Probing the Redox Reactivity of Mycogenic Manganese Oxides with Substituted Quinones

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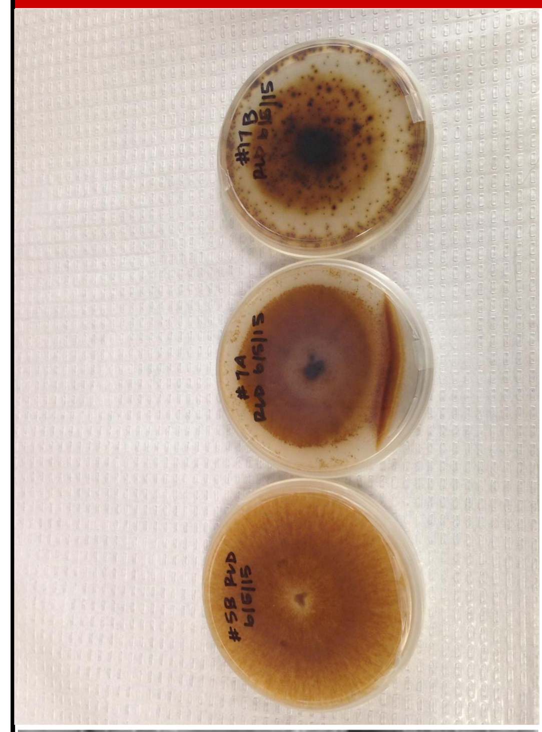
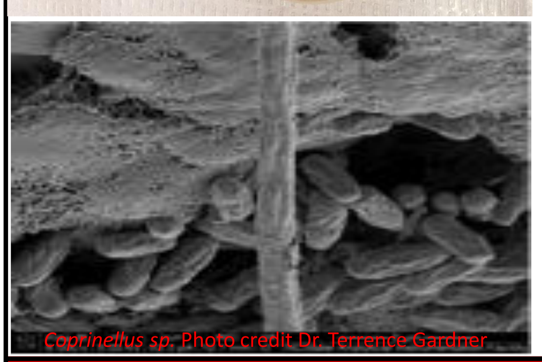
Abstract



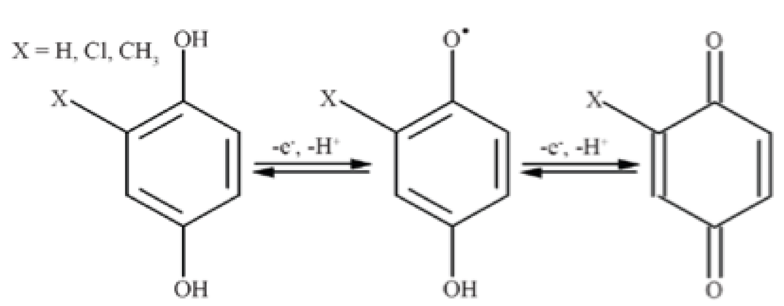


- Manganese oxides can be very useful in bioremediation techniques because they can oxidize metal and organic contaminants
- Mycogenic Mn oxides are of particular interest because fungal species can exist in harsh environments consistent with contaminated areas
- Prior work suggests that the structures of mycogenic Mn oxides are species dependent
- It is important to probe the reactivity of the oxide produced by each fungal specie to determine the redox reactivity of each structure
- Myogenic oxides will also be compared to a synthetic Mn oxide reacted with 3 substituted quinones that function as redox probes

Motivating Questions

It is known that differing Mn minerals react at different rates, but few studies have focused on the reactivity of biominerals.

- How do structure and redox properties interplay to control the redox reactivity of Mn oxide nanoparticles?
- How do reaction rates with redox probes differ between synthetic Mn oxides and those produced biogenically by fungal cultures?

