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Polychlorinated biphenyl dechlorination with palladized magnesium - Development of a sediment remediation technology

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POLYCHLORINATED BIPHENYL DECHLORINATION WITH PALLADIZED MAGNESIUM – DEVELOPMENT OF A SEDIMENT REMEDIATION TECHNOLOGY

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DISSERTATION

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DEDICATION

This dissertation is dedicated to my family: my mom, dad, Előd and Gopal.

Ajánlom ezt a doktori disszertációt családomnak: anyának, apának, Elődnek és Gopálnak.

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by

Emese Hadnagy

University of New Hampshire, September, 2008

PCB contamination in sediments remains a significant problem in many rivers, harbors, and estuarine areas in the US and around the world. In this work, PCB dechlorination by palladium-coated magnesium (Mg/Pd, 0.01% by weight Pd) has been demonstrated in PCB-contaminated marine and freshwater sediments from New Bedford Harbor (NBH), MA; and the Housatonic River (HSR), MA. Experiments were also conducted in pure solvent systems (10% methanol in distilled water). In addition, the performance of an in-situ sediment remediation system capable of delivering and mixing chemical amendments into sub-aqueous sediments and at the same time providing enclosed conditions was evaluated by mixing activated carbon (AC) into Cocheco River, NH sediment. The higher organic and silt/clay content NBH sediment had lower overall dechlorination than the sandy HSR sediment with lower organic content; PCB desorption from the sediments did not limit dechlorination rates. Formation of lower chlorinated congeners could be observed in the HSR sediment, mostly pentachlorobiphenyls or lesser chlorinated congeners, and was also confirmed in experiments conducted with single

PCB congeners BZ 194 and 204 in pure solvents, indicating that dechlorination was occurring. A stepwise dechlorination process was suggested in which chlorines in the ortho position were removed last. The use of methanol, ethanol and isopropanol to enhance dechlorination by increasing contaminant solubility proved to be inefficient in both sediments when compared to water. The bioavailability of PCBs decreased by 78.0%, 59.9%, and 66.7% in the sandy HSR sediment in the presence of water, ethanol and isopropanol (with associated mass removals of 48.3%, 52.2% and 17.9%, respectively), indicating that the majority of the contaminants that were not accessible for dechlorination were not bioavailable. In the in-situ sediment remediation system evaluation, better amendment recoveries were observed at lower added AC volumes, at lower pump flow rates, at faster mixing speeds, and at horizontal locations closer to the center shaft. In general, poor amendment recoveries could be attributed to the limited capacity of the sediment pore space to accommodate the AC slurry. Even though not all amendment was mixed successfully into the sediment the reagent stayed within the enclosure of the device, indicating that contained mixing conditions were achieved.

CHAPTER 1

INTRODUCTION

Objectives

The main goal of the current research was to develop a contaminated sediment remediation technology for PCB dechlorination by palladized magnesium (Mg/Pd) that can be used either in an in-situ or an ex-situ scenario. Experiments were conducted in PCB-contaminated marine and freshwater sediments from New Bedford Harbor (NBH), MA; and the Housatonic River (HSR), MA and also in pure solvents (10% methanol in distilled water). In addition, the performance of an in-situ sediment remediation system capable of delivering and mixing chemical amendments into sub-aqueous sediments and at the same time providing enclosed conditions was evaluated by mixing activated carbon (AC) into Cocheco River, NH sediment. The specific objectives were:

For experiments conducted in pure solvent:

- Evaluate the reaction kinetics of single PCB congeners and commercially available PCB mixtures;
- Identify the reaction by- and end-products and close the mass balance of the system; and
- Determine congener-specific dechlorination pathways and the relative resistance of positional isomers.

For the sediment experiments:

- Assess the extent of PCB dechlorination by Mg/Pd in unmodified aged, PCB-contaminated sediments;
- Evaluate the effect of sediment characteristics (e.g., gradation, natural organic material content) on the dechlorination reaction;
- Investigate the congener-specificity of the dechlorination reaction in sediments;
- Test various solvents for their potential to enhance PCB dechlorination by increasing contaminant availability; and
- Understand how the treatment affects PCB bioaccumulation and whether the treatment contributes to toxicity to benthic organisms.

