

Project Title: The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems

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RESEARCH OBJECTIVES

Many hydroxylated aromatic compounds (HACs), particularly small molecules such as substituted phenols, are common contaminants of surface and subsurface systems. The high environmental mobility of these contaminants, due to their relatively high water solubilities, is of particular concern. Abiotic and enzymatic oxidative coupling of this class of contaminants by natural sorbents may be significant in controlling the mobility of HACs and facilitate remediation efforts. The principal objectives of this study are to investigate: 1) the role of abiotic/enzymatic coupling reactions on the sequestration of HACs by natural sorbents; 2) the effects of sorbent structure and chemical composition on such sequestration; and 3) optimal conditions for the induction of these abiotic/enzymatic coupling reactions by addition of suitable catalysts and sorbents. Information gathered from the study will be useful in quantifying the behavior of this class of organic compounds in various subsurface contamination scenarios relevant to DOE facilities, and in specifying strategies for the selection and design of remediation technologies.

RESEARCH PROGRESS AND IMPLICATIONS

During the third year of this four-year project, significant advances were achieved in the understanding of hydroxylated aromatic compounds (HACs) sequestration by natural sorbents and the induction of oxidative coupling reactions by metal oxide and enzyme additions. As scheduled, the investigation of HAC coupling in natural systems (Phase I of the project) was fully completed this year. The expansion of the experimental matrix to five natural sorbents (Table 1) further confirmed the work of prior years concerning the effect of diagenesis of the carbon fraction (i.e., chemical structure) on the sequestration of HACs by natural sorbents. In this study, sequestration is quantified in terms of the amount of contaminant remaining on the sorbents after sequential water and solvent extractions.

Table 1. Relevant characteristics of the selected natural sorbents used in this study.

Sorbent	¹ S _A , m ² /g	% organic matter	Type of organic matter	² Chemistry of organic matter	Mn, ppm	Fe, ppm
Lachine shale	15.0	12.6	kerogen	aliphatic, aromatic	23.2	840
Fox Forest	4.5	5.9	humus	O-aliphatic, phenolic, aromatic	44.8	9
Fox Grassland	8.9	2.5	humus	O-aliphatic, phenolic, aromatic	24.2	16
Wagner III	1.5	0.15	kerogen/humus	n/d	n/d	n/d
Canadian Peat	2.3	99.1	peat	O-aliphatic	13	91

1) S_A = BET surface area determined by N₂ adsorption, 2) predominant groups determined by solid state¹³C NMR spectra, n/d = not determined

The results confirm our initial hypothesis that sequestration of HACs in abiotic and non-enzymatic conditions via oxidative coupling is more likely to take place in natural sorbents that have geologically young organic matter (OM) with sufficient reactive groups and mineral catalyst concentrations. Phenolic and oxygen-substituted aliphatic (O-aliphatic) compounds have been reported to participate in oxidative coupling reactions (1). Oxidative coupling reactions are known to be catalyzed by Mn(III/IV) and to a lesser extent by Fe(III) oxides (2). Abiotic and non-enzymatic conditions were maintained by gamma irradiation of the sorbents and additions of the microbial and peroxidase inhibitor sodium azide.

Sorption was non-linear, hysteresis was high, and the sequestration of phenol, o-cresol and p-chlorophenol was significant in the near-surface Fox series soils (Forest and Grassland) (Table 2). These soils contain high concentrations of phenolic and O-aliphatic groups and potentially oxidized forms of Mn/Fe minerals (Table 1). On the contrary, almost total extractability of all three contaminants was observed on Lachine shale and Canadian peat, indicating the absence of oxidative coupling to these sorbents OM (Table 2). The shale, containing diagenetically older kerogen-type OM, may not have sufficient reactive groups for coupling (Table 1). Whereas the peat may not have sufficient oxidized minerals to catalyze the reaction due to the anoxic conditions prevalent in such high organic content soils. In the case of Wagner soil, a sandy material with low organic content composed of mostly kerogen-type OM, similar hysteresis and low sequestration, as seen with shale, were observed (Table 2).

Table 2. Selected parameters that illustrate the sorption linearity (n), sorption-desorption hysteresis (H.I.₂₅₀) and extractability (% Seq) of phenol, o-cresol, and p-chlorophenol in natural sorbents described in Table 1.

	phenol			o-cresol			p-chlorophenol		
	¹ n	² H.I. ₂₅₀	³ %Seq	¹ n	² H.I. ₂₅₀	³ %Seq	¹ n	² H.I. ₂₅₀	³ %Seq
Lachine shale	0.80	0.18	4.5 ± 1.1	0.74	0.25	4.6 ± 1.1	0.54	0.31	2.1 ± 0.3
Canadian Peat	n/d	n/d	n/d	0.91	0.05	4.6 ± 1.6	0.85	0.001	1.0 ± 0.07
Fox Forest	0.76	0.67	74 ± 10	0.87	0.49	19 ± 3	0.61	0.24	61 ± 18
Fox Grassland	0.78	0.51	48 ± 6	n/d	n/d	n/d	0.65	0.49	n/d
Wagner III soil	n/d	n/d	n/d	0.82	0.22	4.7 ± 0.2	0.74	0.29	1.3 ± 0.2

1) n = Freundlich n ($q_e = K_F C_e^n$), 2) H.I.₂₅₀ = hysteresis index at $C_e = 250 \mu\text{M}$. $H.I. = (q_{e,des} - q_{e,ads}) / q_{e,ads}$, 3) % Seq is the percentage of the sorbed fraction (q_e) that remains in the solid after water/solvent extraction averaged for all organic concentrations tested $10 \mu\text{M} \leq C_o \leq 1000 \mu\text{M}$.

