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Mechanisms of the In Situ Ozonation of Recalcitrant Organics

George Skladany (george.skladany@erm.com) and Richard A. Brown, Ph.D.,
(ERM, Ewing NJ, USA)

ABSTRACT: Many remedial technologies are not effective in treating high-molecular weight, recalcitrant organics. The commonly accepted reasons for this failure are: 1) the reaction mechanisms are in general aqueous-based, and, 2) high molecular weight compounds are generally not soluble. For example, the solubility and the rate of biodegradation of polyaromatic hydrocarbons (PAHs) decreases with increasing ring number. For each ring added, the solubility decreases approximately an order of magnitude. This results in a significant reduction in the rate of biodegradation. Solubility limitations are also a concern with chemical oxidation. Much of the current research on *in situ* chemical oxidation of non-aqueous phase liquids (NAPL) or adsorbed phase contaminants with water-based oxidants (such as potassium permanganate) has focused on the dissolution of the contaminant as the rate limiting step.

In situ ozonation, which generally involves the injection of an ozone-containing gas stream, does not appear to have the same solubility-derived limitations of reactivity as do other reactive remedial technologies. Not only does ozone dissolve in and react in the aqueous phase but it also reacts in the gas phase. This creates gas-solid or gas-NAPL interactions, which are independent of solubility.

INTRODUCTION

It has long been recognized that a limitation to the effectiveness of many *in situ* technologies is the sorption of recalcitrant organics to the soil matrix (Sposito, 1994). In general, it is believed that the contaminant must first desorb/dissolve into the aqueous phase before it can react. Desorption is, thus, often the rate limiting step in the remediation of contaminated soils. If the contaminant is strongly sorbed it will be slow to react.

Methods of enhancing the desorption of hydrophobic organic compounds as a means of enhancing degradation have often been a focus of research on the biodegradation of these contaminants (Radosevich, 1997). This research recognizes that biodegradation is limited by the desorption of the contaminant from the soil matrix (Pavlostathis, 2003). The central importance of desorption in biodegradation is acknowledged by the term, "bioavailability," which generally denotes the portion of the sorbed contaminant that enters the aqueous phase. (Luthy, 1996; Reid, 2000).

The role of desorption is also recognized in the application of In Situ Chemical Oxidation (ISCO): "…there is evidence that reaction times may depend on the desorption of adsorbed organics from the soil particles into the aqueous phase." (h2o2.com, 2006). Watts (1999) has shown that some of the reactivity of modified Fenton's reactions with sorbed, hydrophobic contaminants is due to enhanced desorption.

While there has been an increasing utilization of ISCO for treating recalcitrant contaminants such as chlorinated solvents, *in situ* ozonation, in particular, has been demonstrated to be highly effective in treating high molecular weight recalcitrant contaminants such as PAHs (Dablow 2002) and PCBs (Brown 2001). *In situ* ozonation, which involves the injection of an ozone-containing gas stream, does not appear to have the same solubility-derived limitations of reactivity as do the aqueous ISCO reagents such as permanganate, persulfate or peroxide. Not only does ozone dissolve in and react in the aqueous phase but it also appears to react in the gas phase. This creates gas-solid or gas-NAPL interactions, which are independent of solubility. Laboratory studies of the ozonation of soils containing PAHs and polychlorinated biphenyls (PCBs), discussed below, document the gas phase reactions of ozone. When the response for the individual PAHs or PCB congeners is tracked, there is no apparent preferential reactivity for the lower molecular weight compounds. The degree of destruction that is observed for an individual PAH or PCB congener is proportional to the initial level of the compound and not its size or solubility. This suggests that the reaction is a gas phase reaction. By contrast, the biodegradation of PAHs and the chemical oxidation of PAHs and PCBs using aqueous reactants show a strong correlation to solubility.

TREATMENT PROCESSES

Biodegradation of PAHs. Biodegradation is an aqueous phase reaction. Both the solubility and the rate of biodegradation of polyaromatic hydrocarbons (PAHs) decrease with increasing ring number. As shown in Table 1, for each ring added, PAH solubility decreases approximately an order of magnitude. As shown in Figure 1, this results in a significant reduction in the rate of biodegradation with an increasing number of rings. The data presented in Figure 1 are from a slurry-phase microcosm study. Soil and water from an MGP site were mixed in a sealed flask with an oxygen headspace. The oxygen in the headspace was replenished daily. After three and five weeks, an aliquot of the slurry was removed and fractionated. Both the solid and aqueous phases were analyzed for PAHs.

