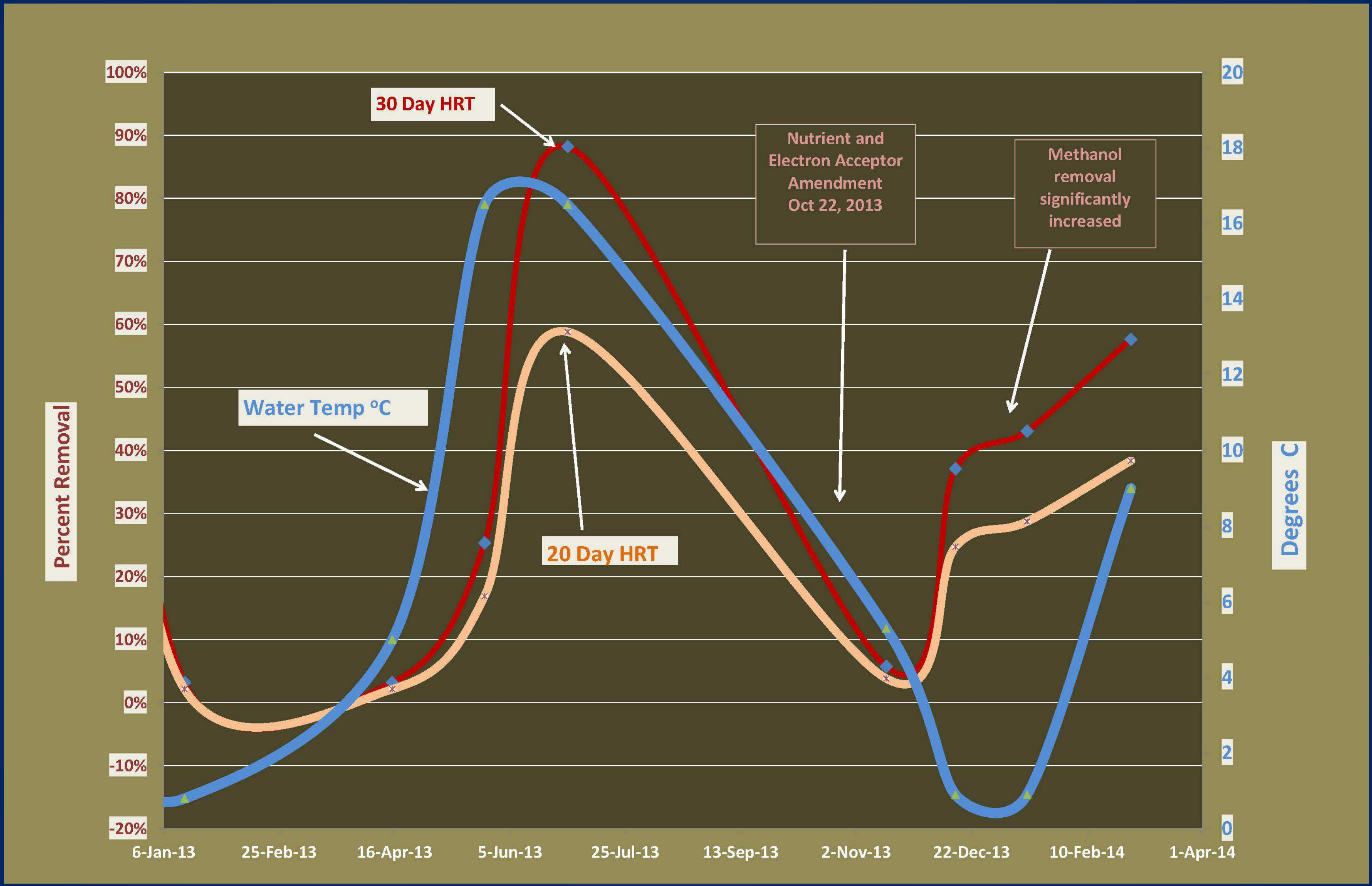
Determining the Rates of Metabolism
For Covered Bioreactor and Uncovered Evaporation Ponds