For the in-situ sediment remediation system evaluation:

- Quantify and evaluate the amendment delivery and mixing efficiency of the remediation system in terms of reagent yield and homogeneity of the mixing; and
- Monitor sediment resuspension and reagent release into the water column.

Dissertation Organization

The chapters of this dissertation were written as individual papers addressing unanswered research questions. Contributions are in the areas of PCB dechlorination by Mg/Pd in pure solvents (Chapter 2) and in aged, contaminated sediments (Chapter 3), and an in-situ sediment remediation system evaluation (Chapter 4).

Chapter 2 summarizes the results of PCB dechlorination experiments conducted in pure solvents (a 10% methanol solution in distilled water spiked with known amounts of the contaminant). Complete and rapid dechlorination (i.e., in the matter of few minutes) of single PCB congeners was achieved in these experiments. The formation of lower chlorinated PCB compounds indicated that dechlorination was occurring. A stepwise dechlorination process was suggested in which chlorines in the ortho position were removed last. Understanding the reaction kinetics and the dechlorination pathways of single congeners, and identifying the reaction end products in pure solvents helped understand the reactions and products formed in more complex sediment systems.

The extent of the dechlorination reaction in sediments is described in chapter 3 including observations related to the apparent connection between dechlorination and sediment characteristics. The role of various solvents in enhancing PCB dechlorination is also presented. Finally, the effect of treatment on PCB bioavailability and toxicity is discussed and scenarios for the practical applicability of PCB dechlorination by Mg/Pd in sediments are stated. Lower PCB mass reduction was observed in sediments than in pure solvents; e.g., 48% in the sandy Housatonic River sediment after 24 hours. PCB bioavailability measured over 14 days decreased by 78% in the same sediment, indicating that not all the contaminants remaining were available for uptake by benthic organism. A comparative cost analysis reported by Calante (2006) shows that in-situ PCB dechlorination using Mg/Pd is a potential cheaper technology than dredging, which is currently the most common remediation method for contaminated sediment management. The study reports actual and estimated dredging costs for the New Bedford Harbor and the Hudson River remediation sites, respectively. Therefore, the cost comparison between PCB dechlorination by Mg/Pd and dredging in the New Bedford Harbor project is more realistic.

While chapters 2 and 3 discuss the viability of the dechlorination reaction in different matrices when using the Mg/Pd bimetal, chapter 4 addresses another important issue: ways to deliver and mix reagents into sediments in-situ. The performance of an in-situ sediment remediation system that is capable of delivering and mixing chemical amendments into sub-aqueous sediments is evaluated in chapter 4. Activated carbon amendment was used for system evaluation in this work instead of the Mg/Pd because the carbon was easier to measure, it was cheaper and there were no safety concerns regarding its application.

Chapter 2 has been published in a peer-reviewed journal. The other two chapters will also be submitted for publication in the future. The appropriate citations are as follows:

Chapter 2:

Hadnagy, E.; Rauch, L.M.; Gardner, K.H. Dechlorination of polychlorinated biphenyls, naphthalenes and dibenzo-p-dioxins by magnesium/palladium bimetallic particles. *Journal of Environmental Science and Health: Part A* **2007**, 42, 685-695.

Chapter 3:

Hadnagy, E.; Calante, I.; Gardner, K.H. Polychlorinated biphenyl dechlorination and bioavailability in marine and freshwater sediments in the presence of various solvents (not yet submitted)

Chapter 4:

Hadnagy, E.; Gardner, K.H.; Chesner, W.H.; Justus, H.; Maxwell, G.; Forgione, M. Pilot scale evaluation of an in-situ amendment mixing device in dredged river sediment (not yet submitted)

CHAPTER 2

DECHLORINATION OF POLYCHLORINATED BIPHENYLS, NAPHTHALENES AND DIBENZO-P-DIOXINS BY MAGNESIUM/PALLADIUM BIMETALLIC PARTICLES

