Naval Facilities Engineering Service Center
Port Hueneme, California

Treatability Study Results

for ESTCP Project ER-0825

In Situ Wetland Restoration Demonstration

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Contents

List of Acronyms

AFB	Air Force Base
AFCEE	AirForceCenterforEnvironmentalExcellence
APG	Aberdeen Proving Grounds
ASE	Accelerated Solvent Extraction
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DDD	Dichloro-Diphenyl-Dichloroethane
DDE	Dichloro-Diphenyl-Dichloroethylene
DDT	Dichloro-Diphenyl-Trichloroethane
DDx	Total DDT, i.e. the sum of DDT, DDE, and DDD
DoD	Department of Defense
EPA	(United States) Environmental Protection Agency
ERDC	Engineer Research and Development Center
ERDC WES	Engineer Research and Development Center Waterways Experiment Station
ESTCP	Environmental Security Technology Certification Program
FRTR	Federal Remediation Technologies Roundtable
GC/MS	Gas Chromatograph/Mass Spectrometer
ITRC	Interstate Technology and Regulatory Council
NAVFAC	Naval Facilities Engineering Command
NAVFAC ESC	Naval Facilities Engineering Command, Engineering Service Center
NAVFAC LANT	Naval Facilities Engineering Command, Atlantic Division
NFESC	Naval Facilities Engineering Service Center
PBT	Persistent, Bioaccumulative, and Toxic

PCB	Polychlorinated Biphenyl
PMO	Project Management Office
SPMD	Semipermeable Membrane Device
SPME	Solid Phase Microextraction
TOC	Total Organic Carbon
UNH	University of New Hampshire
USACHPPM	United States Army Center for Health Promotion and Preventive Medicine
USEPA	United States Environmental Protection Agency
WQS	Water Quality Standard
ZVI	Zero-Valent Iron

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1.0 Introduction

The Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) has funded the Naval Facilities Engineering Service Center (NFESC) and its DoD partners [Naval Facilities Engineering Command (NAVFAC), U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM), Naval Facilities Engineering Command Atlantic Division (NAVFAC Atlantic), AirForceCenterforEnvironmentalExcellence (AFCEE), and Engineer Research and Development Center (ERDC) Waterways Experiment Station], as well as their contractors AECOM Environment (formerly ENSR) and the University of New Hampshire (UNH), to demonstrate and validate an innovative technology for the *in situ* sequestration of contaminants present in hydric soils of palustrine wetlands (ESTCP Project ER-0825: *In Situ* Wetland Restoration Demonstration).

The Treatability Study Work Plan described laboratory experiments to be performed in support of the Field Demonstration. This report provides the results from the experiments performed, the analytical testing and statistical data evaluation.

1.1 Objectives of the Treatability Study

The overall objective of ESTCP Project ER-0825 is to demonstrate and validate *in situ* wetland remediation technologies designed to sequester contaminants in wetlands without devastating the ecology of these systems. The primary objective of the Treatability Study is to determine the most effective amendment agent to be used for Field Demonstration. Effectiveness was determined based upon decreases in hydrophobic organic contaminant concentrations in pore water of amended hydric soils compared to pre-treatment conditions and decreases in bioaccumulation in *Lumbriculus* assays. The Treatability Study and the Field Demonstration include evaluation of several sequestration agents and delivery systems to determine which combination(s) provides the most cost-effective and environmentally protective solution(s). Monitoring will be conducted following the Field Demonstration to validate project success. Performance objectives are described in detail in Section 3 of the Treatability Study Workplan, however, specific objectives of the Treatability Study include:

- Determine the effectiveness of a variety of demonstrated reagents in terms of their ability to sequester or dechlorinate contaminants (i.e., PCBs and DDx) in wetland hydric soils obtained from APG Canal Creek. This Treatability Study estimates the potential effectiveness of the *in situ* treatment under ideal laboratory conditions; it is anticipated that field demonstration site conditions may achieve less thorough mixing and thus a less effective treatment than will be observed in the Treatability Studies;

- Optimize amendment application dose;

- Demonstrate reduced contaminant bioavailability through laboratory bioaccumulation studies and pore water concentration measurements.

- Recommend the most effective amendment(s) and its application dose(s) for use at the APG Canal Creek wetland site during the Field Demonstration to reduce the bioavailability of PCBs and DDx in contaminated hydric soils. Once this recommendation has been made, the Field Demonstration Work Plan will be prepared to present the scope of work for the Field Demonstration phase of work.

The types and selection of amendment delivery methods and the evaluation of the potential impacts of amendment addition to wetland ecosystems will be described in the Field Demonstration Work Plan. In addition to field application at the APG, the Field Demonstration will also include laboratory microcosm studies conducted at the Jackson Estuarine Laboratory in Durham, NH to evaluate the effectiveness of amendment mixing into hydric soils by organisms under controlled conditions.