Sampling Program

Accutest	Method
Alkalinity, Total as $CaCO_3$ COD	SM2320B
Individual BTEX Compounds	SM 5210B-2011
Hexane	8260B
Methane	8260B RSK175
GRO	MOD
DRO	8015B
Methanol	8015B
HEM Oil and Grease	8015B
TDS	1664A
TSS	SM 2540C-2011
VSS	SM 2540C-2011
pH	SM 2540E-2011
VFAs (Microseeps Subcontract)	
Ammonia	AM21G
Sulfate	SM 4500NH3 D-2011
	EPA 300.0/SW846 9056

Methanol Removal By Metabolism



Pond Emissions

Dr. Seth Lyman – Energy Dynamics – Utah State University – Vernal Campus

Calculating Methanol Emissions From Uncovered Ponds

Step 1:

(mg/m^2/hr in March) x (surface area of pond) x (hrs in a month) = monthly emissions March = 4.7 tons

Step 2: Calculate total mass passing through the pond that month.
Conc in water x total volume of water = total mass accepted into pond = 59.7 tons

Step 3: Convert emissions to a percent of the total 4.7 tons of emissions / 59.7 tons total = 7.9%

Step 4: Seasonal adjustment in emissions

(lake evaporation for a specific month / lake evaporation for March) x % emitted in March =

% emissions for the specific month

Example Calculation Pond Emissions

Lake Evaporation for Roosevelt Utah

Jan in	Feb in	March in	April in	May in	June in	July in	Aug in	Sept in	Oct in	Nov in	Dec in
0.65	0.95	2.17	3.6	5.43	5.6	6.17	5.63	3.97	2.71	1.41	0.79

Methanol Flux Estimates Assuming Variations are Roughly Proportional to Lake Evaporation Rates

Jan tons	Feb tons	March tons	April tons	May tons	June tons	July tons	Aug tons	Sept tons	Oct tons	Nov tons	Dec tons
1.4	2.1	4.7	7.9	11.9	12.2	13.5	12.3	8.7	5.9	3.1	1.7

Flux as a percent of the Measured March Field Measurements

30%	44%	100%	166%	250%	258%	284%	259%	183%	125%	65%	36%

March Pond Emissions = 7.9% percent of the total methanol mass accepted into ponds

August Pond Emissions = 7.9% x (5.63 / 2.17) = 20.5 % of total mass accepted into the ponds.

Additional studies of season effects on pond emissions are planned by Utah State.

Putting It All Together

Bioreactor performance, modeled emissions for covered bioreactor, flux sampling of uncovered ponds