Abstract

The contamination of sediments with polychlorinated organics such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (Dioxins) and polychlorinated naphthalenes (PCNs) remains a significant problem in many rivers, harbors, and estuarine areas in the US and around the world. In this work, rapid dechlorination of PCBs, PCNs, and Dioxins by palladium-coated magnesium (0.01% by weight Pd) has been demonstrated in pure solvent systems (10% methanol in distilled water). This reaction was investigated with the goal of developing it as a future sediment treatment method. More than 90% of the initial single PCB congeners BZ 3 and 170 were removed in 1 to 10 minutes and about 58% of the total initial Arochlor 1260 was removed in 4 minutes. The removal of single Dioxin and PCN congeners also occurred rapidly resulting in a 69 to 95% reduction in 30 minutes. Rapid removal of biphenyl, the expected degradation end product for PCBs, was also observed (80% removal in 5 minutes). Experiments conducted with Arochlor 1260 and biphenyl did not identify significant volatile fractions. A significant amount of PCBs were extracted from the filtered Mg/Pd material suggesting that PCBs first adsorb to the surface of the bimetal

and then dechlorination occurs; lesser chlorinated congeners and biphenyl adsorbed to the Mg/Pd material. Experiments conducted with single PCB congeners BZ 194 and 204 demonstrated the formation of lower-chlorinated PCB congeners, indicating that dechlorination was occurring. A stepwise dechlorination process was suggested in which chlorines in the ortho position were removed last. A satisfactory mass balance could not be achieved because of the reaction of the biphenyl.

Introduction

Polychlorinated biphenyl (PCB) contamination in sediments remains a significant problem in many rivers, harbors, and estuarine areas in the US and around the world. These contaminated sediments continue to provide PCBs to the food chain despite the long ban on PCB manufacture and use. Of further concern is the presence of similar persistent chlorinated compounds such as polychlorinated dibenzo-p-dioxins (Dioxins) and polychlorinated naphthalenes (PCNs). Although PCBs are often present in the environment at higher concentrations, these other compounds can be more significant contributors than PCBs to overall sediment toxicity (Eljarrat et al., 2003; Kannan et al., 2001). Yet the treatment of dioxin and PCN contaminated sediments has been relatively little studied to date.

Current contaminated sediment management options include: natural attenuation, dredging followed by containment or ex-situ treatment, capping, and in-situ chemical or biological treatment. Dredging, the most commonly used alternative, has been reported to be unsuccessful in reducing PCB levels in biota (Voie et al., 2002). In-situ treatment technologies and among them the chemical degradation of chlorinated organics through reductive dehalogenation using metals or bimetals is one of the alternatives that could be applied for sediment treatment. Zero-valent iron is the most widely studied reducing agent that has been tested to dechlorinate organics. Grittini et al. (1995) was the first to report effective dechlorination of PCBs by palladized iron (Fe/Pd) in a pure solvent system under ambient conditions. Complete dechlorination of Arochlors 1260 and 1254 was achieved in 5-10 minutes. The bimetal was extracted after the reaction to confirm that the removal was not due to adsorption. No PCBs were found in the extracts. Wang and Zhang (1997) also observed complete dechlorination of Arochlor 1254 at ambient temperature but by synthesized nanoscale Fe/Pd particles in a 17-hour time frame. Less than 25% dechlorination was achieved with nanoscale iron alone within the same time period. One difference in this study was that the measured PCB concentrations were based on the dissolved phase only. Korte et al. (2002) reported complete dechlorination of 2,2',3,5'-tetrachlorobiphenyl (BZ 44) in 9 hours by Fe/Pd. The initial rapid dechlorination rate decreased with increasing reaction times for both BZ 44 and Arochlor 1260. At the end of each reaction the Fe/Pd material was extracted and the amount of unreacted PCBs was quantified. This amount did not exceed 10% of the removed PCBs in any of the experiments. Lowry et al. (2004) also observed rapid dechlorination rates of selected PCB congeners by Fe/Pd for the first 2 days of the reaction. After that time period no additional products were formed for a month. Both the aqueous and solid phases were extracted in all batches.

