The influence of in situ activated carbon on microbial transformation of chlorinated solvents and explosives

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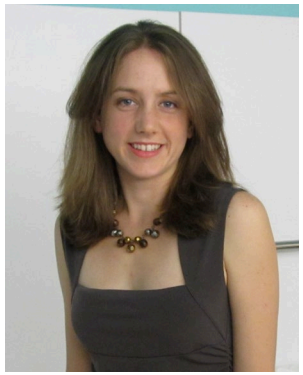
Overview

- Graduate students that have worked on these data, and funding sources
- Combined reactions, and how in situ activated carbon relates to past work
- Activated carbon chemistry and how it can impact microbiology
- Data
  - RDX both ex situ and in situ
  - Electron transfer at and through activated carbon
  - Chlorinated solvents
  - Impacts on methane production
- Future directions and conclusions

Up front acknowledgements, the real work!



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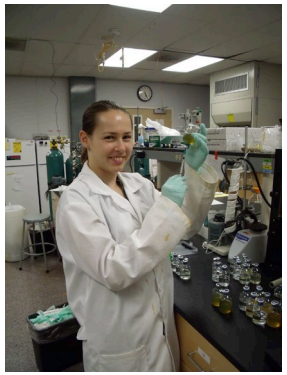

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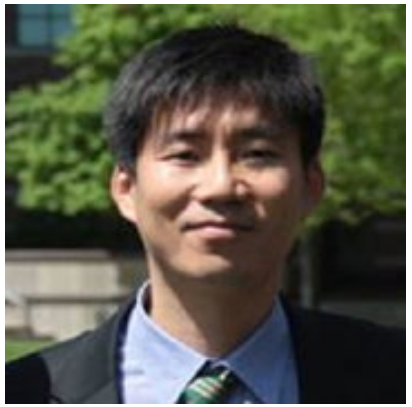

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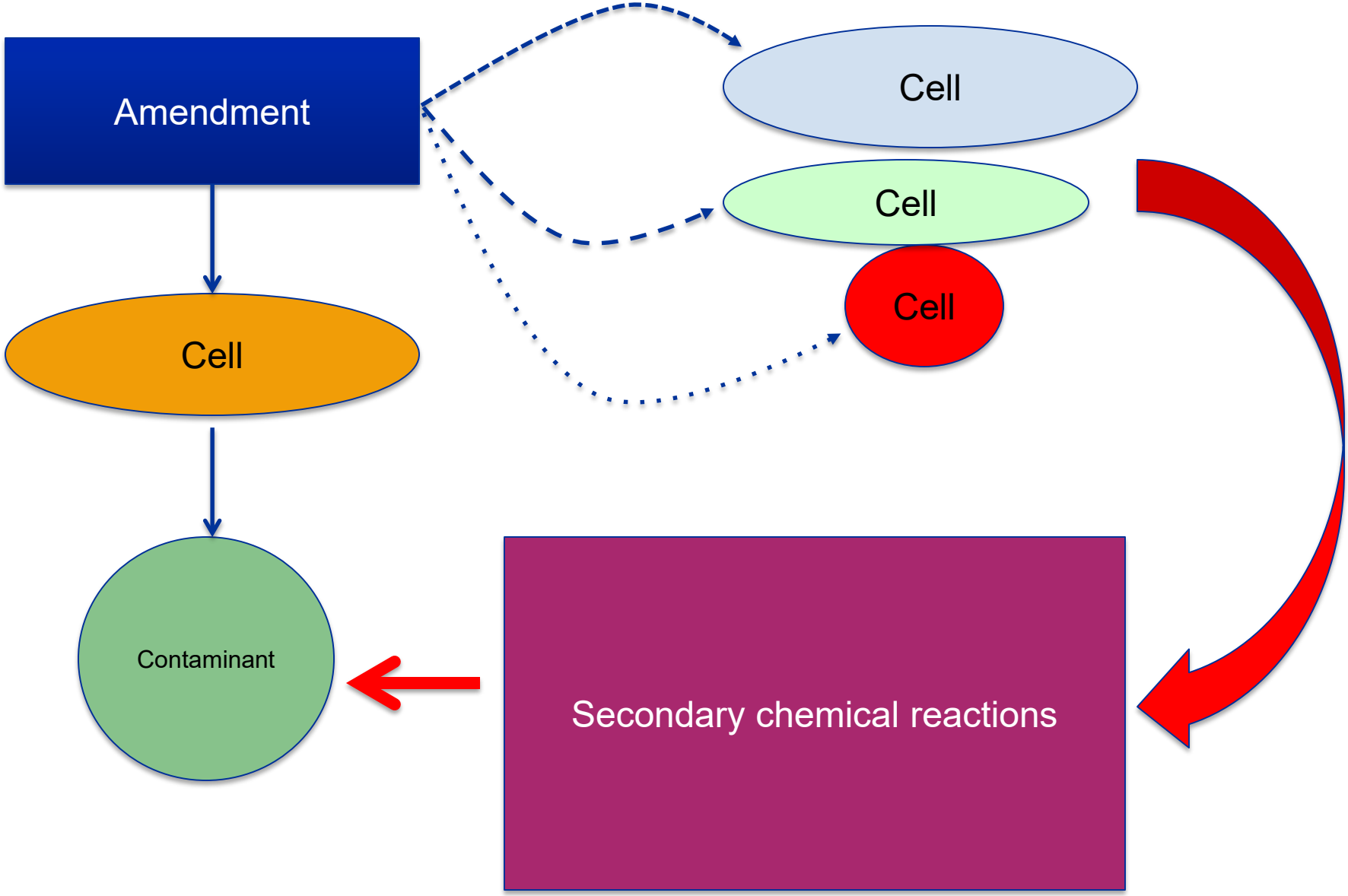
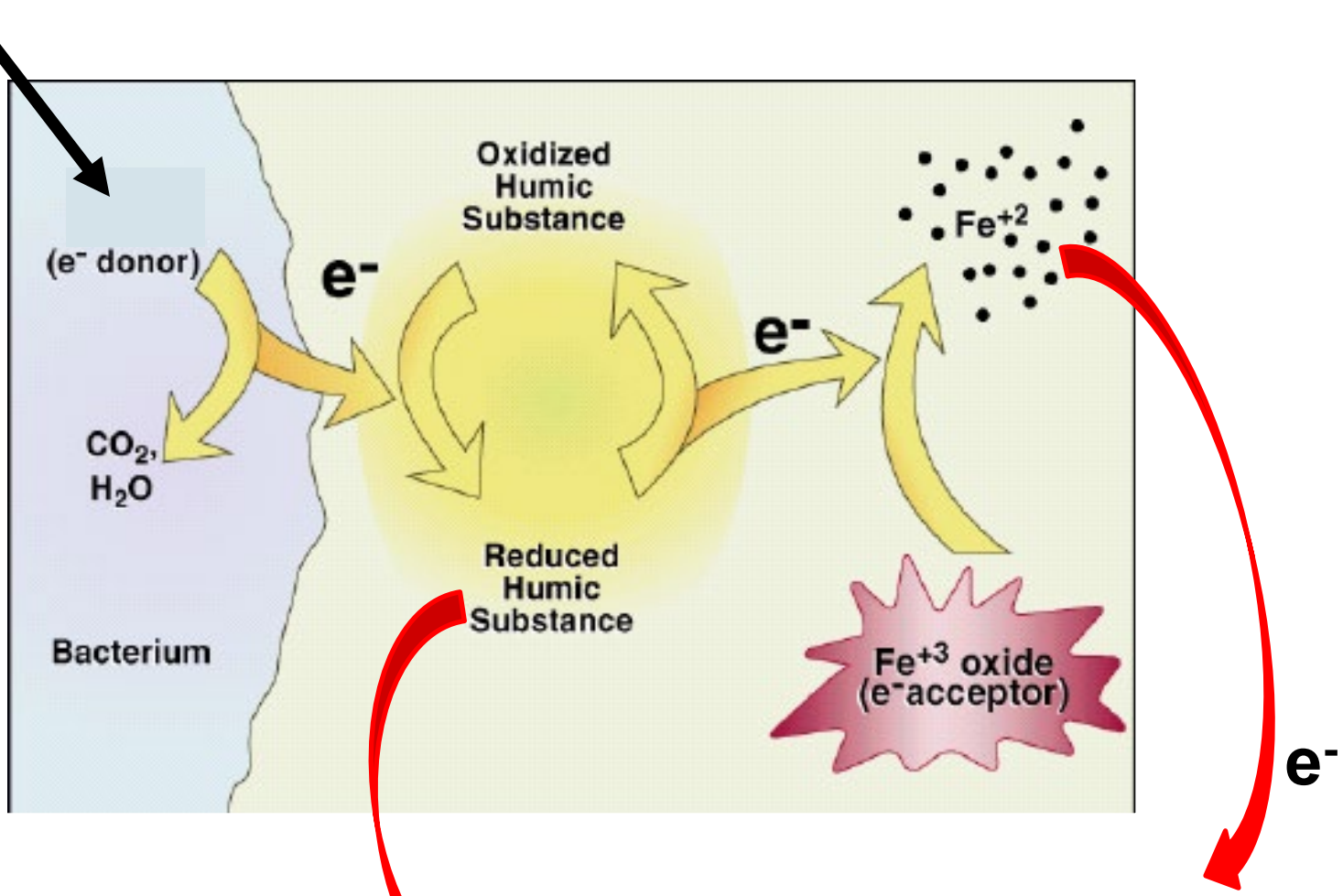
Masters Students: Yang Zhang (Consulting, China); Patricia Shin (Consulting, US); Neeraja Ramasubramanian (Consulting, India); Ayusha Khanna (Consulting, India); Sarah Galloway (Consulting, Ryder Truck Company Remediation, US), Kameryn McGee (in progress)