2.0 Test Design

2.1 Experimental Design Method Summary

A detailed description of the Test Design for this study can be found in section 5 of the Treatability Study Work Plan. To support the Field Demonstration Work Plan, focused laboratory Treatability Testing with hydric soils from the primary selected demonstration site (Canal Creek APG) was performed to screen engineered amendment agents. Based on the site-specific conditions presented in the January 2009*Site Selection Memorandumfor ESTCP Project ER-0825In Situ Wetland Restoration Demonstration*, and considering that the primary contaminants of concern are DDx and PCBs, promising amendments evaluated in this Treatability Study included activated carbon and organoclay for sequestration, and zero-valent iron (ZVI) for reductive abioticdechlorination of DDx.

The Treatability Study was performed using a phased approach. Major phases of the design include: 1) evaluation of amendment effectiveness, 2) amendment dose optimization, and 3) bioaccumulation study. The effectiveness of amendments selected based on literature review were tested in laboratory batch experiments to evaluate if the reagents successfully sequestered or dechlorinated PCBs and/or DDx in Canal Creek APG wetland hydric soils. Amendments were evaluated at different doses to understand the dose-response characteristics of each amendment. Effectiveness was measured based on decrease in pore water contaminant concentrations . Microcosms containing amended hydric soils were subjected to standard laboratory bioaccumulation tests to demonstrate decrease in contaminant tissue residues using the freshwater oligochaete*Lumbriculusvariegat*us(work conducted by UpalGhosh as part of the ESTCP ER-0835 collaboration).

2.2 Pore Water Test Methods

Sediment samples were obtained from Aberdeen Proving Ground, Maryland by AECOM and shipped to the University of New Hampshire. Samples were analyzed for total PCB and DDx concentrations and the results are shown below in Table 2.1. Those samples with the highest PCB and DDx concentrations (sample APG-SED-2C for PCBs and APG-SED-4C for DDx)were selected for the treatability study.

Table 2.1PCB and DDx concentrations detected in surficial sediments of Canal Creek (December 19 sampling event).

Sample ID	Total PCBs, μg/kg	Total DDx, μg/kg
APG-SED-1A	4700	410
APG-SED-1B	2700	316

APG-SED-1C	740	0
APG-SED-2A	1100	233
APG-SED-2B	4900	0
APG-SED-2C	5700	0
APG-SED-3A	2500	178
APG-SED-3B	1180	87
APG-SED-4A	0	1150
APG-SED-4B	0	6000
APG-SED-4C	0	6920
APG-SED-4D	0	408

Two sets of experiments were performed: one with PCB and one with DDT contaminated sediments. The sample for PCB analysis (SED-2C) contained Total Organic Carbon (TOC) of 15.9% and total PCB concentration of 5.70 mg/kg. The sediment sample for DDx (SED-4C) contained 14.2% TOC and total DDx concentration of 6.92 mg/kg. Both hydric soil samples were homogenized prior to taking subsamples to prepare batches. The samples were split into 4 sets of 50 gram subsamples and were either amended with powdered activated carbon, granular organoclay or granular ZVI or were used as controls (i.e., unamendedhydric soils). Samples amended with activated carbon and organoclay were added at levels of 3% and 6% of the total dry weight of the sediments amended (w/w) while the samples amended with zero valent iron were added at levels of 5% and 10% (w/w). All experiments were allowed to equilibrate for eight weeks, were performed in duplicates and two controls were maintained for the entire experiment.

After eight weeks, porewater samples were obtained from both non-amended and amended sediments APG-SED-2C and APG-SED-4C following the standard method for porewater separation (ASTM D7363 – 07). Briefly, sediment samples were centrifuged and flocculated with alum and sodium hydroxide to remove colloids. Porewater was decanted and SPME fibers were added to the porewater and allowed to equilibrate for 48 hours. SPME fibers were then removed from the porewater and extracted in hexane. Vials with fibers and hexane were sent to Dr. KannanKurunthachalam, Laboratory of Organic Analytical Chemistry, Albany, New York for analysis using high resolution gas chromatography / high resolution mass spectrometry for congener-specific PCB analysis and analysis of individual DDx compounds. The results of this analysis are indicated below in section 3.

2.3 Bioaccumulation Test Methods

Sediment characterization. In order to provide sufficient sample for bioaccumulation testing, sediment samples used for amendment testing above (SED-2C and SED-4C were composited and shipped from the University of New Hampshire to the University of Maryland Baltimore County. Total DDx (2,4’-DDD, 4,4’-DDD, 2,4’-DDT, 4,4’-DDT and

4,4'-DDE) concentration the study sediment was 25.4 mg/kg with 4,4' DDD comprising the dominant compound. There was very little parent DDT remaining in the sediment sample with the degradation products forming most of the DDx remaining in the sediment. Total PCB concentration in the compositedsediment was 2.7 mg/kg with tri, tetra, penta, and hexachlorobiphenyls comprising the dominant congeners. Total organic carbon (TOC) content in the sediment was 5.7 % by sediment dry weight.

