Quarterly Report July 13, 2016

MUS Research Initiative Project 51060-MUSRI2015-01:
Remediation Technology for Chlorinated Pollutants Based on Natural Product from Soil Bacteria

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This project's objectives address the programmatic goal of growing important research sectors that increase the diversity of Montana's economy and lies within the 'Materials' category. The work is aimed at deriving improved materials for chlorinated pollutant remediation and is based on an effective process for carbon tetrachloride (CT) destruction in contaminated water. Progress toward specific goals to date are given below.

Objective 1: Have verified, chemically pure PDTC sulfonate, polymer-linked PDTC, and their copper complexes: December 10, 2017

- **Progress Towards Objective:** The lithiation of brominated test compounds has been verified as an effective means of adding monothiocarboxylate substituents to pyridine starting compounds. The addition of carbonyl sulfide, and carbon disulfide are now being optimized to avoid unwanted side products and maximize yields. Citrazinic acid has proven to be a viable means of accessing water soluble derivatives of PDTC via compounds 1a and 1b (Figure 1) and the dilithiation/thiocarboxylation process.

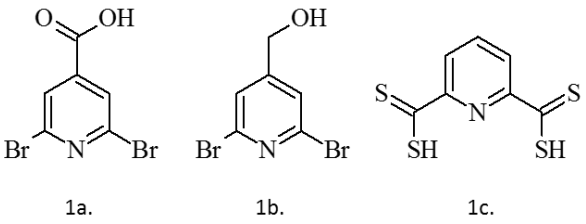

Figure 1. PDTC-derivative precursor ligands (1a,b), and the bis-dithiocarboxylic acid analog made using carbon disulfide (1c).

Objective 2: Have data regarding solubility and dechlorination rates for new derivatives of PDTC: April 1, 2017

- **Progress Towards Objective:** A gas chromatographic method for separation and quantitation of CCl_4, $CHCl_3$, and CS_2 has been developed: Column, PoraBond Q 25m x 0.25mm; He carrier 1.5 mL/min; Inlet 220°C, split 20:1; Oven 130°C 2 min, 20°C/min to 200°C 0.5 min; Detector, (MS) source 220°C, quadrupole 150°C. Using this method, CT removal by the natural compound (PDTC) has been monitored and showed first order kinetics with respect to CT (Fig 2). The pseudo first order rate constant derived from these data will be used to compare synthetic analogs with PDTC for their effectiveness.

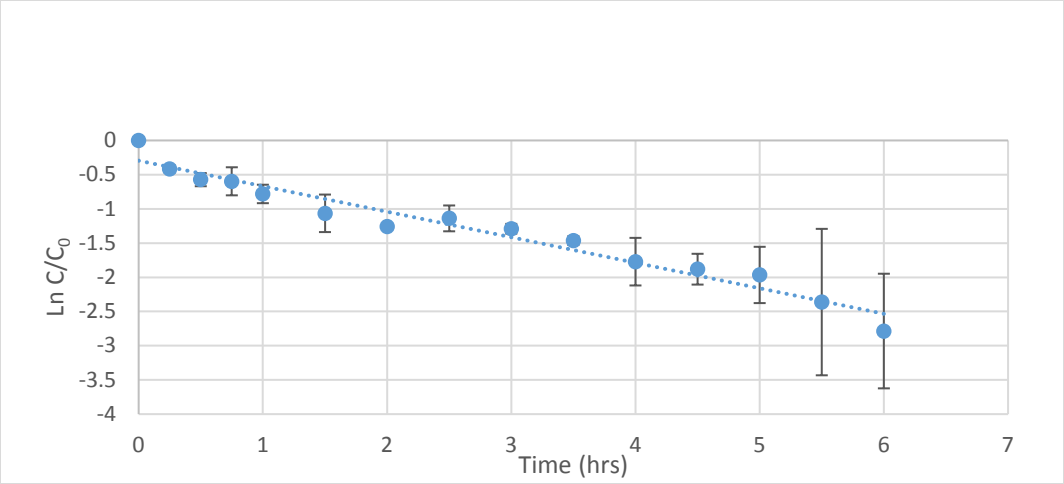

Figure 2. CT removal kinetics with excess Cu:PDTC. The data show the natural logarithm of the ratio of the measured concentration at a given time divided by the initial concentration (C_0). Error bars represent standard deviations of triplicate reactions quantitated after killing at the indicated time points with $KMnO_4$.

We are also quantifying PDTC and Cu:PDTC solubility characteristics using saturated solutions in a constant temperature and ionic strength phosphate buffer and a spectro-photometric assay involving titration with $FeCl_3$.

Objective 3: Have initial toxicology assessment of simulated remediation mixtures, refined dechlorination data to include other solvents, effects of aquifer solids: July 1, 2017

- **Progress Towards Objective:** work on this objective will await deliverables of Objective 1.

Expenditures to Date

Category	Budget Total	As of 06/30/2016
Salaries	148,405	38,677.15
Equipment	35,000	34,822.61
Supplies (MSUB)	5,000	4,118.13
Subcontracts (MSU)	71,940	10,586.48
Travel, other	1,600	1,473.46