Undergraduates Trained on these projects: Ivy Choi, Anna Knussmann, Rachel Castillo, Erin Grubbs, Kathryn Fauerby, Jessica Bush, Gina Straga, Alexandra McIntyre, Kelsey Herring, and Olivia Felber

Our expertise is combined reactions; what do we mean by that?



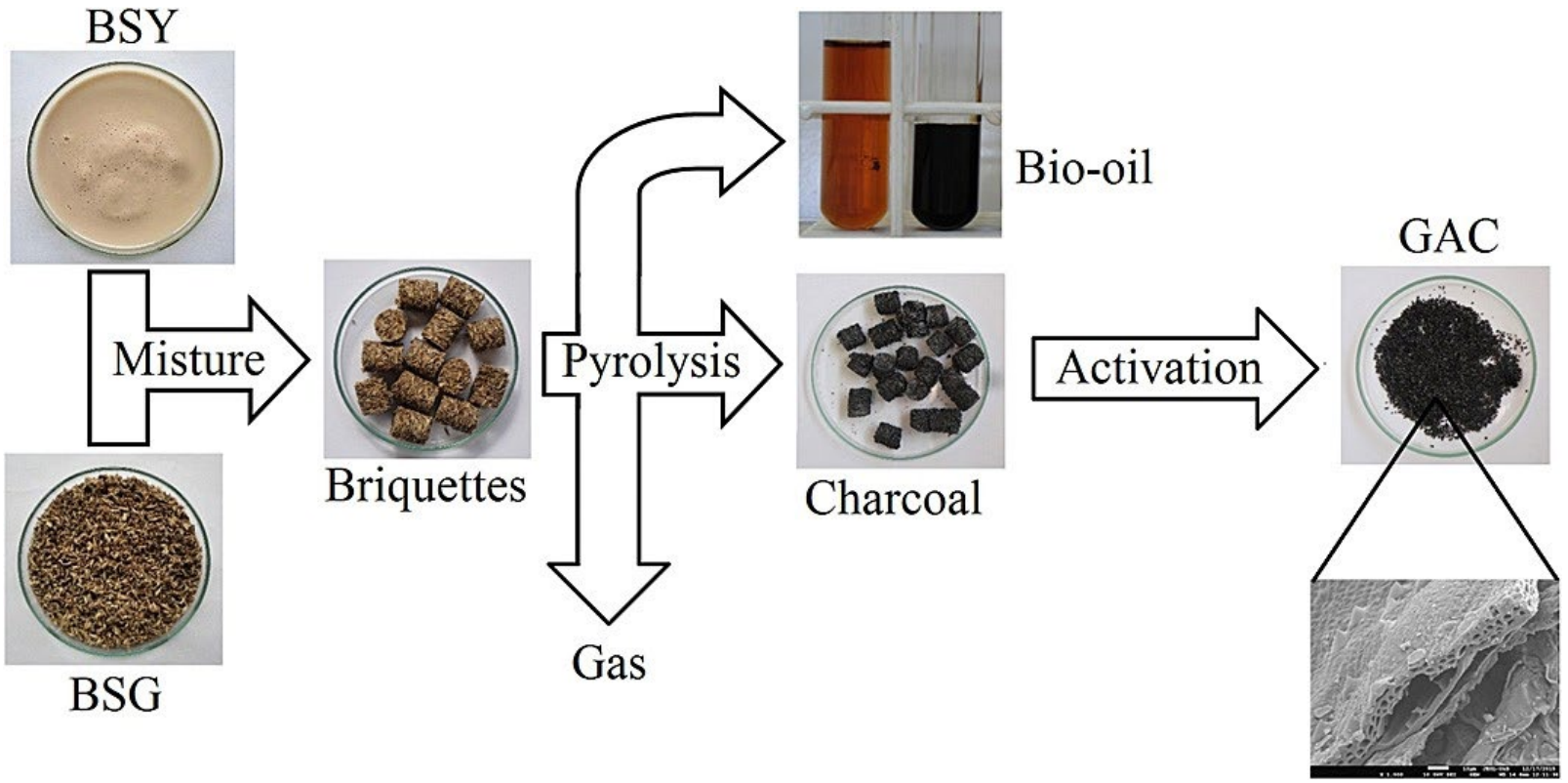
Electron donors can be contaminants or labile substrates



Reduced extracellular electron shuttles can transfer electrons to electronegative contaminants (organic and inorganic compounds)