Annual Summary

@ 3000 bbls/day = 20 Day HRT

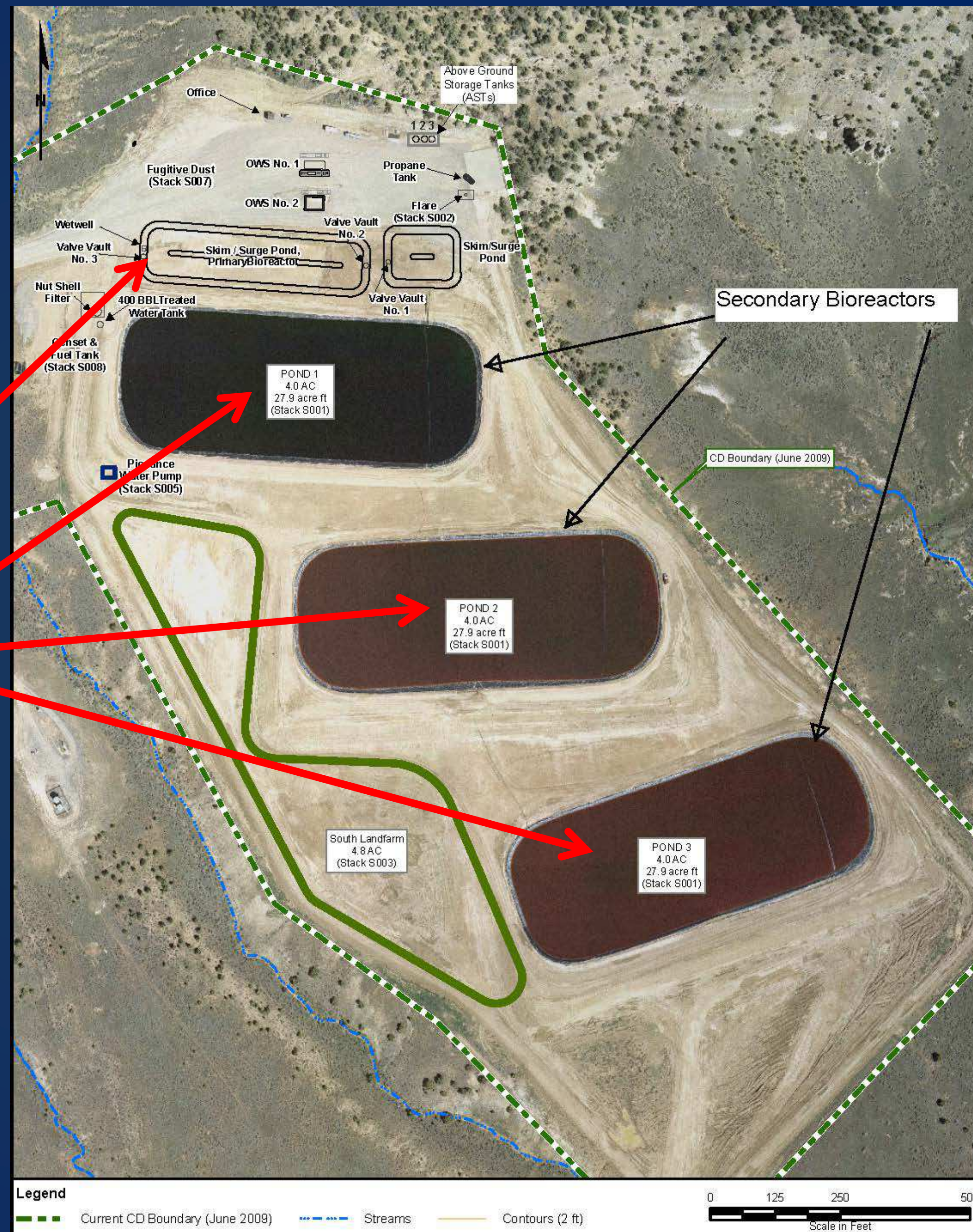
Emissions vs Metabolism

Received = 502 tpy of Methanol

Primary Bioreactor = 157 tpy = 31.2%

Secondary Reactors = 155 tpy = 31%

Emissions = 199.7 tons = 37.8 %



Current system

Constituents	RN Industries Average Facility Inlet Concentrations based on RNI Facilities in Utah sampled seasonally	Estimated Total Annual Mass in 3000 bbls/day	Overall Treatment Facility Efficiency	Overall Treatment System Mass Removal	Evaporation Pond Emissions
	mg/L	tons/year	%	tons/year	tons/yr
GRO	**42.50**	8.2	34.2%	2.8	5.4
DRO	**88.47**	17.0	79.8%	13.5	3.4
Benzene	**12.17**	2.3	0.0%	0.0	2.3
Ethylbenzene	**0.54**	0.1	5.3%	0.0	0.1
Toluene	**18.83**	3.6	8.7%	0.3	3.3
Xylene	**6.82**	1.3	7.0%	0.1	1.2
Hexane	**0.24**	0.05	0.0%	0.0	0.05
Methanol	**2619**	502.4	0.0%	0.0	502.4
Total VOCs	**2750.0**	**527.5**		**16.3**	**511.2**
Total HAPS	**2657.6**	**509.8**		**0.4**	**509.4**