Sediment treatment with Activated Carbon. Prior to processing, the sediment was stored in a refrigerator at 4 degree Celsius temperature. Twelve beakers of 500 ml volume were filled with 150 ml of homogenized sediment slurry and 300 ml of filtered stream water obtained from a natural stream in the UMBC campus. The beakers were allowed to aerate for 1 week to reduce ammonia content in the overlying water to less than 1.5 mg/L to minimize any toxic effect on the test organisms. The following treatments were performed:

1) Control: 4 beakers for control (no amendment),

2) Activated carbon-Low: 4 beakers with a low dose of activated carbon(2.7%)

3) Activated carbon-High: 4 beakers with a high dose of activated carbon(5.7%)

Activated carbon was added as SediMite pellets, and were applied on the sediment surface and allowed to soften overnight before being manually mixed into the sediment. The beakers after mixing the treatments were allowed to settle for one day before starting the bioaccumulation test.

14 day Bioaccumulation Study of PCBs and DDx. PCB uptake in the freshwater oligochaete*L. variegatus* was measured to assess the change in PCB bioavailability to benthic organisms after amending with activated carbon. The bioaccumulation test method used was based on the method described in USEPA (2000). Fresh *L. variegatus* were obtained from Aquatic Research Organisms, Hampton, New Hampshire. The worms were maintained in the laboratory using standard culturing procedures outlined in the USEPA (2000). Essentially the culturing method involves maintaining the worms in plastic containers with pureed unbleached paper towel and stream or site water with daily renewal of the overlying water. The water in the culture chamber is aerated using an aquarium air pump and an air stone.

At the initiation of the bioaccumulation test, 0.5 g wet worms were weighed and added to each test beaker described above. The worms were exposed to the test sediment for 14 days and maintained at $23 \pm 1\ ^{o}C$ in an aquarium maintained with a 16 hour light:8 hour dark photoperiod (14 day has been shown to be sufficient for observation of bioaccumulation reduction; see Sun and Ghosh, 2007). The aquarium contained water to a depth of 3" (partially immersing the exposure beakers) to maintain a constant temperature for all the beakers. A thermometer placed in the aquarium water was used to monitor temperature of the test. Average values of water quality parameters in overlying water at test initiation were: temperature 23 °C, DO 5.5 mg/L, pH 6.8, general hardness 280 mg/L as $CaCO_3$, alkalinity 160 mg/L as $CaCO_3$**.**

At the termination of the experiment, worms were removed from the sediments and allowed to depurate for 6 hours in clean beakers containing stream water. The worm wet tissue mass was measured after removing the excess water and frozen until further analysis.

PCB and DDx analysis. The organisms were ground with anhydrous sodium sulfate and extracted by sonication using three volumes of 40 ml each of hexane-acetone mixture (1:1) according to EPA SW846 method 3550B. Total extracted solvent wassplit into two for DDT and PCB analysis. Sample cleanup was performed based on EPA SW846 methods 3660B (activated copper cleanup), 3665A (sulfuric acid cleanup), 3620B (activate florosil cleanup for DDT) and 3630C (silica gel cleanup for PCB). DDT andPCB analyses were performed using an Agilent 6890 gas chromatograph with a micro electron capture detector. One of the PCB congeners (#153) coeluted with a contaminant peak in the tissue extracts and was removed from the analysis from all samples. This congener contributed less than 0.2% of total PCB in the sediment extraction.

3.0 Results of Laboratory Experiments

3.1 Pore Water Study Results

Amendments of activated carbon (AC), organoclay (OC) and zero valent iron (ZVI) were added to sediment. AC and OC were added at 3% and 6% (dry sediment weight), and ZVI was added at 5% and 10%. The results for both sediments are discussed below.

<u>Amendment Effectiveness for PCB Contaminated Sediment</u>

Figure 3.1 below shows % reduction in porewater concentrations of five PCB congeners detected using the analytical procedures outlined above. Table 3.1 below shows the concentration data collected that forms the basis for the % reductions calculated and shown in Figure 3.1. Organoclay was added at 3% (OC-3) and 6 % (OC-6), ZVI was added at 5% (ZVI-5) and 10% (ZVI-10) and activated carbon was added at 3% (AC-3) and 6% (AC-6). These data indicate that organoclays had marginal effectiveness for reducing porewater concentrations of detected congeners at these very low levels, ZVI resulted in increases in PCB availability, and activated carbon significantly reduced PCB porewater concentrations.