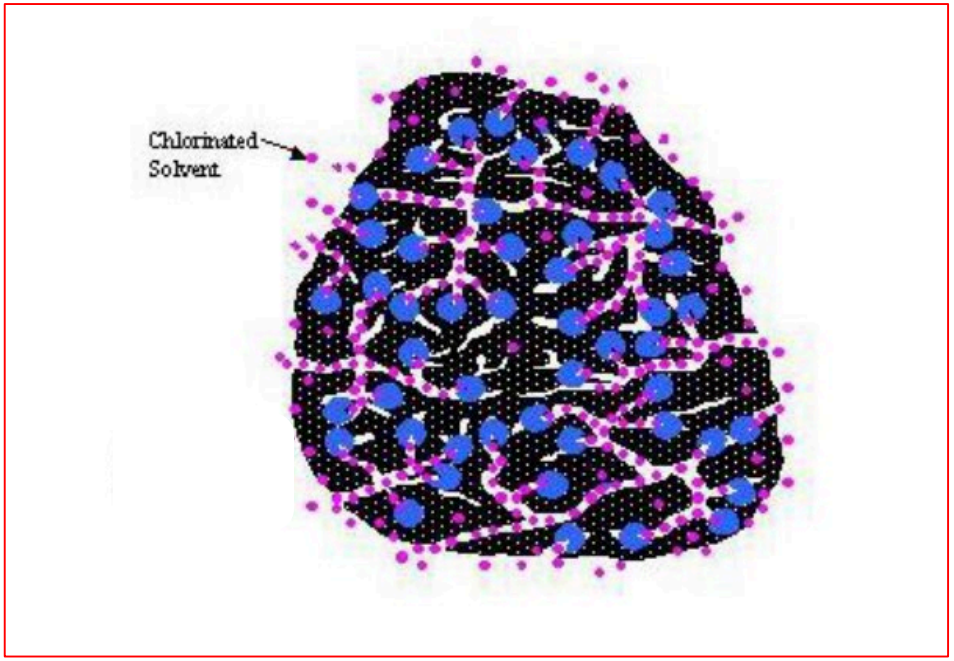
Activated Carbon

GAC is merely pyrolyzed high molecular mass organic matter

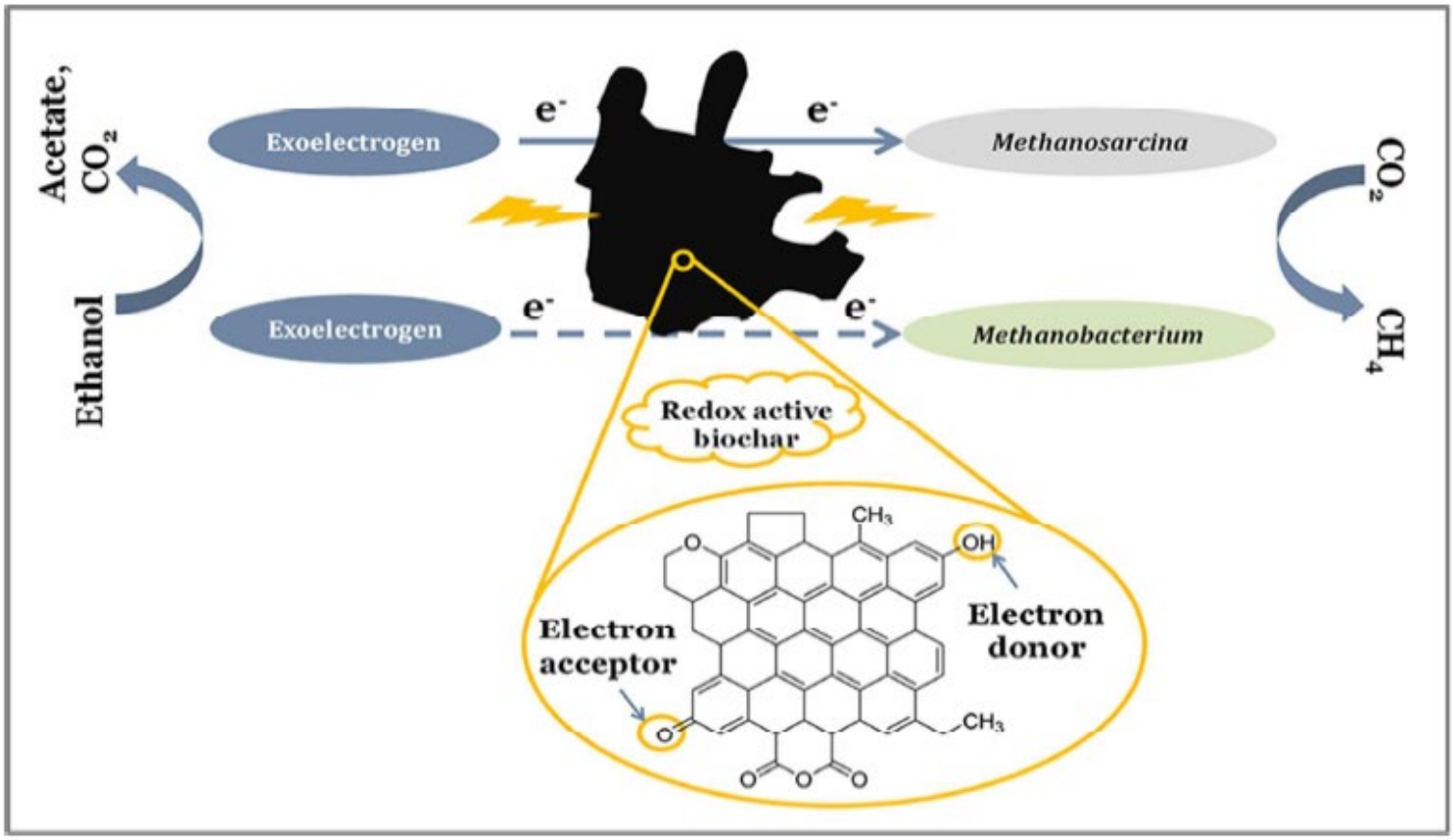


Activated Carbon Chemistry

- Activated Carbon
  - Porous
  - Provides large surface area
  - High affinity for organic pollutants
- Granular Activated Carbon (GAC)
  - Large internal surface area
  - Small pores
- Powder Activated Carbon (PAC)
  - Larger pore diameters
  - Smaller internal surface area

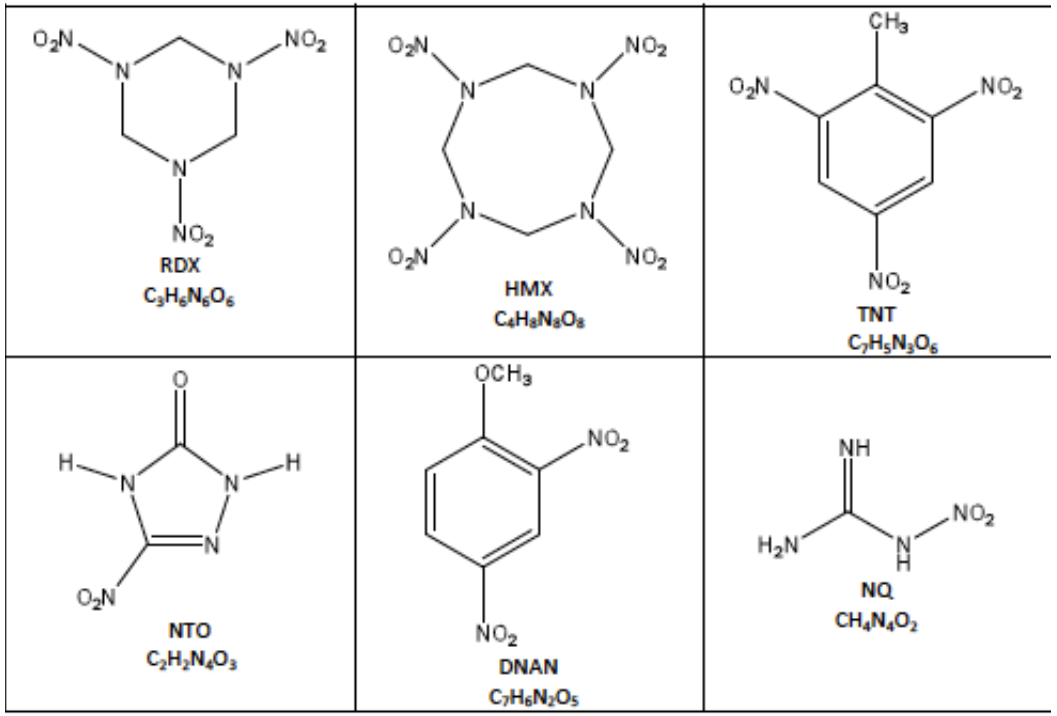


The chemical structure of activated carbon allows for electron transfer through the structure



Biodegradation of GAC-Adsorbed RDX using EES

Over 1,200 sites in the U.S. and 2,000 sites in Europe have been contaminated by explosives



Explosive	Molecular mass [g/mol]	Solubility in water [g/L]	Reduction potential [V]
RDX	222.12	38.9 mg/L (low to negligible)	-0.55
HMX	296.16	6.63 mg/L (low)	-0.66
TNT	227.13	insoluble	N/A
NTO	130.07	12.8	N/A
DNAN	198.13	sparingly soluble	-0.40
NQ	104.07	3	-0.70

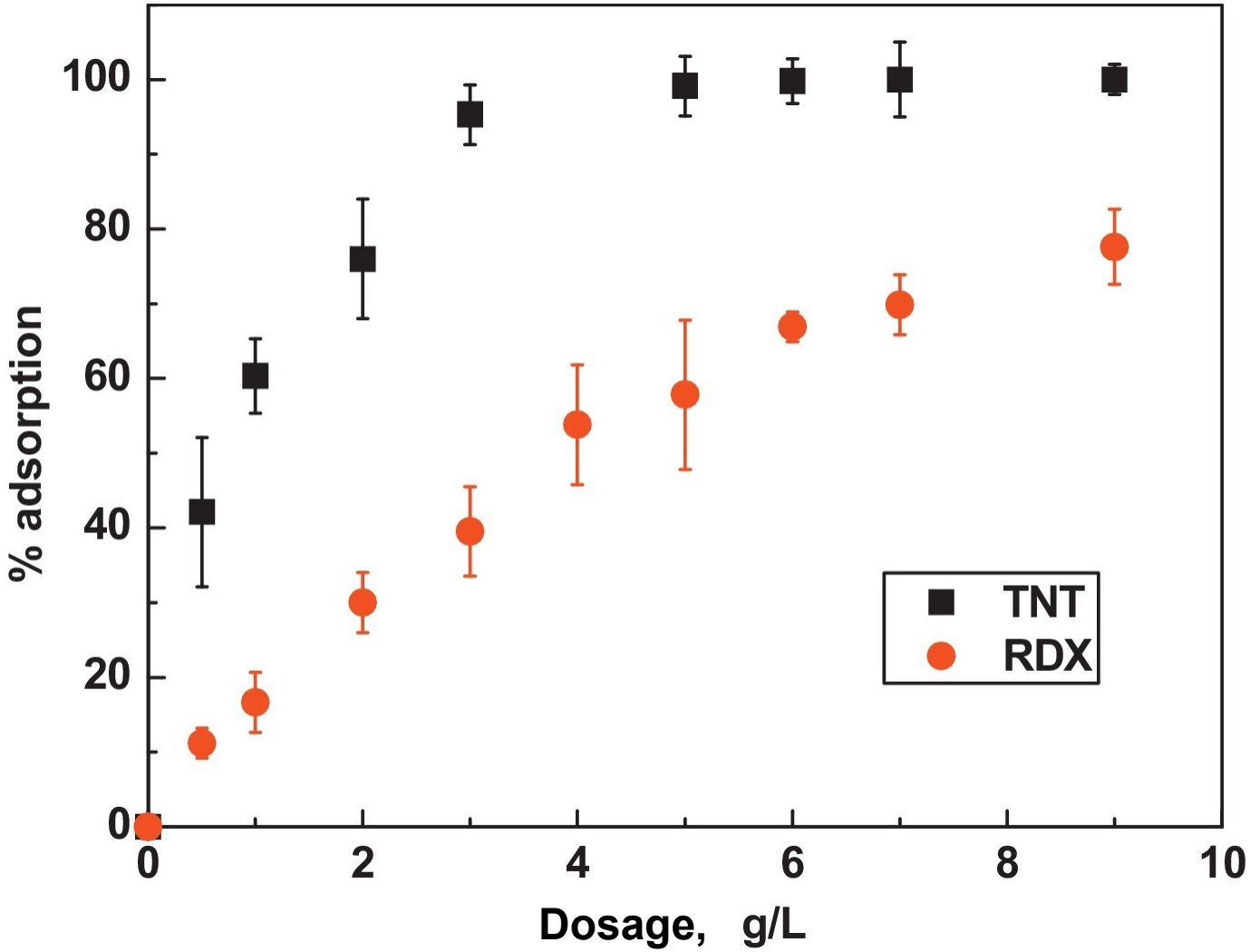
RDX is a possible human carcinogen (the lifetime health advisory in drinking water is 2μg/l)