Table 1: Properties of PAHs as a Function of Ring Size

Compound	Number of Rings	Solubility (mg/L)	Adsorption (log k_{ow})	Volatility ($\mathrm{mm_{Hg}}$ [20°C])
Naphthalene	2	31.7	3.01/3.45	4.92×10^{-2}
Anthracene	3	0.045	4.45	1.95×10^{-4}
Benzo(a)anthracene	4	0.0057	5.6	2.2×10^{-6}
Benzo(a)pyrene	5	0.0012	8.06	5.6×10^{-9}
Benzo(g,h,i)perylene	6	0.0007	6.51	1.03×10^{-10}

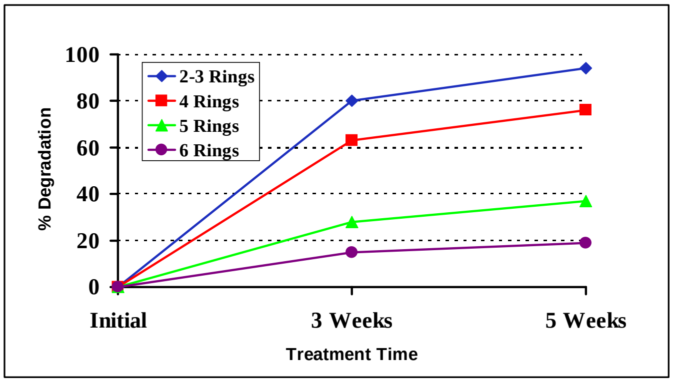


Figure 1: Biodegradation of PAHS

Biodegradation is an aqueous phase reaction. Therefore, as shown in Figure 1, the lower the solubility of a PAH, the more slowly it will biodegrade. The biodegradation rate is correlated to the solubility of the PAH, which, in turn, is correlated to the number of aromatic rings present. The more rings, the lower is the compound's solubility which correlates with a slower rate of biodegradation.

Oxidation of PAHs. A similar correlation between reactivity and solubility was observed for the permanganate oxidation of PAHs. Figure 2 shows the results from a slurry-phase oxidation study with aqueous potassium permanganate. The soil was obtained from an MGP site and was treated with 10,000 mg/L of $KMnO_4$. Treatment time was 7 days. The average removal rate, mg/Kg/Day, is plotted against the number of rings in the PAH. As can be seen from Figure 2, the rate of oxidation averaged for each type (number of rings of PAH) decreases with an increase in the number of rings present. Thus, as with biodegradation, the oxidation of PAHs with permanganate is affected by solubility. This suggests that the reaction of permanganate occurs primarily in the aqueous phase.

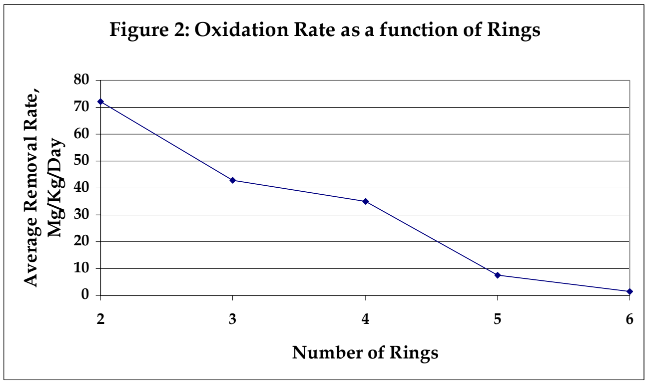


Figure 2: Oxidation Rate as a function of Rings

Figures 3 and 4 plot the average removal rate (mg/Kg/Day) versus the initial concentration (Figure 3) and the number of rings (Figure 4). If the reaction of permanganate occurs directly with the adsorbed PAH and solubility is <u>**not**</u> a controlling factor, one would expect that there would be a strong correlation between the average removal rate and the initial concentration. The expectation would be that the higher the concentration of a PAH, the more likely the permanganate would be to contact and oxidize that PAH versus a PAH at a lower concentration. What can be seen from Figures 3 and 4 is that there is a poor correlation of removal rate to initial concentration but a good correlation of removal rate to number of rings, and therefore solubility. The conclusions that can be drawn from this data are that the oxidation of PAHs by permanganate is an aqueous phase reaction, and that the reaction is controlled by the solubility of the PAH, which is, in turn, a function of the number of rings.