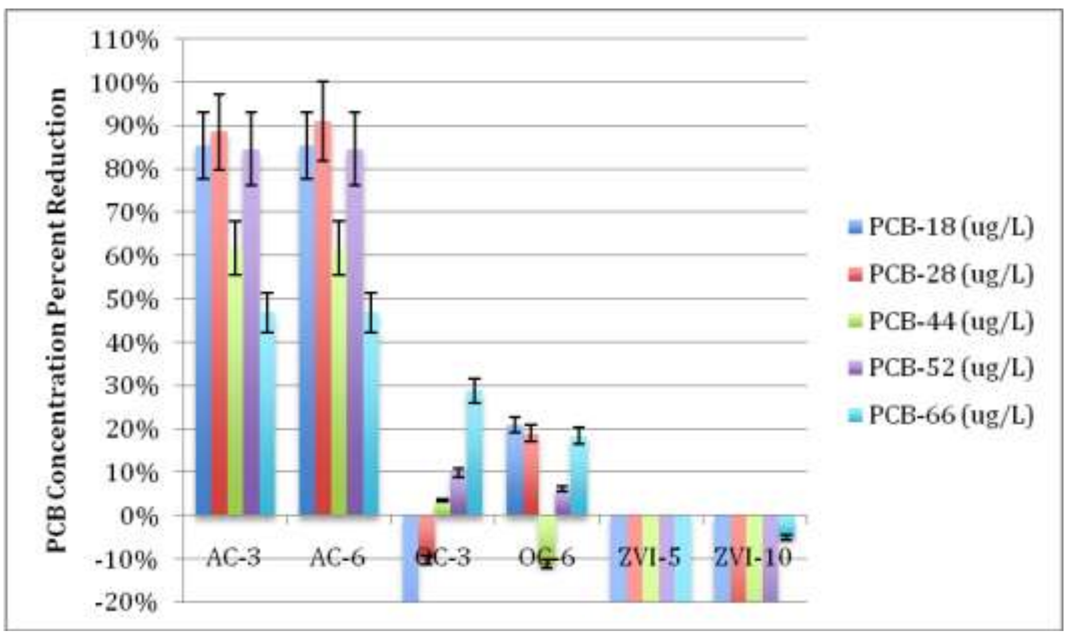

Figure 3.1 PCB Porewater Reduction for Different Amendments

Table 3.1PCBs concentrations in porewater (ug/L)

	pcb-18	pcb-28	pcb-44	pcb-52	pcb-66
Control (avg)	1.05E-03	5.61E-05	3.23E-05	7.71E-05	1.02E-05
oc3a	1.84E-03	6.57E-05	3.68E-05	7.41E-05	5.72E-06
oc3b	1.35E-03	5.78E-05	2.55E-05	6.49E-05	8.76E-06
oc6a	9.36E-04	5.07E-05	3.80E-05	7.36E-05	7.01E-06
oc6b	7.24E-04	4.01E-05	3.38E-05	7.12E-05	9.58E-06
zv1-10b	2.39E-03	9.49E-05	6.44E-05	1.39E-04	1.21E-05
zv1-10b	1.31E-03	5.27E-05	3.24E-05	6.56E-05	9.27E-06
zv1-5a	2.12E-03	7.91E-05	5.10E-05	1.17E-04	1.26E-05
zv1-5b	5.39E-03	2.25E-04	1.16E-04	2.38E-04	2.74E-05
ac6a	1.52E-04	3.78E-06	1.24E-05	1.18E-05	5.40E-06
ac6b	1.52E-04	6.18E-06	1.24E-05	1.18E-05	5.40E-06
ac3a	1.52E-04	4.47E-06	1.24E-05	1.18E-05	5.40E-06
ac3b	1.52E-04	8.37E-06	1.24E-05	1.18E-05	5.40E-06

Assuming a normal distribution and a confidence interval of 90%, the data in table 3.2 show whether the PCB porewater change was statistically significant. Organoclay shows a statistically significant decrease in PCB concentrations for only congener 18 at a dose of 3% (w/w). Zero valent iron results in statistically significant increases in porewater concentrations for every congener at 5% (w/w) amendment and an increase of congener 18 at 10% (w/w). Activated carbon resulted in statistically significant PCB concentration decreases, with the exception of congener 44, further indicating its potential as the appropriate amendment agent for the field demonstration.

Table 3.2Statistical Significance for PCB Changes

	pcb-18	pcb-28	pcb-44	pcb-52	pcb-66
Control (avg)	0.35	1.16	0.26	0.65	0.19
Std Dev	0.079	0.411	0.138	0.272	0.033
OC-3	**YES**	NO	NO	NO	NO
OC-6	NO	NO	NO	NO	NO
ZVI-5	**YES**	**YES**	**YES**	**YES**	**YES**
ZVI-10	**YES**	NO	NO	NO	NO
AC-3	**YES**	**YES**	NO	**YES**	**YES**
AC-6	**YES**	**YES**	NO	**YES**	**YES**

Figure 3.2 shows the relative effectiveness of activated carbon added at 0%, 3% and 6%. Because there is little difference observed between 3% and 6% and both levels are statistically significant (as shown in table 3.2), 3% activated carbon appears to be the most cost-effective approach for amendment addition based on this set of porewater concentration data for PCBs. Therefore, activated carbon is indicated for the field demonstration.