HMX may damage the central nerve system (the lifetime health advisory in drinking water is 0.4mg/l)

IM such as 2,4-dinitroaniosole and 3-nitro-1,2,4-triazole-5-one (NTO) are currently being investigated in novel explosives composites for DoD use

Niedzwiecka and Finneran , RSC ES:WR&T, 2015, V1(1), Page 34-39

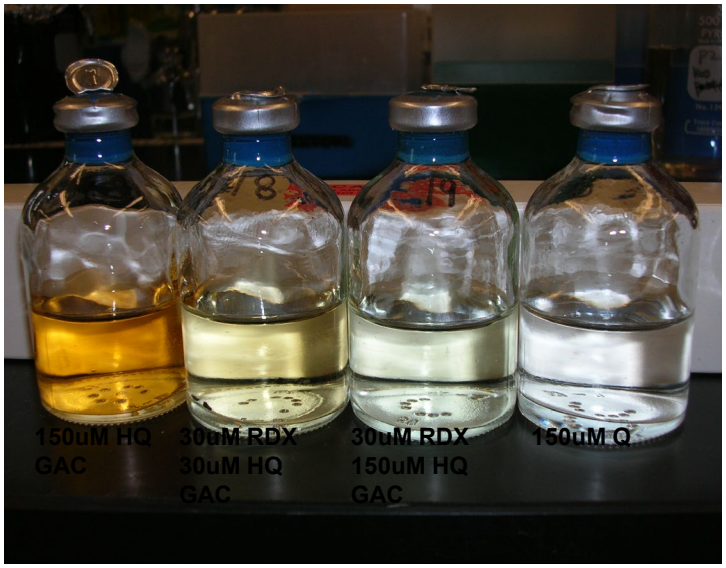
GAC sorbs explosives easily

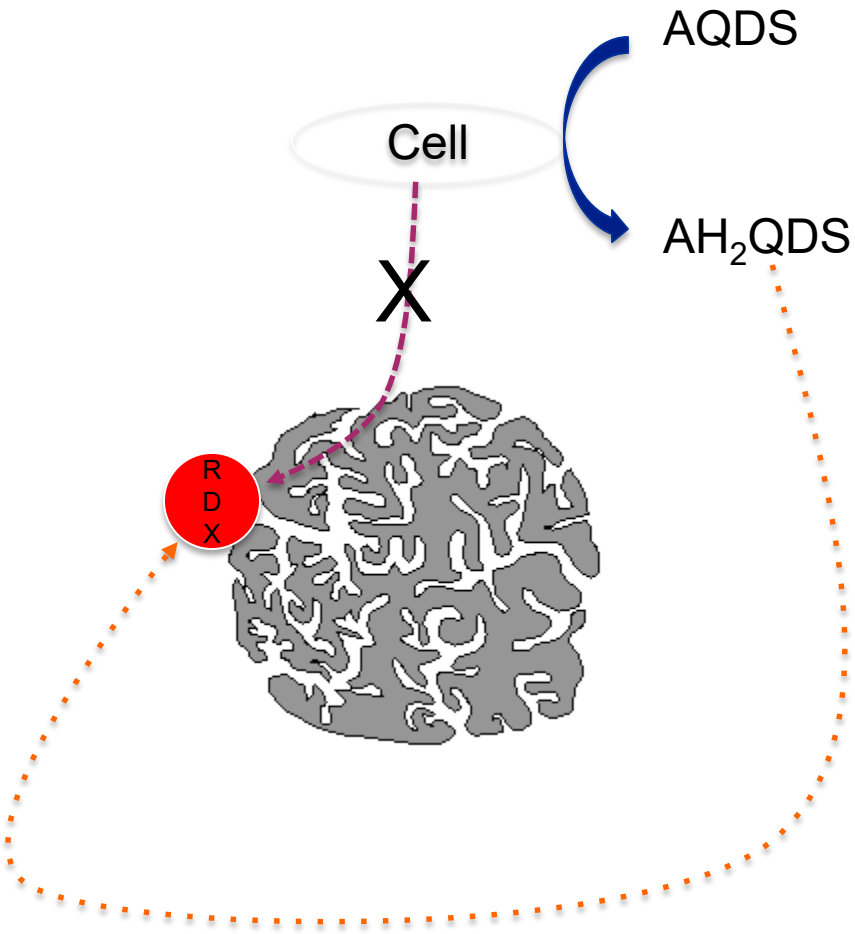


Pump and treat using granular activated carbon (GAC), the most common form of porous carbon, is the “de facto” treatment strategy utilized in RDX remediation.

Adsorption of over 12% (w/w) RDX per GAC constitutes an explosive hazard; therefore, carbon must be continually replaced.

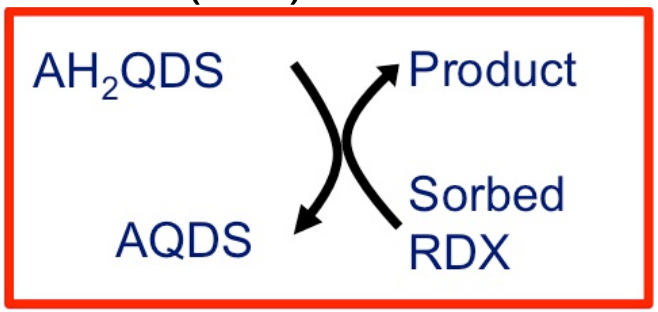
The spent carbon is typically treated as hazardous waste and landfilled. This process is very costly.



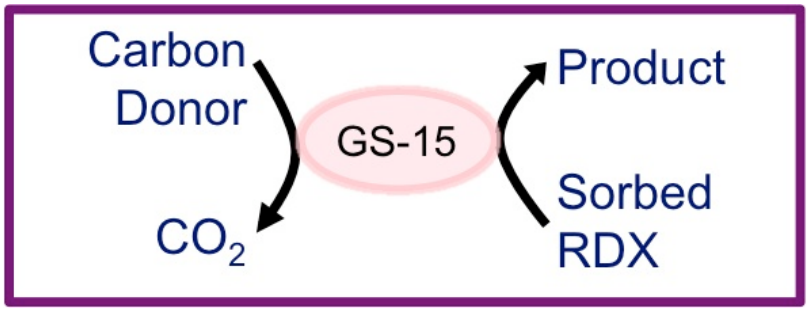


Electrons are added to sorbed RDX

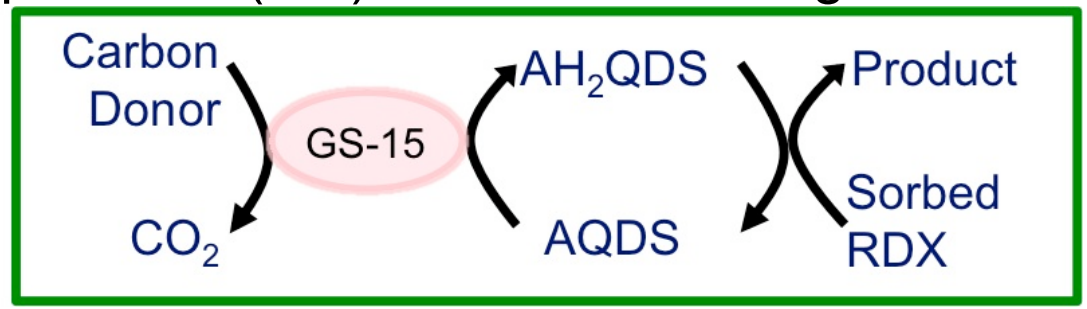
Treatment Approach 1 (T-1): Chemical Reduction System



