



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

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Alexander M. Orlov, Alok Bhandari, Walter J. Weber, Jr.
Environmental and Water Resources
Engineering, Civil and Environmental Engineering
University of Michigan, Ann Arbor, Michigan

Introduction

Hydroxylated aromatic compounds (HAC) and their precursors are common contaminants of surface and subsurface systems at DOE facilities. The environmental fate and transport of HAC, particularly in subsurface systems, is generally dominated by their sorption and desorption by soils and sediments. Certain secondary chemical reactions, most specifically abiotic (i.e. catalyzed by metal oxides) and/or enzymatic oxidative coupling, may be significant in controlling the sorption and subsequent desorption of such hydroxylated aromatics.

A simplified reaction mechanism of oxidative coupling (Figure 1) includes:

1) surface complex formation; 2) electron transfer and release of a phenoxy radical; and 3) coupling and further oxidation [1]. Mineral oxides play an important role in the first and second steps of the reaction [2]. Coupling of HAC to soils has been attributed to the reactivity of the intermediate radical with dissolved organic constituents of soils [3]. Molecular oxygen has been reported to enhance the reaction rate [4].

Figure 1. Illustration of oxidative coupling of phenol mediated by enzymes (E) or metal oxides (HO-Me) in soils.



Significance and Relevance

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 in the selection and design of remediation technologies.

Research Objectives

The objectives of this study are to investigate:

- The role of abiotic/enzymatic coupling reactions on the immobilization of HAC.
- The effects of environmental factors on such immobilization.
- Preliminary engineering approaches to induce abiotic/enzymatic coupling of HAC in situ.

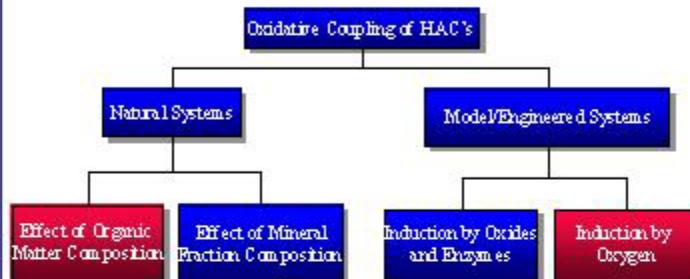
Main Hypotheses

- Oxidative coupling can be induced in contaminated subsurface systems by addition of oxygen, enzymes or/and metal oxides to immobilize hydroxylated aromatic compounds on soil organic and inorganic matrices.
- Soils comprised by younger organic materials and having a significant fraction of phenolic functional groups exhibit the greatest potential for oxidative coupling and immobilization of hydroxylated aromatic compounds.

Project Outline

This study is composed of two main areas of investigation: natural systems and model/engineered systems (Figure 2). The natural systems studies include the abiotic oxidative coupling of HAC as a function of soil composition in three natural materials. The model/engineered systems include evaluation of induced immobilization by addition of oxygen, metal oxides, and enzymes in batch and continuous-flow reactors.

Figure 2. Schematic diagram of the project research focus. The completed sections are represented in red, while blue boxes represent on-going studies.



Experimental Approach

The chemical and physical properties of the soils selected are shown in Table 1. Two of the three sorbents studied to date are near-surface soil, characterized by geologically younger organic material (Fox Forest and Fox Grassland soils). The third sorbent is an older and diagenetically altered soil (Lachine Shale).

Table 1. Physical and chemical properties of the natural geo-sorbents

Type of Soil	Fox Grassland <i>loam</i>	Fox Forest <i>sandy loam</i>	Warksworth <i>sandy loam</i>	Lachine Shale <i>silt loam</i>
% sand	47.1	53.1	65.1	13.1
% silt	31.4	33.4	23.4	73.4
% clay	21.4	13.4	11.4	13.4
Total Iron (ppm)	16	9	147	840
Total Manganese (ppm)	242	448	19.0	23.2
% organic matter	2.5	5.9	0.6	12.6

Immobilized HAC in soils is defined as the sorbate remaining after multiple water and solvent extractions, and is quantified by combustion and CO₂ entrainment of the residual. Abiotic conditions are maintained by suppressing microbiological/enzymatic activity with gamma irradiation and sodium azide additions. ¹⁴C radio-labeled forms of the target compounds are used for analysis.

Three different experimental approaches have been used to demonstrate the occurrence of abiotic oxidative coupling in immobilization of HAC: 1) comparison of equilibrium adsorption isotherms, 2) evaluation of sorption/desorption hysteresis, and 3) determination of extractable and non-extractable fractions of the sorbate.

Effect of Oxygen on Sorption Characteristics of Soils Containing Geologically Young Organic Carbon

The presence of oxygen significantly enhances oxidative coupling of HAC on soils containing geologically young organic carbon:

- Up to 75 % of sorbed phenol is immobilized by Fox Forest Soil (non-extractable fraction) (Figure 4).
- A significant decrease in immobilization capacity was observed under anoxic conditions (Figure 5).