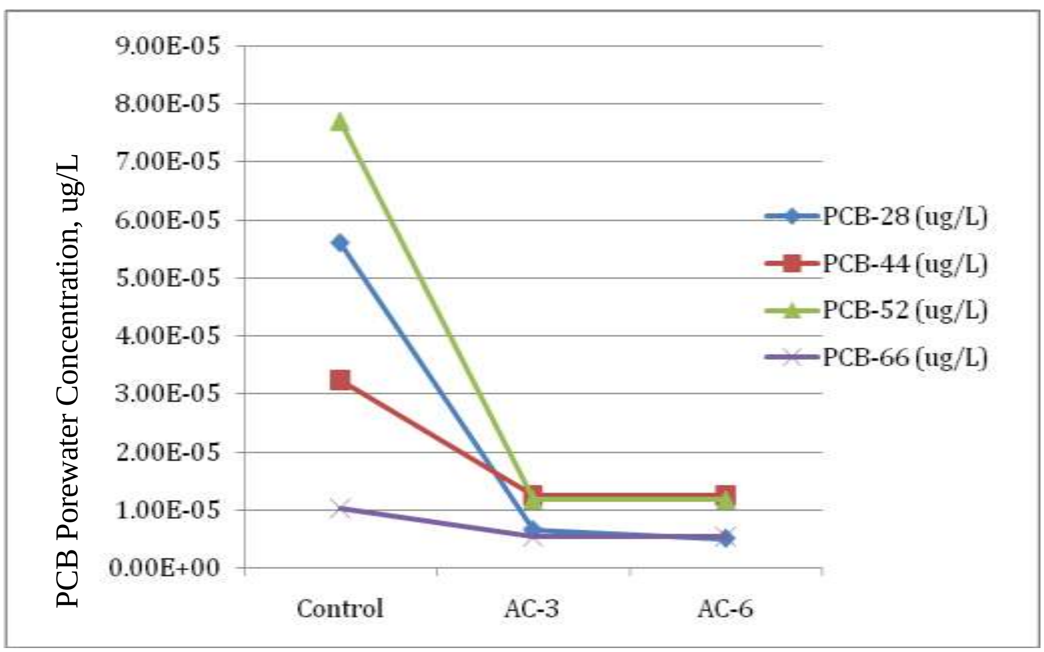

Figure 3.2 Activated Carbon Effectiveness for PCBs

Amendment Effectiveness for DDx Contaminated Sediment

Figure 3.3 below shows % reduction in porewater concentrations of DDT and its reduced forms while Table 3.3 provides the concentration data for average porewater concentrations of DDx. These data show that organoclays had marginal effectiveness for reducing these porewater concentrations, ZVI resulted in increases in DDxconcentrations, and activated carbon significantly reduced DDxporewater concentrations.

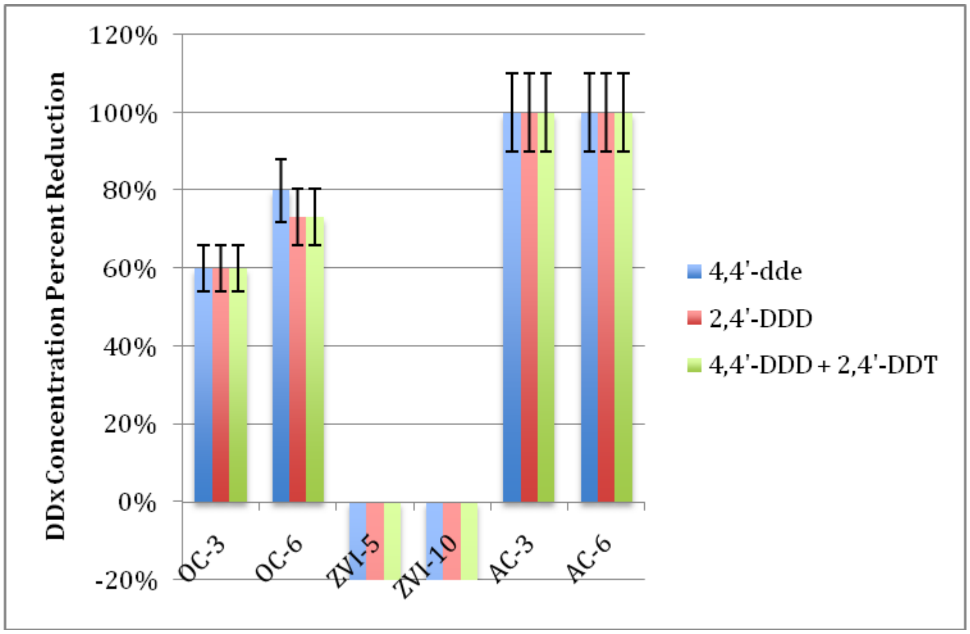

Figure 3.3DDxPorewater Reduction for Different Amendments

Table 3.3DDx concentrations in porewater (ug/L)

	2,4'-dde	4,4'-dde	2,4'-DDD	4,4'-DDD + 2,4'-DDT
Control (avg)	1.67E-05	1.40E-04	5.00E-04	6.14E-04
OC-3	<MDL	5.61E-05	2.00E-04	2.45E-04
OC-6	<MDL	2.81E-05	1.34E-04	1.64E-04
ZVI-5	<MDL	2.10E-04	9.19E-04	1.13E-03
ZVI-10	<MDL	2.54E-04	1.08E-03	1.33E-03
AC-3	<MDL	<MDL	<MDL	<MDL
AC-6	<MDL	<MDL	<MDL	<MDL

Assuming a normal distribution and a confidence interval of 90%, the data in table 3.4 shows the statistical significance of the DDx amendment agents. Zero-valent iron results in statistically significant increases of DDx concentration while organoclay and activated carbon result in statistically significant decreases. However, given the raw data in Table 3.3 and the information in Figure 3.3, it is clear that activated carbon is the best amendment agent for the field demonstration.