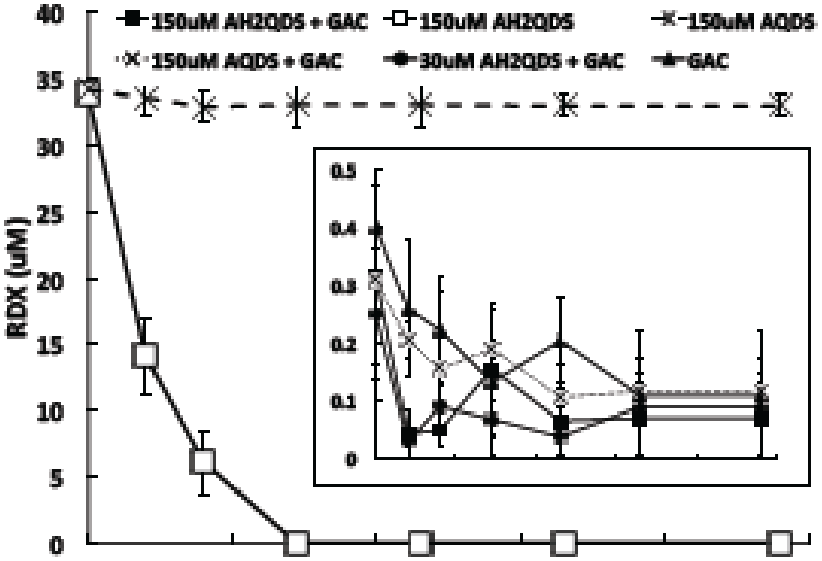
Treatment Approach 2 (T-2): Biological Reduction System



Treatment Approach 3 (T-3): Chemical-Biological Reduction System

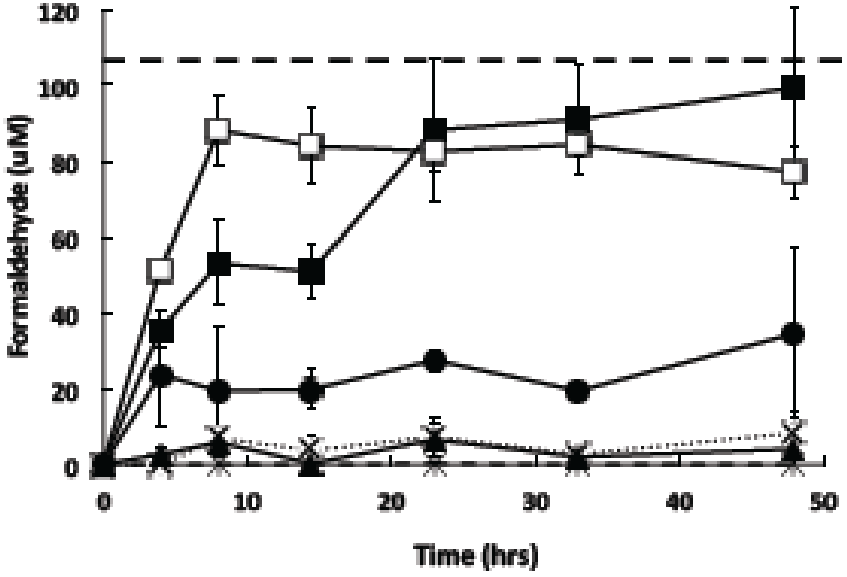


Adsorption of RDX to GAC and HCHO production from AH_2QDS amendment



A

RDX rapidly adsorbs to minimal GAC mass, and mass transfer back into the aqueous phase is negligible unless a strong organic extractant is added

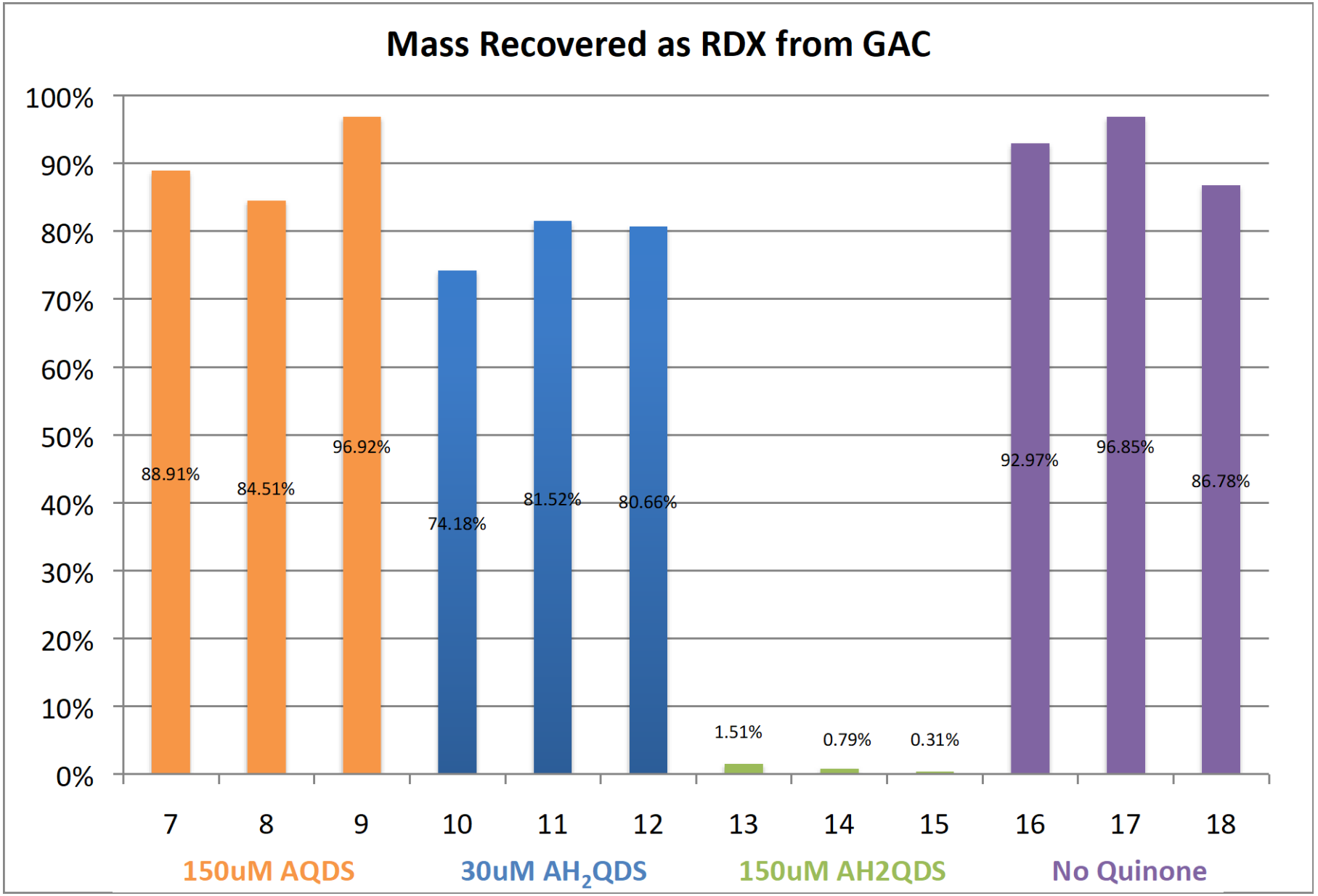


B

HCHO formation agrees with the predicted 3:1 stoichiometry when AH_2QDS is present in "excess" relative to the RDX adsorbed to GAC