System w/o nutshell and with biotechnology

Constituents	RN Industries Average Facility Inlet Concentrations based on RNI Facilities in Utah sampled seasonally	Estimated Total Annual Mass in 3000 bbls/day	Overall Treatment Facility Efficiency	Overall Treatment System Mass Removal	Evaporation Pond Emissions
	mg/L	**tons/year**	%	tons/year	tons/year
GRO	**42.50**	**8.2**	34.0%	2.8	5.4
DRO	**88.47**	**17.0**	75.4%	12.8	4.2
Benzene	**12.17**	**2.3**	0.0%	0.00	2.3
Ethylbenzene	**0.54**	**0.1**	8.8%	0.01	0.1
Toluene	**18.83**	**3.6**	1.3%	0.05	3.6
Xylene	**6.82**	**1.3**	0.0%	0.00	1.3
Hexane	**0.24**	**0.0**	0.0%	0.00	0.0
Methanol	**2619**	**502.4**	62.2%	312.3	190.1
Total VOCs	**2750.0**	**527.5**		**327.9**	**199.7**
Total HAPS	**2657.6**	**509.8**		**312.3**	**197.5**
% of total VOCs represented by methanol =		**95.2%**			

Biotechnology removes 300 tons more VOCs / year.

Conclusions

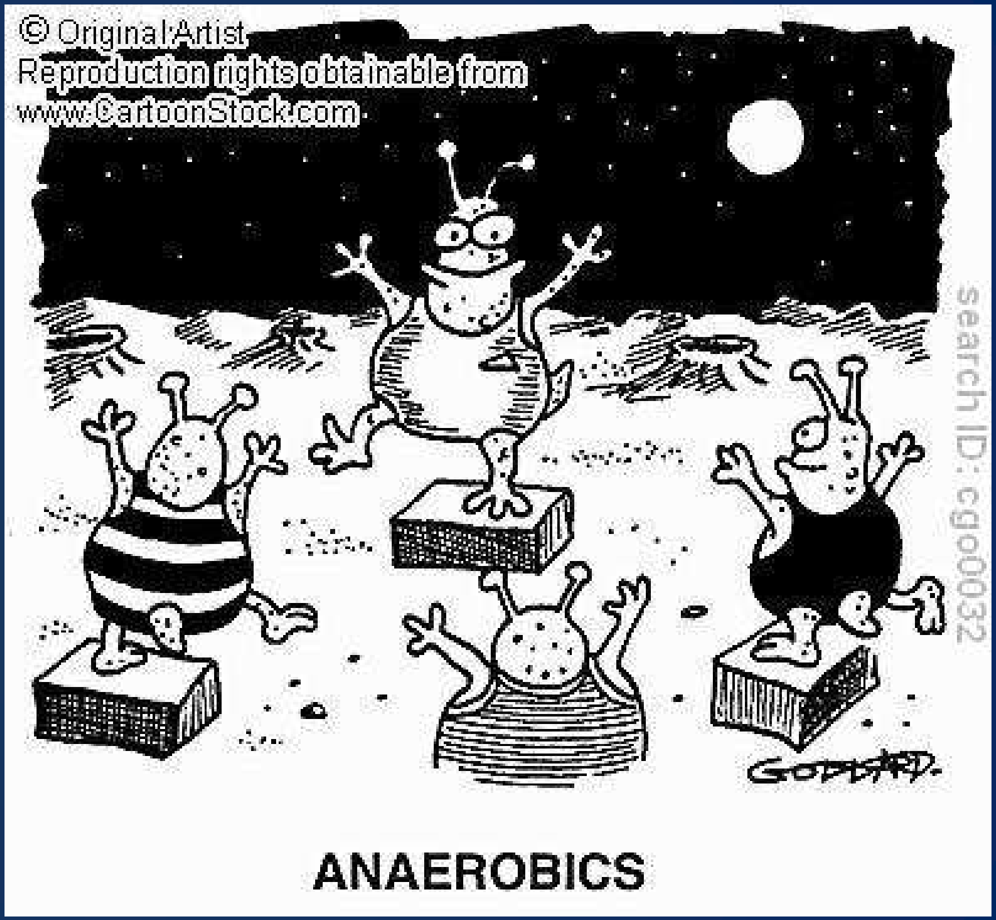
Temperature of pond water is critical to the rate of metabolism.