Table 3.4Statistical Significance for DDxPorewater Change

	2,4'-ddt	**2,4'-DDD**	**4,4'-DDD +2,4'-DDT**
control (avg)	0.46	1.65	2.02
std dev	0.05	0.11	0.14
ZVI-5	**YES**	**YES**	**YES**
ZVI-10	**YES**	**YES**	**YES**
AC-3	**YES**	**YES**	**YES**
AC-6	**YES**	**YES**	**YES**
OC-3	**YES**	**YES**	**YES**
OC-6	**YES**	**YES**	**YES**

Figure 3.4shows the effectiveness of activated carbon added at 0%, 3% and 6%. Because there is little difference observed between 3% and 6% and both levels are statistically significant (as shown in table 3.4), 3% activated carbon appears to be the most cost-effective approach for amendment addition based on these data sets.

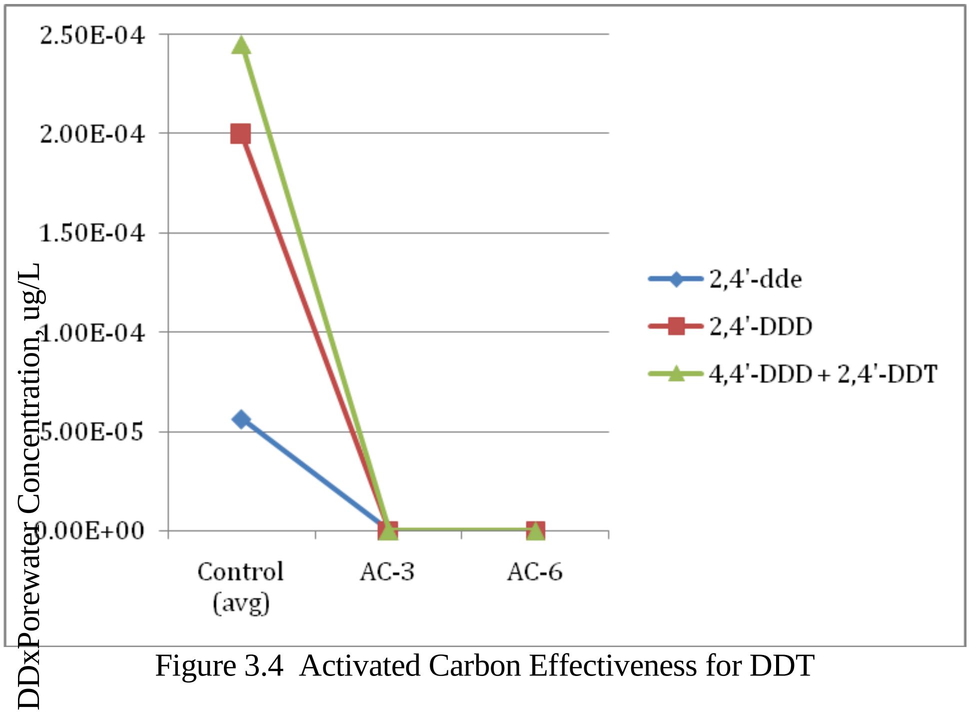

Figure 3.4 Activated Carbon Effectiveness for DDT

3.2 Bioaccumulation Study Results

Water quality parameters (DO, pH, temperature, hardness, and conductivity) remained within acceptable range during the 14-day bioaccumulation study. Worms applied to control and treated sediments exhibited normal burrowing and feeding behavior during the study. The recovery of worm tissue at the end of the exposure period was acceptable for all exposure beakers and was greater than 70%. PCB concentration measured in recovered worm tissue from control and exposure beakers are shown in Figure 3.5 by homolog groups. For the untreated sediment, PCB homolog distribution in worm tissue showed the tetra, penta, and hexachlorobiphenylsasthe most abundant homologs in worms exposed to untreated sediment. Treatment at the low dose of activated carbon (2.7%) reduced total PCB bioaccumulation in worms by 81%. At the higher dose of activated carbon (5.7%), PCB bioaccumulation by the worms was reduced further to 95%.