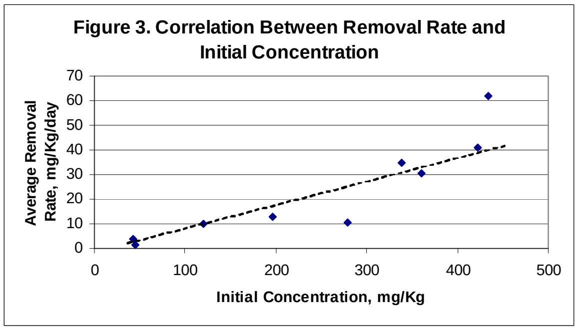


Figure 3. Correlation Between Removal Rate and Initial Concentration

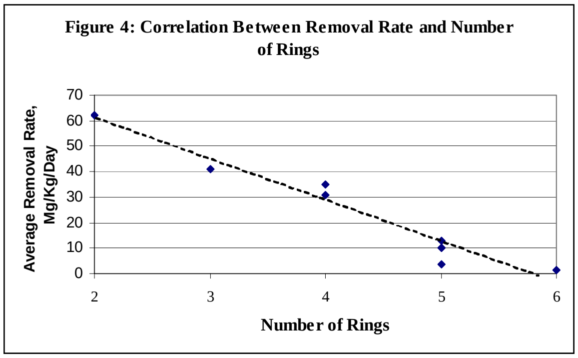


Figure 4: Correlation Between Removal Rate and Number of Rings

Ozonation of PAHs. A study was conducted to examine the ozonation of PAHs. A soil slurry was placed in a stirred, 3-neck round bottom flask. The soil was collected from an MGP site. Ozone (5-7% in oxygen) was sparged into the flask at 300 mL/min and the slurry was treated for 18 days. There were 13 PAHs present. The number of rings increases with increasing PAH number, varying from 2 to 6 rings. In Figure 5, PAH 1 is naphthalene; PAH numbers 2 to 4 are 3-Ring compounds; PAH numbers 5 to 8 are 4-ring compounds; PAH numbers 9 to 11 are 5-ring compounds; and PAH numbers 12 to 13 are 6-ring compounds.

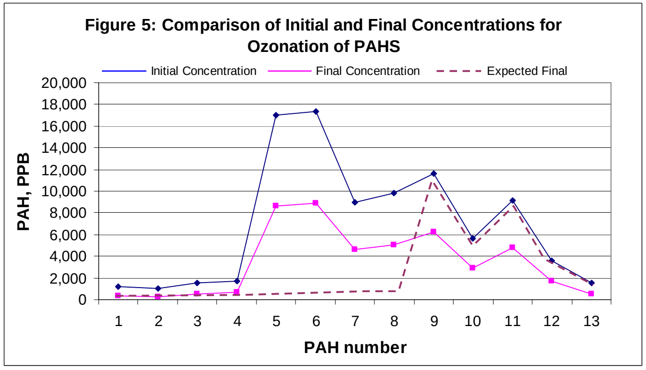


Figure 5: Comparison of Initial and Final Concentrations for Ozonation of PAHS

If the ozonation reaction was limited by solubility, the expected behavior would be represented by the dashed line. One would expect very good removal for the lower numbered PAHs, which have fewer rings and higher solubility, and less removal for the higher ringed PAHs. However, as can be seen in Figure 5, the initial and final concentrations of each compound parallel one another. This suggests that the ozonation reaction is a function of the concentration of the PAH present and not of its solubility. The reaction is independent of the number of rings; all the PAHS have roughly the same degree of removal.

Figures 6 and 7 plot the removal rate for ozone against the initial PAH concentration (Figure 6) and the number of rings (Figure 7). These plots are the same types as those shown in Figures 3 and 4. The results shown in Figures 6 and 7, however, are very different. Figures 3 and 4, which gave the results for permanganate, showed a stronger correlation of the removal to the number of rings than to the initial concentration. This was interpreted as an indication that the permanganate reactivity was limited by the solubility of the PAH. By contrast, the removal rates calculated for ozone are more strongly correlated to the initial concentration than to the number of rings. This indicates that ozonation directly attacks the PAHs adsorbed to the soil. It is not dependent on the PAH first dissolving into the aqueous phase.