In our case metabolism in the uncovered evaporation ponds was more effective than in the primary bioreactor.

BTEX, GRO, DRO metabolism was low. Only 8 % of the GRO and 12 % DRO mass received was removed by metabolism.

The performance varies so you need to quantify your metabolism and emissions monthly.

Amendments of select alternate electron acceptors and nutrients may increase performance without producing undesirable bi-products.



Quick Recap - Why It Worked?

It worked because methanol is

miscible,
readily metabolized, and
represented 95% of the dissolved VOCs.

It did not work well for BTEXH, GRO or DRO because of temp / contact time

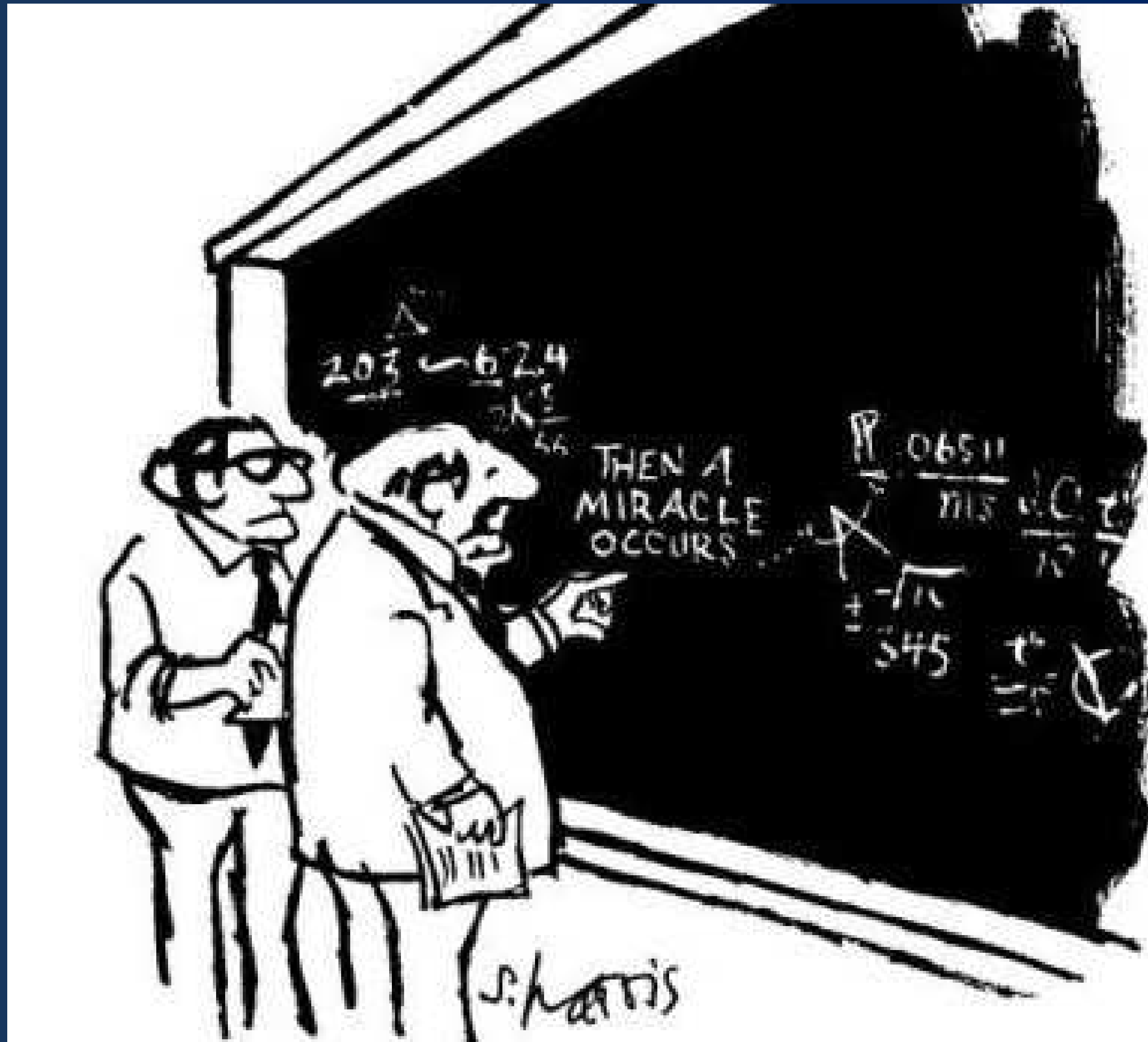
Lessons learned:

Evaporation ponds were more effective – greater retention time.