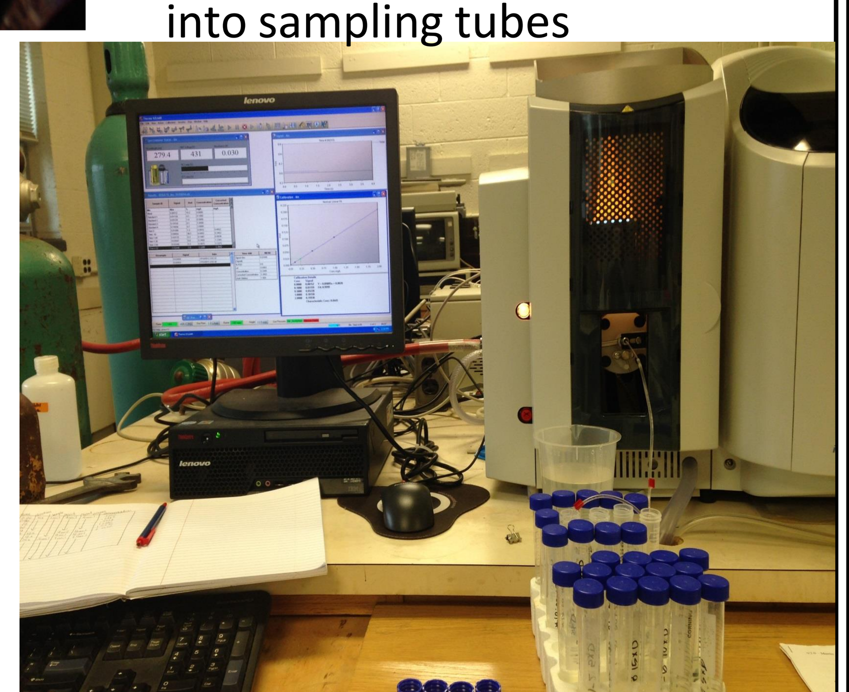


Substituted quinone redox probes

Design and Methods

- The substituted hydroquinone solutions pictured above were introduced to a 10 mM HEPES/0.1 M NaCl buffer containing synthetic Mn oxides or biogenic Mn oxide produced by the fungal species *Coprinellus sp. in* an anaerobic chamber
- Timed samples were filtered into sampling tubes

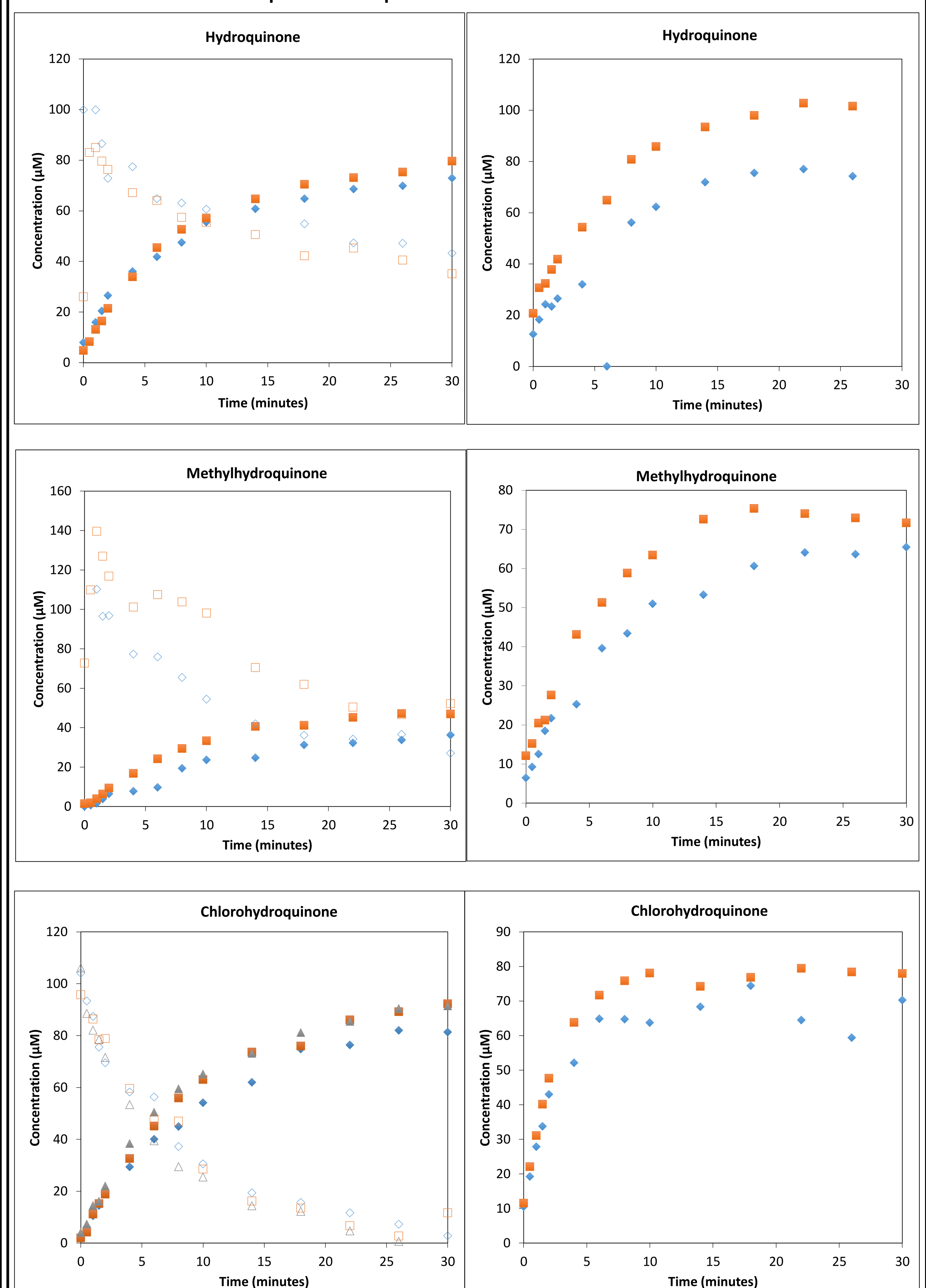
- A UV-visible spectrometer was used to measure the absorbance of the given quinone concentration at each sampling point
- The concentration of the quinone reactant in each sample were measured using Beer's Law
- Atomic absorption spectroscopy was used to measure concentrations of Mn^{2+} reduced from its oxide state