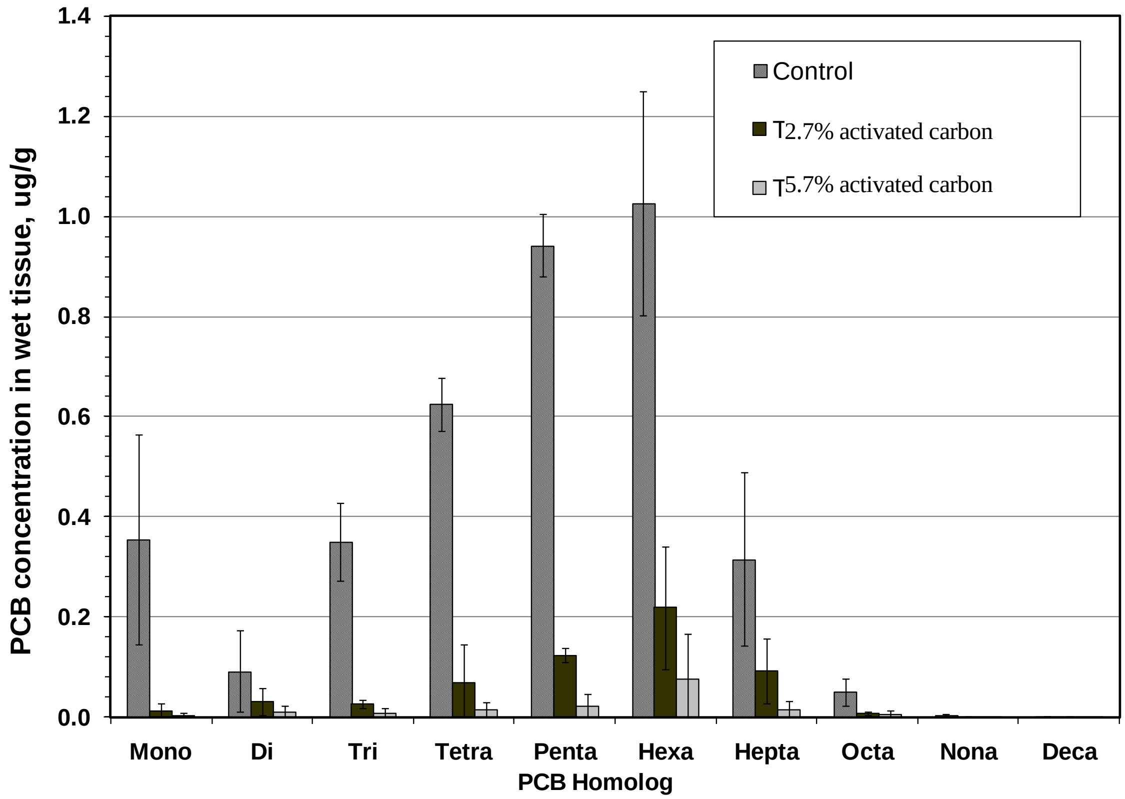

Figure 3.5Concentration of PCB homologs in wet tissue of *L. variegatus* for untreated sediment and sediment treated with different amounts of activated carbon. (Ghosh et al., 2009)

DDx concentration measured in recovered worm tissue from control and exposure beakers are shown in Figure 3.6. After 14 days contact, total DDx bioaccumulation was significantly reduced compared to control. Treatment at the low dose of activated carbon (2.7%) reduced total DDx bioaccumulation in worms by 87%. At the higher dose of 5.7%, DDx bioaccumulation by the worms was reduced further to 92%. The percent reductions in bioaccumulation close to 90% observed in this study are similar to reductions reported previously after amending activated carbon to PCB contaminated sediment (Sun and Ghosh 2007).