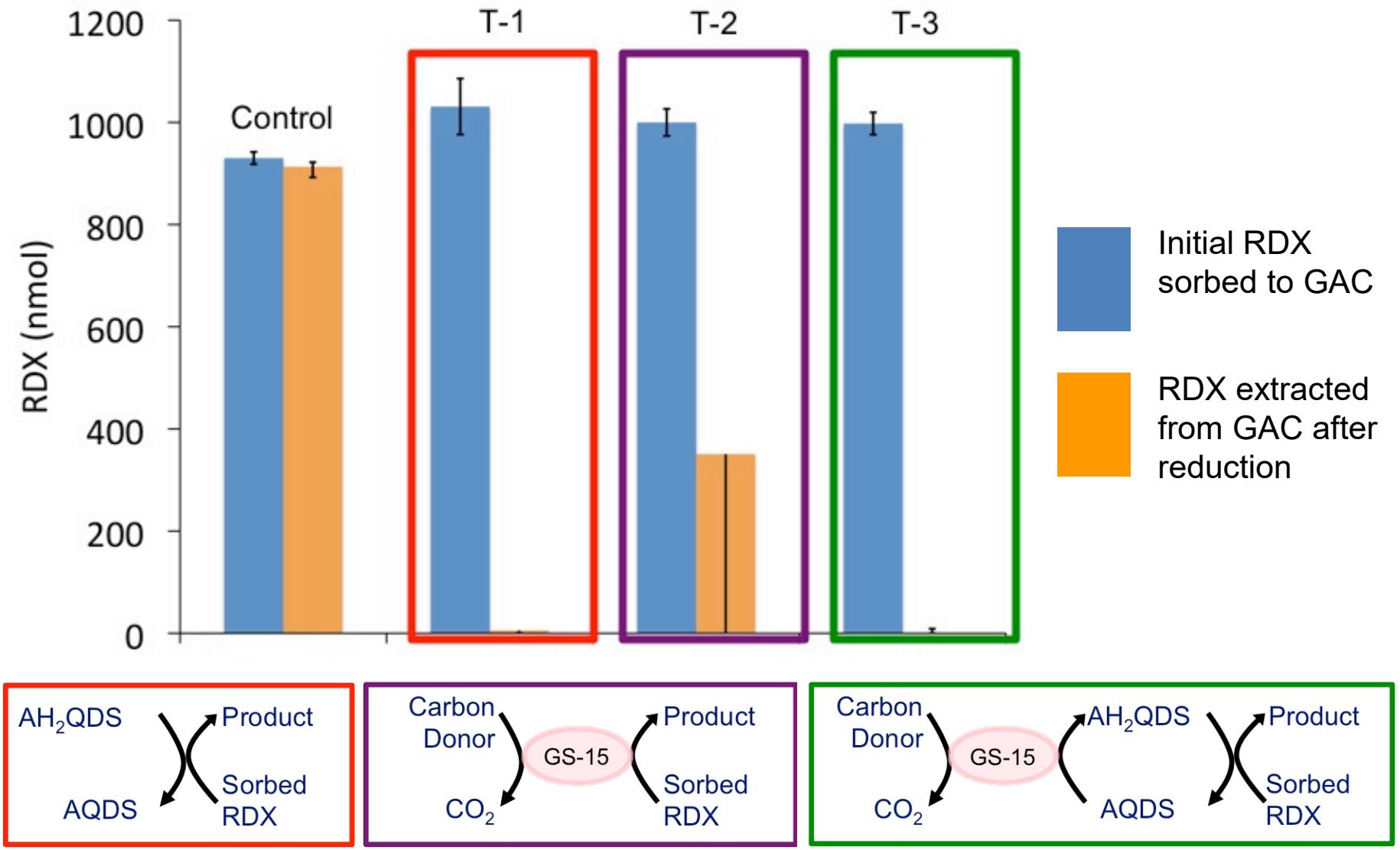
Millerick and Finneran, 2013, ES&T 47: 8743-8750

Post-treatment RDX recovered from GAC after extracting with 100% EtOH



Millerick and Finneran, 2013, ES&T 47: 8743-8750

Systems that incorporate both quinone and quinone-reducing bacteria consistently reduce RDX



GAC treated with combined reactions can be re-used over and over

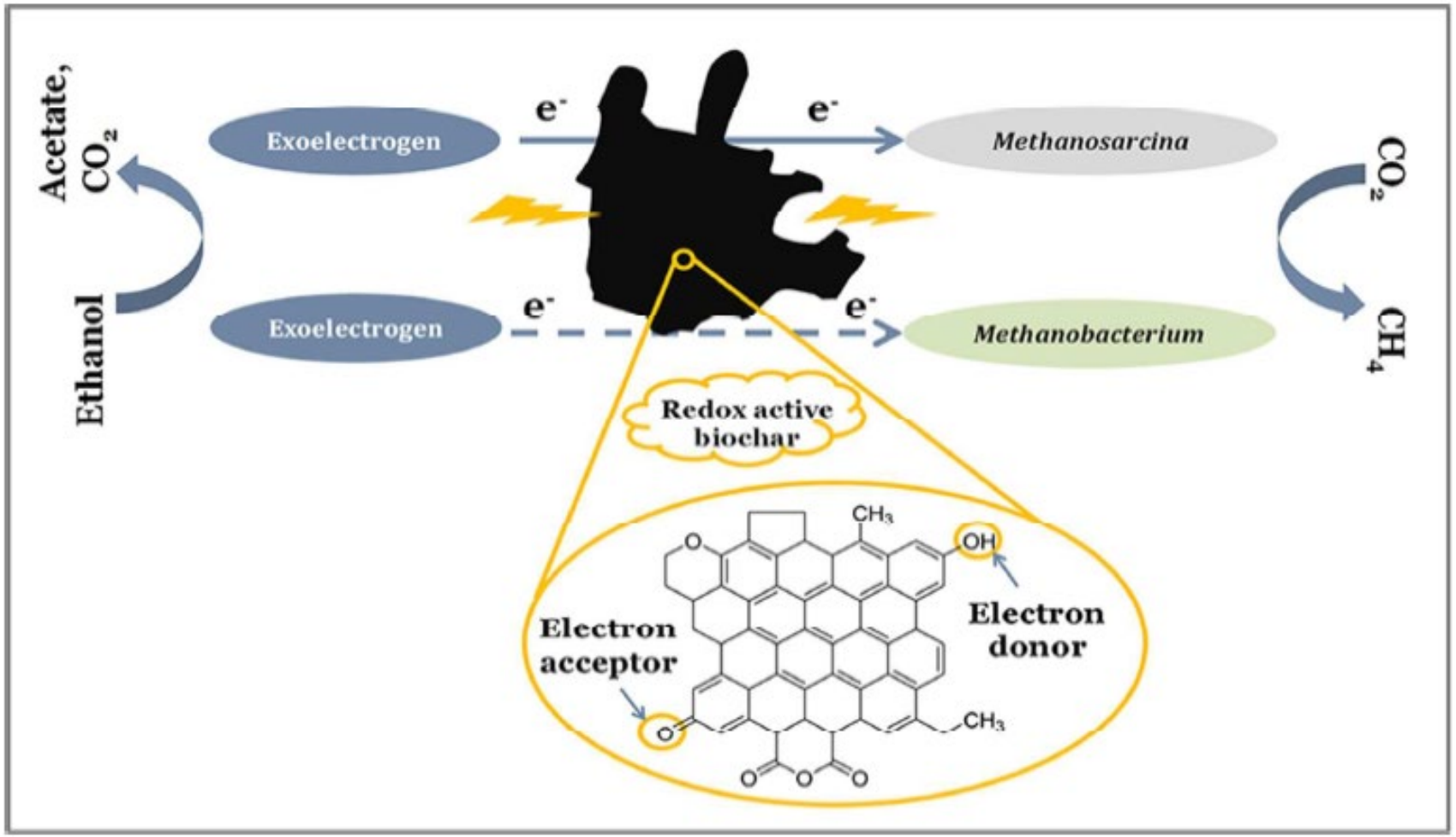
Series	Pretreatment	RDX Removal in 350 hours	Standard Deviation
1	No pretreatment (virgin carbon)	99.22%	0.12%
2	Ethanol extraction (120 hrs)	95.89%	3.98%
3	Hydroquinone (210 hrs)	95.88%	0.77%
4	Hydroquinone (90 hrs), followed by ethanol extraction (120 hrs)	97.08%	1.28%
5	RDX (350 hrs), followed by ethanol extraction (120 hrs)	98.49%	0.31%
6	RDX (350 hrs), followed by hydroquinone (90 hrs), followed by ethanol extraction (120 hrs)	97.54%	0.78%

Influence of activated carbon on TCE biodegradation

Experimental Design

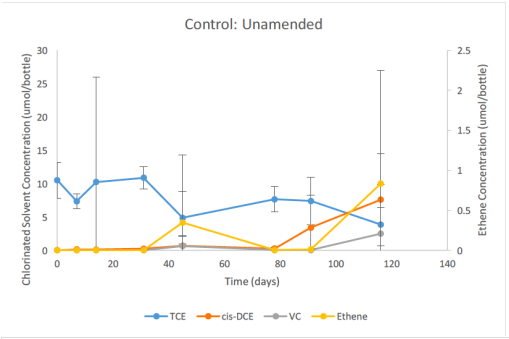
- ❖ Glass serum bottles:
  - 10g of contaminated aquifer material
  - 10mL of water
  - Activated Carbon
    - High GAC (78 mg/mL)
    - Low GAC (26 mg/mL)
    - High PAC (78 mg/mL)
    - Low PAC (26 mg/mL)
  - 20 µmol neat TCE
  - Electron Donor (1x stoichiometry)
    - Lipid (EOS)
    - Acetate + Hydrogen gas
    - Lactate
- ❖ Controls:
  - No electron donor
  - No activated carbon
  - Sterile- autoclaved