Experiments in soil-free systems with MnO₂ minerals (synthetic birnessite) and horseradish peroxidase (Phase II) have brought important insights about oxidative coupling of HACs. Soil-free experiments with these catalysts confirmed the occurrence of oxidative coupling as shown by the formation of more hydrophobic products detected by HPLC and large polymers that precipitate out of solution after centrifugation. Results obtained to date revealed that the rate of polymer formation and the composition of the polymers could be controlled by varying the catalyst/HAC ratio and contact time. For example, at low birnessite concentrations (0.1 mg/mL), only 22% of the HACs precipitate out of solution compared to 68% for higher MnO₂ concentrations (2 mg/mL) after a contact time of 15 days at equal HAC concentrations. When using horseradish peroxidase (HRP) as the catalyst, polymeric precipitates were observed at phenol concentrations of 1000 and 500 μM but not at concentration of 100 μM or lower. Results obtained to date in engineered systems (Phase III), described in the following paragraphs, suggest that the rate of HAC polymerization may affect HAC sequestration by natural sorbents.

As part of Phase III of this study, synthetic birnessite and HRP were independently added to selected natural sorbents to evaluate the sorption-desorption and extractability of the reaction products under batch equilibrium conditions. Based on differences in the sorption/desorption behavior on Lachine shale compared to the four other sorbents, it appears that enzyme or mineral additions may enhance coupling to sorbents with peat and humus-type OM but not to those containing kerogen-type OM. Our results show that addition of both catalysts greatly increased the removal of contaminants from solution for all sorbents tested. However, in the case of Lachine shale, contrary to the peat and humus-type OM sorbents, inspection of the sorption/desorption curves indicate that most of the removal was due to precipitation of polymeric material. Freundlich n parameters much greater than 1, and increased hysteresis with increasing organic concentration are suggestive of precipitation. Since batch equilibration followed by centrifugation cannot discriminate between polymeric precipitates and soil-bound fractions, more conclusive results are expected from our flow-through systems.

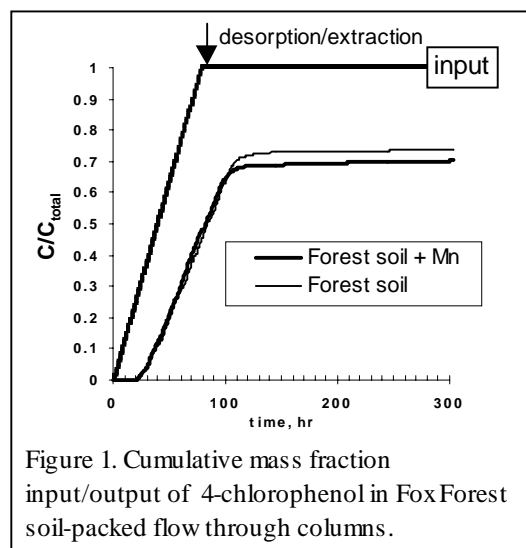


Figure 1. Cumulative mass fraction input/output of 4-chlorophenol in Fox Forest soil-packed flow through columns.

All the experimental procedures to test HAC sequestration by natural sorbents in flow-through systems were developed during this past year. A packed-bed multiple column system was selected over our original multi-port single column design. Each of the two multiple column systems consists of 1) a multiple syringe pump with capacity for four 25-mL gas-tight glass syringes, 2) four air-tight short glass columns (8 mL bed volume), and 3) a four-column capacity automatic fraction collector. These systems have the ability to test up to eight conditions simultaneously, and the short bed gives the advantage of fast experimental times. Different control situations have been tested (e.g., glass bead packed columns and bromide tracer studies) resulting in negligible losses and low dispersivities in the systems. Initial results showed that 30% of the p-chlorophenol added to the MnO₂-amended system and 25% of the p-chlorophenol added to the soil-only system could not be solvent extracted from Fox Forest soil-packed columns (Figure 1). Since settling of large polymeric materials is not expected in flow-

through conditions, the non-extractable fraction is believed to correspond to contaminant incorporated onto the OM by coupling. Parallel investigations in glass bead-packed columns amended or not with MnO₂ showed that large phenolic polymers (i.e., polymers that precipitate after centrifugation) were not formed under the experimental conditions tested. This result independently confirms that coupling to sorbents' OM is the dominant mechanism of removal and suggests that the rate and composition of polymer formation warrants further investigation.

PLANNED ACTIVITIES

Experiments are planned to cover two interrelated areas of research: i) sorbent-free model experiments to determine the rate and composition of reactive products at different catalyst and organic concentrations, and ii) sorbent-packed flow-through columns amended with tested catalyst/organic ratios and organic residence time to determine HAC sequestration. Results obtained are expected to be decisive with respect to evaluating HAC coupling as potential component of reactive barrier remediation strategies.

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