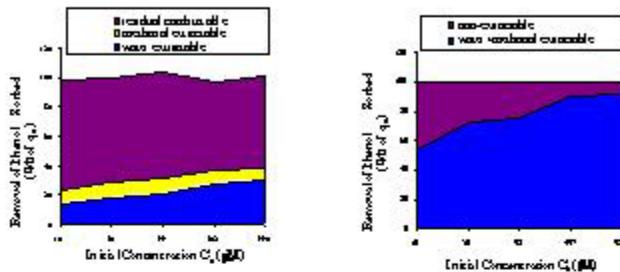


Figure 4. Distribution of phenol sorbed by Fox Forest soil under oxic conditions

Figure 5. Distribution of phenol sorbed by Fox Forest soil under anoxic conditions

- Significant phenol immobilization observed for Fox Grassland and Fox Forest soils translated into detectable differences between their oxic and anoxic isotherms and into increased sorption/desorption hysteresis under oxic conditions (Figure 6).

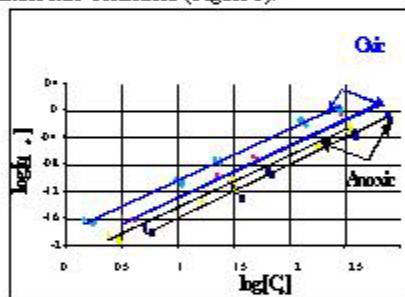


Figure 6. Sorption/desorption isotherms of phenol sorption on Fox Forest soil under oxic/anoxic conditions

Effect of Organic Matter Composition on Oxidative Coupling

- Diagenetically altered materials such as Lachine Shale, although having higher sorption capacity and higher total iron content, do not appear to promote phenol immobilization (Figure 7).

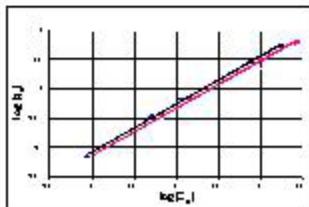
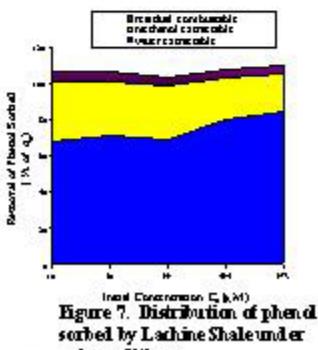


Figure 8. Sorption/desorption isotherms for sorption of phenol on Lachine Shale under oxic conditions



- Low immobilization capacity of Lachine Shale translates into insignificant difference in sorption/desorption isotherms (Figure 8). Contrary to phenol-Fox Forest isotherms (Figure 6), no detectable differences between oxic and anoxic isotherms was observed.

Phenol Extractability and Sorption/Desorption Hysteresis Indices

Hysteresis indices appear to be correlated with the extent of HAC immobilization on natural sediments (Figure 9). Hysteresis Index (*H.I.*) is defined as

$$H.I. = \frac{q_{e(des)} - q_{e(ads)}}{q_{e(ads)}} \Bigg|_{C_e, T}$$

where q_e is the solid phase concentration of sorbed solute at constant C_e and temperature, T . C_e is the apparent equilibrium solution-phase residual concentration. The subscripts (*ads*) and (*des*) refer to the adsorption and desorption phases respectively [5].

At low values of *H.I.*, it appears that the dominant sources of hysteresis are hydrophobic interactions and hydrogen bonding (as shown by the solvent extractable fraction) (Figure 9). Whereas for high values of *H.I.*, these phenomena appear to be less dominant and immobilization by oxidative coupling yields significant hysteresis.

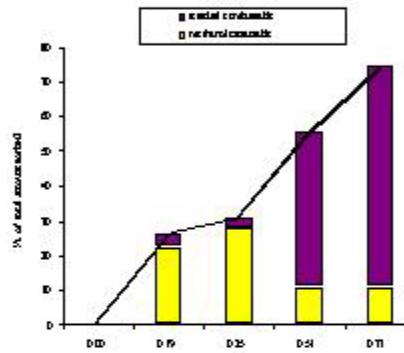


Figure 9. Relationship between the extractability and aqueous phase sorption/desorption hysteresis for phenol on Lachine Shale, Fox Forest and Fox Grassland soils (*H.I.* = 0.19, 0.73, and 0.51, respectively) and for *c*- cresol on Lachine Shale (*H.I.* = 0.25).

Conclusions

- Oxygen has a significant effect on enhancing the HAC immobilization capacity of geologically young organic materials (Fox soils).
- Diagenetically altered soils do not appear to promote HAC immobilization (e.g. Lachine Shale). The effect of oxygen on sorption was found to be negligible.
- Hysteresis index can be used as a rough indicator of HAC immobilization by oxidative coupling.

Literature Cited

- Ulrich, H. J., and A. T. Stone. *Environ. Sci. Technol.* 1989, 23, 421-428.
- McBride, M. B. *Soil Sci. Soc. AM J.* 1987, 51, 1466-1472.
- Bhandari, A., J. T. Novak, W. D. Burgos, and D. F. Berry. *J. of Environ. Eng.* 1997, 123, 506-513.
- Thomson, T. D. and W. F. Moll. *Clays and clay minerals*. 1973, 21, 145-150.
- Huang, W., H. Yu, and W. J. Weber, Jr. *J. Contaminant Hydrology*, 1998, 31, 129-148.

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