# Stimulation of Trichloroethylene Degradation with Natural Organochloride Amendment

M. J. Krzmarzick, X. Wang, and M. Brooks



Mark Krzmarzick Assistant Professor School of Civil & Environmental Engineering Oklahoma State University



# **Environmental Problem**

Chlorinated compounds represent nearly HALF of the EPAs Priority Pollutants.



https://www.epa.gov/sites/production/files/2015-09/documents/priority-pollutant-list-epa.pdf

# **Environmental Problem**

- Soils and groundwater contaminated with chlorinated ethenes is extensive
- PCE and TCE used in dry-cleaning fluids and degreasing



- Many anaerobic bacteria can dechlorinate ethenes
- Dechlorination to ethene represents total remediation

# Organohalide-respiring Physiology

Electron Donor

Electron Acceptor



# Organohalide-respiring Physiology

Electron Donor

#### Electron Acceptor



# Remediation





### Halogenation of 'Natural' chlorinated compounds





### A Natural Organohalogen Cycle



Graphic courtesy of Max Haggblom, Rutgers University: http://dbm.rutgers.edu/labs/haggblom/research/3

#### **Chloroperoxidase reactions**



Speicher, A. Heisel, R. and J. Kolz. Phytochemistry. 62:679-682



FIGURE 2. CI K-edge NEXAFS spectra of plant needles reacted with CPO and HOCI. Spectra of phenol reacted with CI<sup>-</sup> and CPO, and pure CI-containing compounds are also shown for a comparison. (A) Ciorophenol red, (B) phenol + CPO + NaCI +  $H_2O_2$ , (C) NaOCI-(aq), (D) aqueous CI<sup>-</sup>, (E) unpulped redwood needles + 5 mM NaOCI after 2 d, (F) needle pulp + 5 mM NaOCI after 10 min, (G) needle pulp + 5 mM NaOCI after 2 d, (H) needle pulp + 50 mM NaOCI after 2 d, (I) needle pulp + CPO +  $H_2O_2$  (short-term, multiple addition sample), (J) weathered needles attached to tree.

Reina, R. G., Leri, A. C., and S.C.B. Myneni. Env. Sci. Technol. 38:783-789.

### Objectives

- Do dechlorinating bacteria important in bioremediation grow on CPO-produced organochlorides?
- Can CPO-produced organochlorides stimulate trichloroethene biodegradation?







Measure Organohaliderespiring *Chloroflexi* (qPCR)

Measure chloride (IC analysis)

# **CPO produced OM Amended Microcosms**, OM Extract Control Microcosms, and Unamended Control Microcosms



#### Days after Amendment

Members of a family made up of organochloride respirers grew and free chloride increased, indicating chloroperoxidase-produced organochlorides stimulates the growth of organochloride respirers.

Krzmarzick et al., AEM, 2012.

# Other Enriched bacteria

Experiment was repeated, but Illumina-based 16S rRNA sequencing (20,000-40,000 reads per sample; ~400 bp sequences) was used to detect enriched bacterial OTUs in CPO-reacted OM amended vs OM amended microcosms.

OTUs that were much higher (>50×) in CPO-reacted-OM amended reactors over OM-amended control reactors were characterized phylogenetically.

Groups of enriched bacteria were then quantified with qPCR across triplicate microcosms over the time scale of the experiment.









Days



Using water-based soil extraction (for CPO reaction and OM control).

TCE concentrations in Batch Reactors with CPOtreated OM, OM-control extract, and no-coamandment



Degradation occurs within 20 days when co-amended with CPO-treated organic matter. Control extract also stimulates degradation sometime ~60 days. Soil without co-amendment fails to degrade (over several months).

# **Future Objectives**

- Repeat experiment and measure dechlorination products to determine if dechlorination is complete (or, for example, stalls at vinyl chloride.)
- Toxicity assessments of CPO-reacted organic matter.

# Thank you,

Questions?

#### Xuewen Wang and Matt Brooks