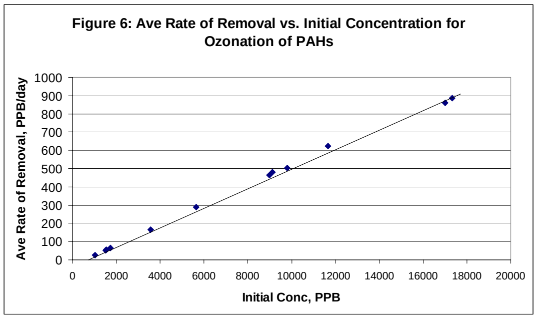


Figure 6: Ave Rate of Removal vs. Initial Concentration for Ozonation of PAHs

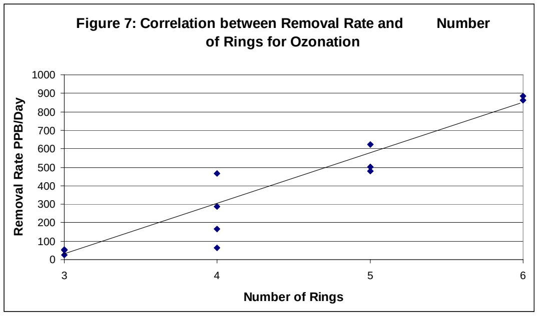


Figure 7: Correlation between Removal Rate and Number of Rings for Ozonation

Ozonation of PCBs. The ozonation of PCBs was also studied. Soil contaminated with Aroclor 1260 was used. The ozonation experiment used the same set-up as the PAH ozonation study.

As shown in Table 2, PCBs products (e.g., Aroclors) are mixtures of chlorinated biphenyls. There are a maximum of 10 carbons that can be chlorinated. Aroclor 1260, is the most highly chlorinated of the Aroclors, having 5 to 9 chlorines. As shown in Table 2, the solubility of the chlorinated biphenyls decreases with increasing chlorination. The sorbtivity (Log K_{OW}) of the PCB also increases with increasing chlorination. Thus, PCBs tend to be strongly sorbed to the soil matrix. The reactivity of PCBs in aqueous systems is depressed by their sorption to the soil matrix. Reaction systems that depend on the PCB being in the dissolved state do not perform well.

Table 2: Composition and Properties of PCBs

Approximate percentage (w/w) of Aroclors with different degrees of chlorination (WHO, 1993)

Compound	Chlorine weight(%)	Aroclor						
		1221	1232	1016	1242	1248	1254	1260
	0	10						
Monochlorobiphenyl	18.8	50	26	2	3			
Dichlorobiphenyl	31.8	35	29	19	13	2		
Trichlorobiphenyl	41.3	4	24	57	28	18		
Tetrachlorobiphenyl	48.6	1	15	22	30	40	11	
Pentachlorobiphenyl	54.4				22	36	49	12
Hexachlorobiphenyl	59.0				4	4	34	38
Heptachlorobiphenyl	62.8						6	41
Octachlorobiphenyl	66.0							8
Nonachlorobiphenyl	68.8							1

Selected values for PCBs congeners groups (from Mackay, et al. 1992)

Congener Group	Mol. Weight (g/mol)	Vap. Pres. (Pa)	Water Solubility (g/m^3)	Log K_{ow}
Monochlorobihenyl	188.7	0.9-2.5	1.21-5.5	4.3-4.6
Dichlorobiphenyl	223.1	0.008-0.60	0.06-2.0	4.9-5.3
Trichlorobiphenyl	257.5	0.003-0.22	0.015-0.4	5.5-5.9
Tetrachlorobiphenyl	292.0	0.002	0.0043-0.010	5.5-6.3
Pentachlorobiphenyl	326.4	0.0023-0.051	0.004-0.02	6.0-6.5
Hexachlorobiphenyl	360.9	0.0007-0.012	0.0004-0.0007	6.9-7.3
Heptachlorobiphenyl	395.3	0.00025	0.000045-0.0002	6.7-7.0
Octachlorobiphenyl	429.8	0.0006	0.0002-0.0003	7.1-7.4
Nonachlorobiphenyl	464.2	--	0.000018-0.000079	7.2-8.16
Decachlorobiphenyl	498.7	0.00003	0.000001	8.26