Results

Synthetic Mn Oxide **_Coprinellus sp._ Mn Oxide**

Closed and open points are Mn2+ and quinone concentration, respectively. Organic matter in mycogenic mineral experiments interfered with quinone quantification.



Manganese Dissolution Rates

	Synthetic Manganese			Biogenic Manganese	
	Test 1	Test 2	Test 3	Test 1	Test 2
Hydroquinone	0.05 ± 0.02	0.06 ± 0.02	0.07 ± 0.01	0.05 ± 0.01	0.09 ± 0.01
Methylhydroquinone	0.034 ± 0.004	0.023 ± 0.005	[redacted]	0.05 ± 0.01	0.07 ± 0.01
Chlorohydroquinone	0.06 ± 0.01	0.07 ± 0.01	0.08 ± 0.01	0.15 ± 0.03	0.18 ± 0.02

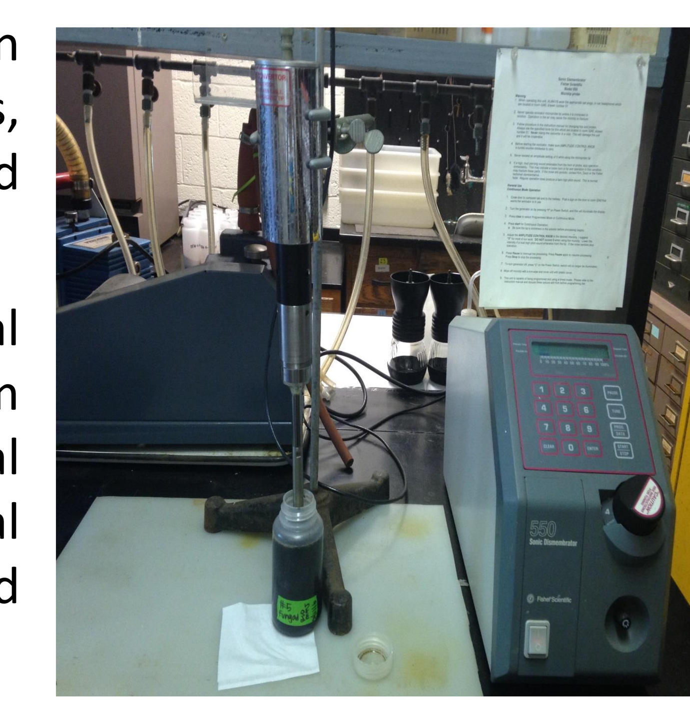
Dissolution rate (mmol min^{-1} g^{-1}) are derived from linear regression (R^2 > 95%) for initial 5-8 data Mn^{2+} points. Uncertainty is based on 95% confidence intervals.

Discussion

- Based on the properties of the quinones, it was anticipated that the reaction between the methylhydroquinone (electron withdrawing substituent) and Mn oxides would be slower than that of the hydroquinone (unsubstituted), which would be slower than chlorohydroquinone (electron donating substituent).
- In general, rates follow the predicted trend, although data is clearer for the synthetic Mn oxide.
- For each quinone, the biogenic oxide had a larger concentration of dissolved Mn^{2+} in the first sample than that the corresponding sample with synthetic oxide.
- With the exception of chlorohydroquinone, the biogenic Mn oxide released more Mn^{2+} over the 30 minute time series.
- Dissolution rates tend to be larger for biogenic oxides that for synthetic oxides under the corresponding conditions.

Conclusion and Future work

- The rapid initial dissolution of biogenic Mn oxide to Mn^{2+} suggests a higher reactivity than the for synthetic Mn oxide.
- With a higher redox reactivity, the biogenic Mn oxides could potentially be more effective in water treatment than synthetic Mn oxides.
- This increased reactivity may be beneficial because biogenic oxides may be more economical to produce in passive treatment systems.
- Future research will test the dissolution rates of biogenic Mn oxides produced by *Paraconiothyrium sp.* and *Coniothyrium sp.* fungal species.
- After measuring rates of Mn dissolution of each fungal species, these rates will then be compared to Mn oxides doped with metals.
- Rates will be compared to electrical properties derived from voltammetry and computational approaches, and structural parameters from spectroscopy and computational approaches.



Acknowledgements

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