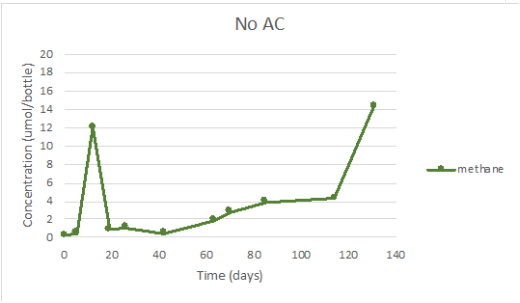
Electron transfer via carbon facilitates methanogenesis (electrons are liberated from organic carbon and flow by “Direct Interspecies Electron Transfer”



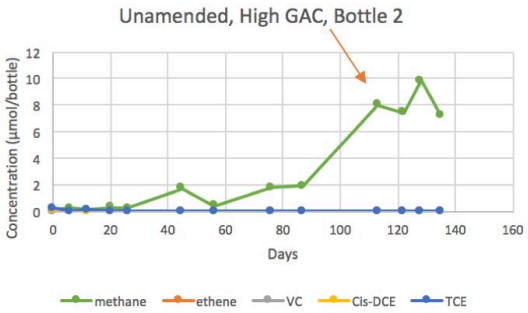
Unamended

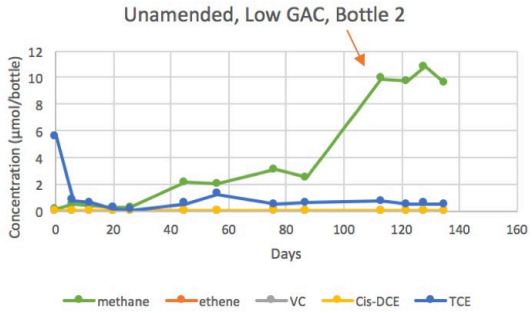
No Activated Carbon



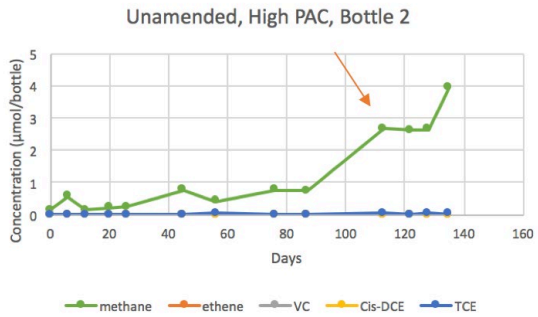


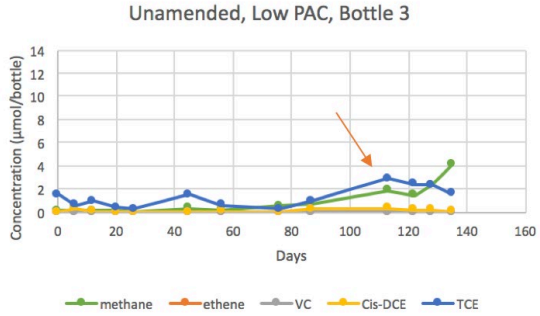
Granular Activated Carbon





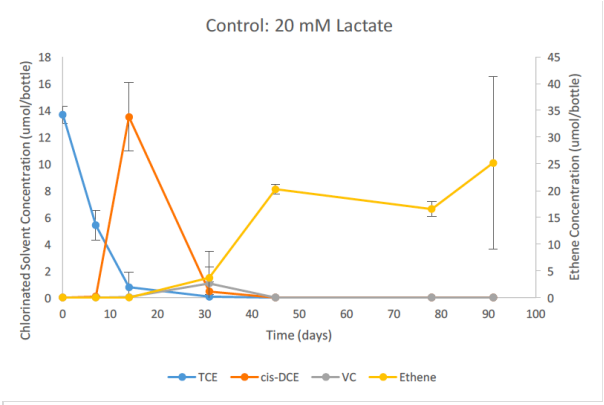
Powdered Activated Carbon

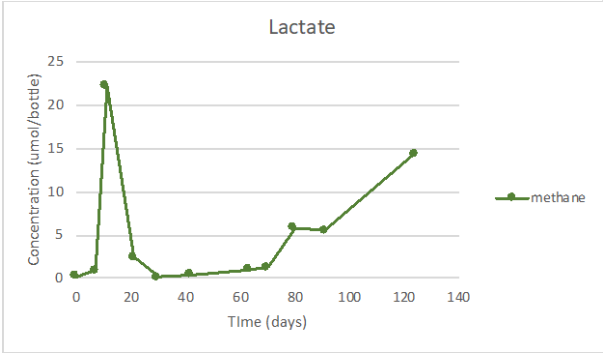




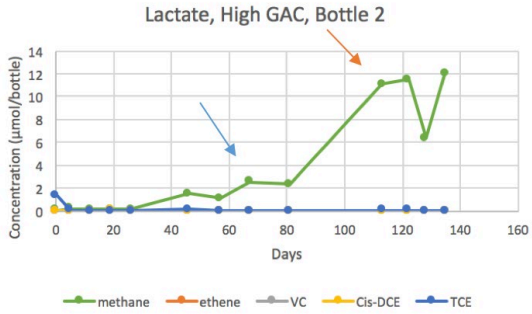
Lactate Amended

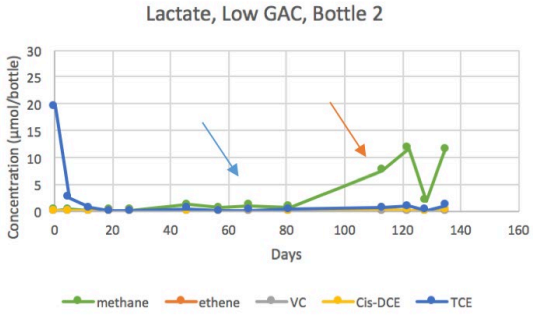
No Activated Carbon





Granular Activated Carbon





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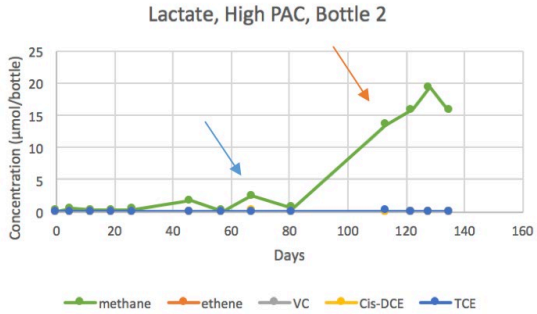
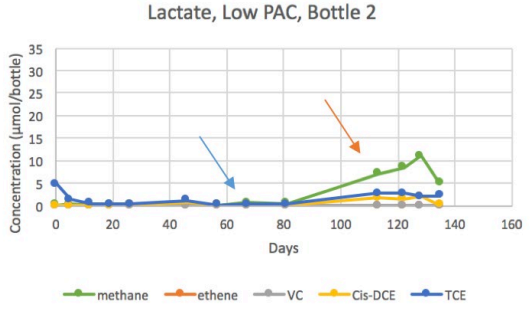
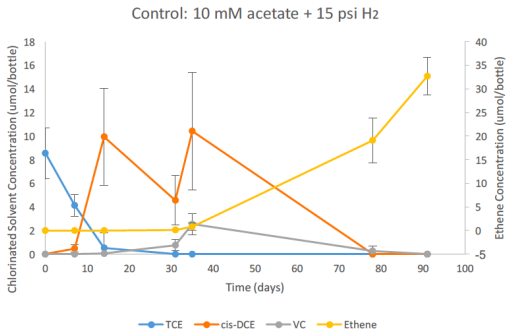
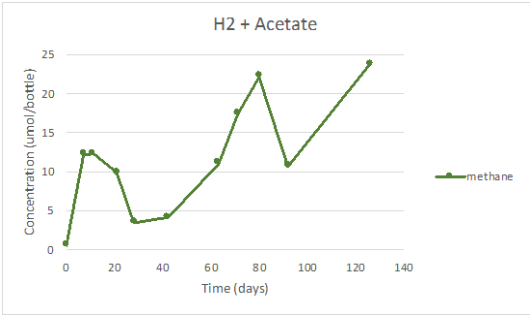