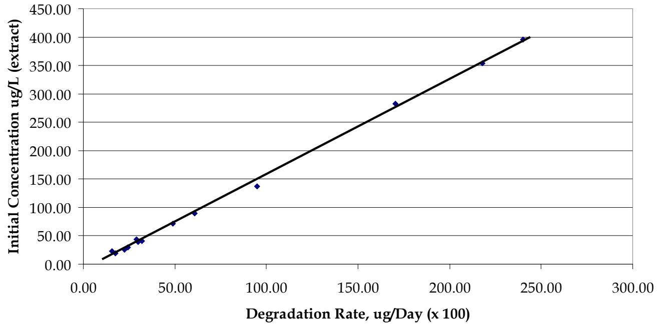
The results of the ozone study are summarized in Table 3. As can be seen ozone was effective in destroying the PCBs in the soil matrix. Over 91% of the PCBs present in the soil were destroyed in eight weeks of ozonation. The control, which used oxygen alone, showed essentially no loss of PCBs over the eight week period. The performance of the ozone system suggests that the reaction is between the ozone gas and the adsorbed PCB.

Table 3: Oxidation of Aroclor 1260 (Slurry)

Treatment	Matrix	T = 0	T = 4 Weeks	T = 8 Weeks
Control	**Soil** (mg/kg)	**9,710**	**9,300**	**9,000**
Control	**Water** (mg/L)	**0.9**	**NA**	**0.36**
Ozone	**Soil** (mg/kg)	**12,400** **12,200**	**7,500** **8,100**	**1,000** **1,100**
Ozone	**Water** (mg/L)	**0.2**	**NA**	**0.07**

Figure 8 plots the rate of PCB removal (ozonation) versus the initial concentration. As can be seen from the figure there is a very strong correlation. This, again, suggests that reaction of ozone with the PCBs sorbed to the soil matrix is a gas-solid reaction. The ozone in the gas-phase contacts and destroys the PCB adsorbed to the soil particle.

Figure 8: Correlation Between Initial Conc. and Rate of PCB Ozonation



A graphic demonstration of the gas-solid reaction of ozone was a laboratory study using a column with pure-phase Aroclor 1260. A 7.6 cm ID column was packed with sand and a 3 mm thick layer of pure-phase Aroclor 1260 (a yellow taffy-like material) was placed in the middle. A 5-7% ozone stream was added to the column at 300 mL/min. An identically constructed column was treated with oxygen as a control. Both columns were kept dry.

A 2 cm thick soil sample was taken from the middle of both column at T=0 and after 40 days. The samples were analyzed for PCBs. The results are shown in Figure 9. As can

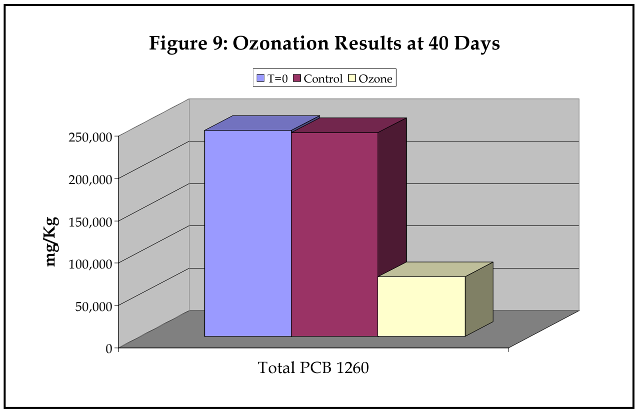
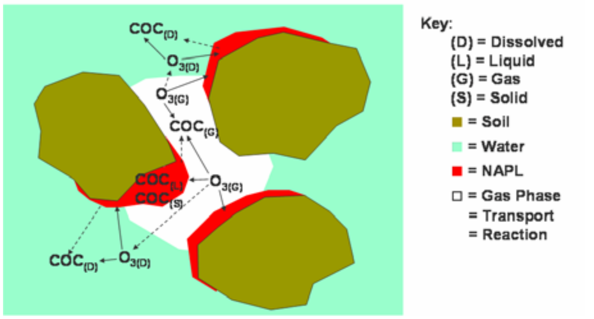


Figure 9: Ozonation Results at 40 Days

Figure 10: Transport and Reaction of Ozone



be seen from the figure, there was essentially no loss of PCBs in the control after 40 days. In the ozone treated column the PCB concentration was reduced from 25% by weight (250,000 mg/Kg) to < 5.5% (55,000 mg/Kg). The only mechanism of reaction that can explain this substantial reduction of pure phase Aroclor 1260 is the direct attack by gaseous ozone on the PCB solid.