Water temperature is the key to success.

15,000 to 20,000 mg/L salinity was not a problem.

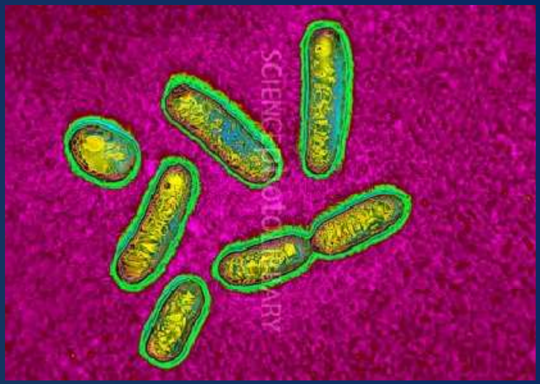
Amendments of alternate electron acceptors nitrate, iron, sulfate or manganese may increase performance without producing metabolic byproducts at levels of regulatory concern. Be careful about H_2S production.



"I THINK YOU SHOULD BE MORE EXPLICIT HERE IN STEP TWO."

Plans For Improving Performance

Nitrate Amendment



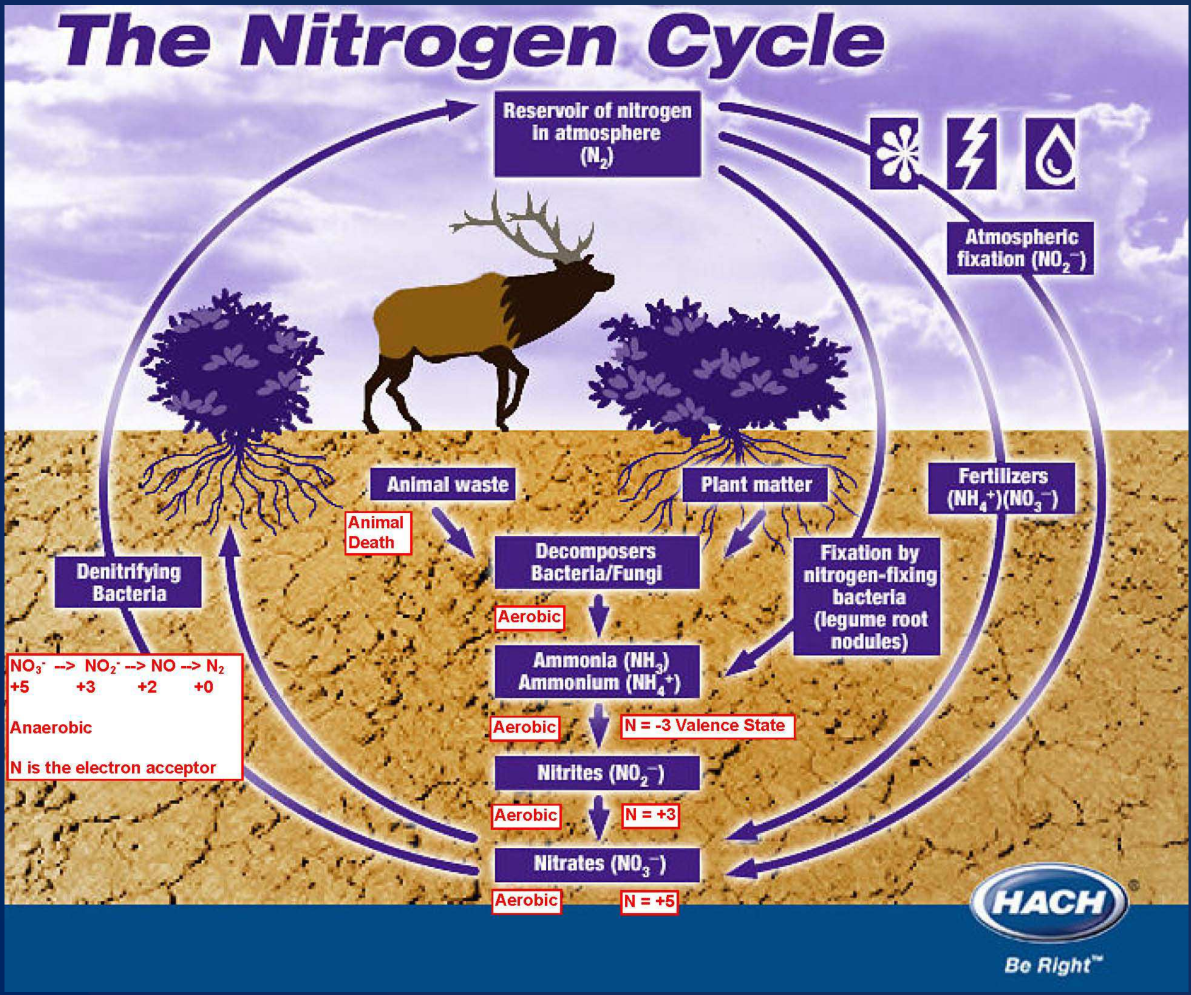
- Electron acceptor (something to breath).