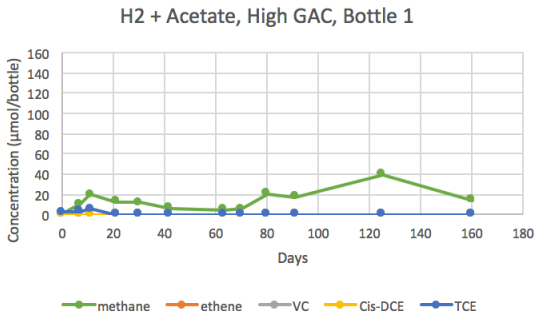
H_2 + Acetate Amended

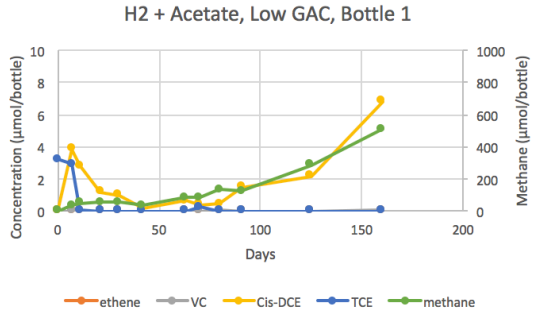
No Activated Carbon





Granular Activated Carbon





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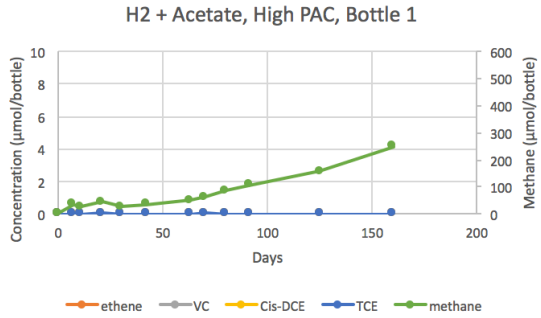
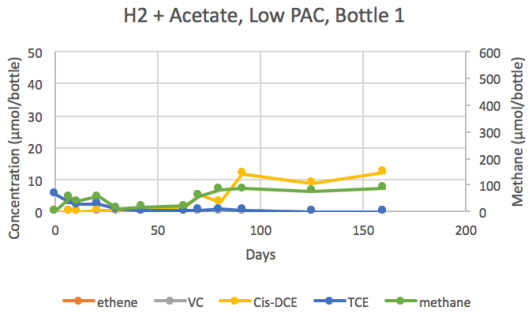
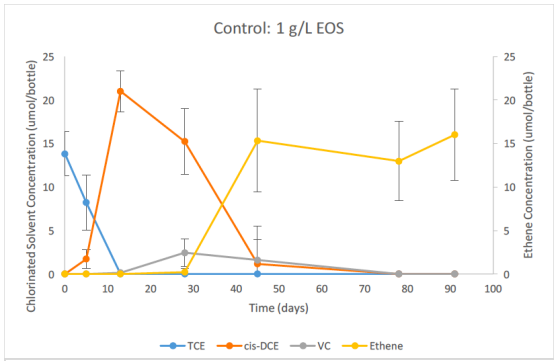
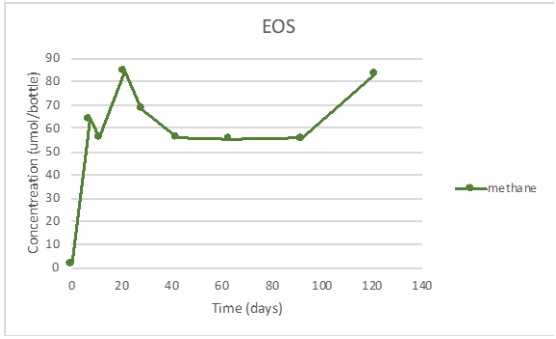




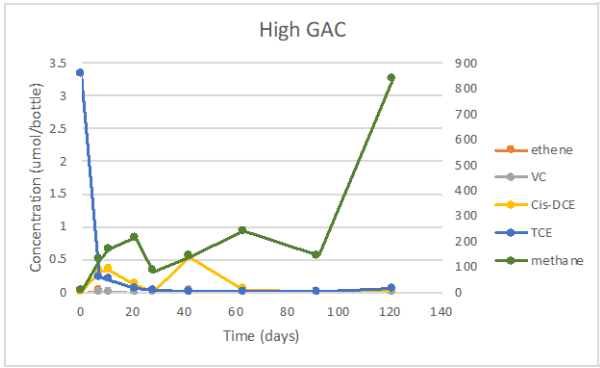
Lipid Amended

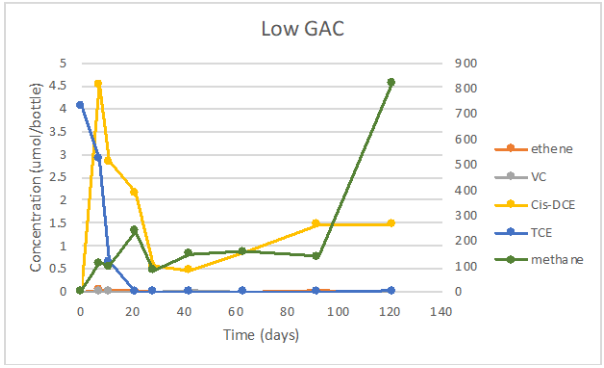
No Activated Carbon





Granular Activated Carbon





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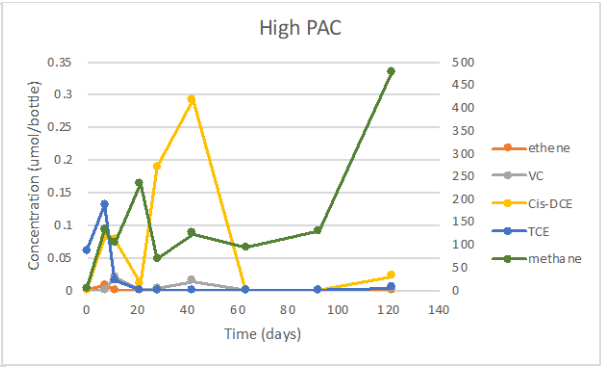
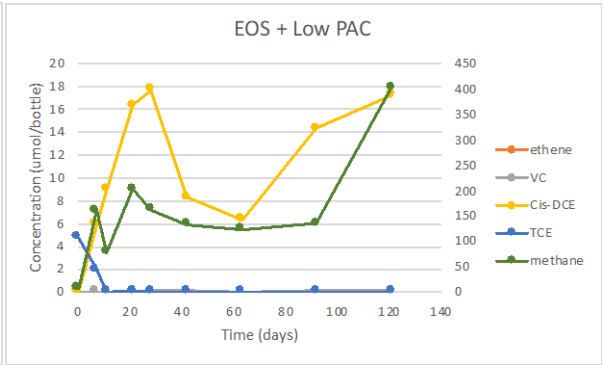
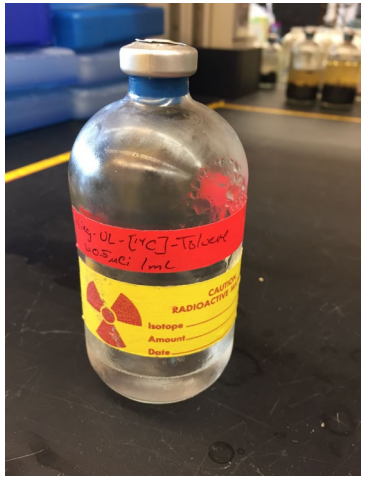




Next Steps: ^{14}C-BTEX research

- Using uniformly radiolabeled ^{14}C-benzene and ^{14}C-toluene we are testing for direct mineralization to $^{14}CO_2$ (thereby eliminating any of the uncertainty associated with partitioning, because the $^{14}CO_2$ will not sorb to the activated carbon)
- All conditions are being tested (aerobic metabolism and the standard anaerobic respiratory pathways)
- GAC/PAC versus no activated carbon controls



Special thanks to BP for funding this work

Conclusions

1. Combined biological and chemical reactions can be more effective than either biological reaction or chemical reactions alone

2. Granular activated carbon is primarily a sorption technology – the question is still “what happens to microbial activity with sorbed contaminants”

3. While activated carbon readily adsorbs explosives, it is more critical to understand electron transfer through this conductive material to the explosives of interest

4. Explosives and energetics degradation is actually accelerated by direct electron transfer, so activated carbon based technologies become destructive/attenuation technologies

5. Data thus far suggest that activated carbon limits or completely inhibits TCE reduction; it is likely that TCE or cis-DCE will desorb at points in the future not having been transformed at all; at the very least “complete dechlorination” was absent

6. Excessive methane production is an unintended consequence of activated carbon amendment that is at the least very wasteful, and at the most a dangerous explosion hazard

7. Levels of methane developed were extreme