Ozonation is a complex reaction system where a number of reaction pathways that are possible. Ozone dissolves in the aqueous phase and reacts with dissolved contaminants or NAPL. Ozone gas can contact and react with adsorbed or dissolved contaminants or with NAPL. Figure 10 provides a conceptual diagram of the reaction pathways that can exist and contribute to the effectiveness of in situ ozonation. The existence of multiple pathways enhances the effectiveness of ozone for . The gas phase reactions enhance the ability of ozone to effectively treat adsorbed, hydrophobic contaminants.

CONCLUSIONS

One of the difficult types of contamination to remediate is soils or sediments that are contaminated with hydrophobic, recalcitrant contaminants such as PAHs or PCBs. Many treatment technologies are aqueous based. That is, contaminants must be dissolved in water before they can be treated. For these technologies, the lack of substrate solubility and/or the slow desorption of the contaminant impedes effectiveness.

In situ ozonation is a particularly effective treatment method for dealing with hydrophobic, adsorbed phase contaminants. This is because ozone reactivity is not dependent on the dissolution of ozone from the gas phase into the aqueous phase, nor is it dependent on the dissolution of the contaminant. Ozone gas can react directly with adsorbed phase contaminants such as PAHs or PCBs.

The existence of this gas-phase reaction pathway provides several treatment benefits in addition to the ability to treat strongly adsorbed contaminants. First, ozone distribution in the gas phase is more facile than in the aqueous phase. This is based on two factors. First, gas permeability in soils is generally one to two orders of magnitude higher than water permeability. Second, gaseous ozone provides more mass than dissolved ozone. One cubic meter of water in contact with a 5-7% ozone stream contains 30 to 40 grams of ozone. One cubic meter of the ozone gas contains 70 to 90 grams of ozone. Third, the gas phase reactions of ozone are rapid, thus reducing treatment times.

In situ ozonation does have some limitations. First, it is a gaseous mixture with an ozone content of generally less than 10%. This means that there is significant quantities of carrier gas, typically oxygen or air. The presence of the carrier gas can cause stripping and volatilization of contaminants with a moderate to high vapor pressure such as chlorinated and/or aromatic solvents. Using ozone to treat these materials may require vapor capture and treatment. Second ozone is a toxic gas. The PEL (personal exposure limit) is 0.5 mg/m^3. In areas with potential for human exposure, excess ozone must be captured and destroyed.

Treating low-solubility, low-volatility contaminants such as PAHs PCBs, pesticide, and energetics is an ideal application of *in situ* ozonation. In fact, *in situ* ozonation may be the only effective *in situ* treatment technology for these types of contaminants.

REFERENCES

Brown R. A., G. J. Skladany, J. R. Lute, T. Moore, and D. Ferriter. 2001. "Bench-Scale Oxidation of PCB's Using Ozonation." The First International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, Niagara Falls, Ont. CA.

Dablow J., M. Seaman, and B. Marvin. 2002. "*In Situ* Ozonation to Remediate Recalcitrant Organic Contamination," Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA;

h2o2.com. 2005. "Soil Treatment: In-Situ Chemical Oxidation of Contaminated Soils." http://www.h2o2.com/applications/hazardouswaste/soil.html

Luthy, R. G., and S. Ghoshal. 1996. "Bioavailability Of Hydrophobic Organic Compounds From Nonaqueous-Phase Liquids: The Biodegradation of Naphthalene From Coal Tar." In: *Environmental Toxicology and Chemistry*. Volume: 15 Issue: 11

Pavlostathis, S.G., M. T. Prytula, and D. H. Yeh. 2003, "Potential and Limitations of Microbial Reductive Dechlorination for Bioremediation Applications." In: *Water, Air, & Soil Pollution: Focus.* Volume 3, Number 3

Radosevich M., Y. Jin, and D. K. Cha. 1997. *The Effect of Biosurfactants on the Fate and Transport of Nonpolar Organic Contaminants in Porous Media*." USGS Water Resources Research Grant Proposal

Reid, B.J., K.C. Jones, and K.T. Semple. 2000. "Bioavailability of persistent organic pollutants in soils and sediments—a perspective on mechanisms, consequences and assessment." In: Environ. Pollut. 108(1): 103-12

Sposito, G. 1994. *Chemical Equilibria and Kinetics in Soils*. Oxford University Press, Oxford

Watts, R. J., B.C. Bottenberg, T. F. Hess, M.D. Jensen, and A.L. Teel. 1999. "Mechanism of the enhanced treatment of chloroaliphatic compounds by Fenton-like reactions." In: *Environ. Sci. Technol*. 33, 3432-3437.

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