$6NO_3^- + 6H^+ + C_6H_6$ ----> $6CO_2(g) + 6H_2O + 3N_2(g)$

- $150 of ammonium nitrate amended in fall . Removal rate for 20 day HRT jumped from 5% to 30%. Low cost big benefit.

- Inert nitrogen gas is the primary bi-product of metabolism.

Nitrogen Cycle – Electron Acceptor

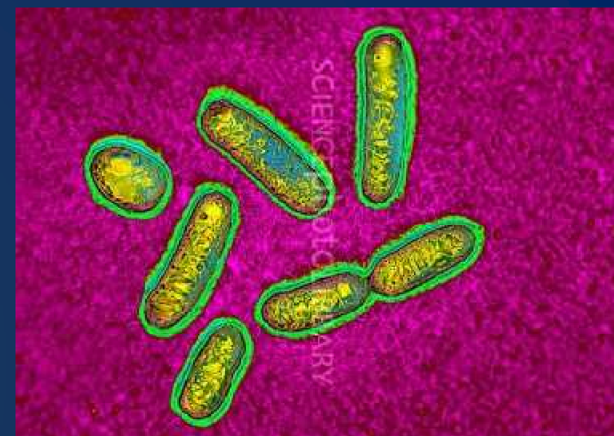


- Nitrogen accepts electrons and becomes less positive
- (+5 -- > 0) Valence
- Nitrate = Something for anaerobic bacteria to breath when O_2 is absent.
- Consume methanol , GRO, DRO (food)
- Produce inert gas.
- Pseudomonis , and other common bacterial species.

Other Potential Amendments / Improvements

Ferric Iron (Electron Acceptor)

$60H^+ + 30Fe(OH)_3 + C_6H_6 \rightarrow 6CO_2 + 30Fe_2+ + 78H_2O$



Sulfate (Electron Acceptor)

$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \rightarrow 6CO_2(g) + 3.75H_2S^o + 3H_2O$

Be careful to monitor for H_2S!

Manganese (Electron Acceptor)

$30H^+ + 15MnO_2 + C_6H_6 \rightarrow 6CO_2 + 15Mn^{2+} + 18H_2O$

Nutrients (ammonium, phosphorous)

Micro Nutrients
(Nickel, Cobalt, Molybdenum, Calcium, Sulfide, Magnesium, Potassium, Zinc, others as needed).

Heat retention strategies (insulated covers, hot reservoir water, natural hot springs, deeper ponds)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