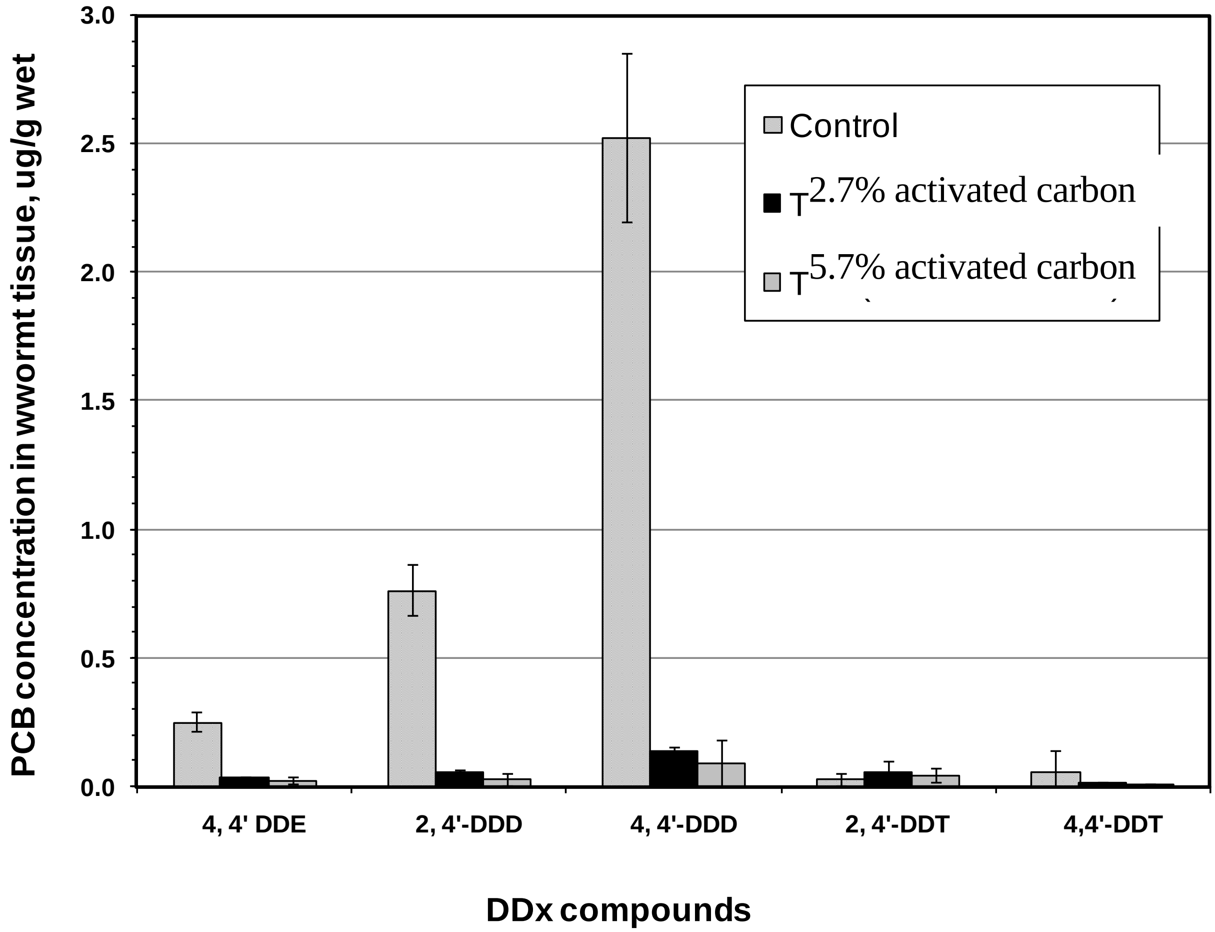

Figure 3.6Concentration ofDDx in wet tissue of*L. variegatus* for untreated sediment and sediment treated with two doses of activated carbon. (Ghosh et al, 2009)

3.3 Bioaccumulation Study Conclusions

Amendment of sediment with activated carbonreduced PCB and DDx uptake in the freshwater oligochaete*L. variegatus*. Although a dose higher than 5.7% could not be tested due to lack of enough sediment volume available for testing, results obtained from this study indicate greater than 90% reduction in PCB and DDx bioaccumulation after amendment with 5.7% activated carbon. Recent treatability work with Hg-impacted sediment from the Lower Canal Creek demonstrated an optimal dose of activated carbon at 1xTOC as carbon, or 5.7% in the case of this sediment. These results suggest some increase in activated carbon effectiveness between 2.7% and 5.7%; however, there is clearly diminishing return at the higher activated carbon dosage, depending on the risk reduction targets for a particular site.

4.0 Summary, Conclusions and Recommendations

The objectives of the treatability study were to determine the effectiveness of a variety of amendment agents, optimize the amendment application dose and demonstrate reduced contaminant bioavailability. Several amendment agents, including activated carbon, organoclay and zero-valent iron, were evaluated. Activated carbon resulted in the most significant reductions in DDx and PCB porewater concentrations. Activated carbon was found to be equally effective at dose levels of 3% and 6% (w/w) in the analysis of sediment porewaters, therefore, based on cost savings, a reduced need for materials, and reduced wetland impact in the application, the lower dose of 3% was recommended.

Sediments amended with zero valent iron (ZVI) resulted in significant increase of PCBs and DDxporewater concentrations while those amended with organoclay (OC) resulted in marginal reductions of PCBs and DDX. Amendment of sediments with activated carbon resulted in significant PCB and DDxporewater concentration reductions at levels ranging from 40 to greater than 90%. Bioaccumulation study results also indicate significant decreases in bioavailable PCBs and DDx with activated carbon addition. The porewater data and the bioaccumulation data are consistent in that they show significant reductions of bioavailable PCBs and DDx with activated carbon addition. The difference in PCB congener distribution between the two sets of studies is due to the differences in SPME fiber efficacy for higher chlorinated PCB congeners relative to

Both studies are in agreement that amendments with activated carbon provide promising results. The optimal activated carbon dose was clearly different between the two studies (little benefit was seen in the porewater for doses higher than 3% while the bioaccumulation study showed a difference between 2.7% and 5.7%). Again, this is likely due to the differences in the sediments tested.

We recommend that activated carbon dose levels for the field application be 3% (dry weight basis for the surficial soils). We base this recommendation on the bioaccumulation test results, which showed greatest cost-effectiveness for 2.7% activated carbon dose (although increases in treatment effectiveness were shown when dose was increased to 5.7%). In addition, there are considerations for the field deployment, such as the cost and the impact of the amendment on the ecosystem. Lower amendment concentrations were still very effective at reducing contaminant bioavailability, and a lower dose would be more cost-effective and minimize adverse ecological impacts. A greater activated carbon dose would require a thicker application, the impact of whichwould vary depending on the type of delivery (e.g. in a slurry vs. in a clay matrix such as Aquablok). The various delivery systems will be evaluated in the field demonstration and are further addressed in the demonstration plan.