Palladized magnesium (Mg/Pd) is another bimetal that has a very strong reducing potential and has been shown to effectively dechlorinate PCBs under ambient conditions in pure solvents in a matter of minutes or just a few hours (Agarwal et al., 2006; Halle et al., 2005; Engelmann et al., 2003; Wu et al., 2001; Engelmann et al., 2000; Doyle et al., 1998). The purpose of most of these studies was to improve the precision of chromatographic measurement and quantification of complex PCB mixtures by reducing the compounds to biphenyl, a single molecule easily detected by gas chromatography. Doyle et al. (1998) and Engelmann et al. (2000) did report almost complete conversion to this compound. Doyle et al. (1998) warned about potential volatilization of the biphenyl during the dechlorination reaction, but this was not observed in their study on the time scale of 10 minutes. Agarwal et al. (2006) also reported complete conversion of 2-chlorobiphenyl to biphenyl in 1 hour. A kinetic curve was presented for the reaction with a mass balance ranging from 85% to 100% at different time intervals. In addition to pure solvents, Wu et al. (2001) investigated the applicability of the method for total PCB determination in soils and found that the amount of biphenyl formed correlated well with the expected values. On the other hand, Engelmann et al. (2003) observed strong interferences and very small amounts of biphenyl when adding Mg/Pd directly to PCB contaminated soils in solvent slurries. They were more successful when first extracting the PCBs from the soils into acetone and then treating the extract with the bimetal, achieving reasonable biphenyl yields in the latter case.

All of the previous studies that achieved almost complete conversion of PCBs to biphenyl conducted experiments with about 50-60% volume of organic solvents and only 40-50% water. Deviations from these optimum conditions resulted in poor biphenyl yields. Engelmann et al. (2003) observed only very low biphenyl yields as the reactivity of the dechlorination reactions increased, i.e. when using higher %Pd or pure aqueous medium or when dechlorinating higher chlorinated PCBs. The same researchers also observed that in pure water one of the two phenyl rings in biphenyl was saturated with hydrogen and phenylcyclohexane was formed. This process was less significant in mixed aqueous/organic solvents. Morales et al. (2002) reported that only 25% of the reaction products could be accounted for in the dechlorination of chlorinated phenols with Mg/Pd. Both Morales et al. (2002) and Engelmann et al. (2003) hypothesized that the missing mass had been lost through low molecular weight volatile compounds that formed during the dechlorination process.

Halle et al. (2005) investigated the PCB dechlorination potential of Mg/Pd from a different perspective, i.e. the applicability of the process as a remediation technology. The dechlorination of decachlorobiphenyl (BZ 209) and 2,4,5-trichlorobiphenyl (BZ 29) was tested in pure solvents. More than 90% removal was achieved for both congeners in a few hours, 24 hrs for BZ 209 and 2 hrs for BZ 29, but a kinetic curve was only presented for BZ 209. No byproducts were observed for BZ 209 due to the use of selected ion scan mode in the gas chromatographic measurements. In experiments run with BZ 29, biphenyl, mono- and dichlorobiphenyl were identified as byproducts, but the specific congeners and their concentrations were not reported.

Literature specifically describing the reaction of Mg/Pd with Dioxins and PCNs could not be found. However other bimetal catalysts (e.g. $NiCl_2/NaBH_4$) in solvents have been used at laboratory scale for analytical purposes to reduce these compounds to dibenzo-p-dioxin and naphthalene, respectively (Stojkovski et al., 1992; Stojkovski et al., 1991; Kennedy et al., 1982). Stojkovski et al. (1992 and 1991) noted that this approach could also be used as a treatment method. The reaction was very rapid for PCNs (<1 hour) and for Dioxins (<3 hours). This was attributed to the planar structure of both of these compounds. When the reaction was allowed to run longer, further hydrogenation occurred resulting in tetralin ($C_{10}H_{12}$) and decalin ($C_{10}H_{18}$) for the PCN compounds (Stojkovski et al., 1991; Kennedy et al., 1982). Other metal catalyst and solvent-based dechlorination approaches have been studied for the treatment of Dioxins: supported Pd catalysts (Yang et al., 2006; Ukisu et al., 2004; Ukisu et al., 2003), metallic calcium in ethanol (Mitoma et al., 2004), and zerovalent zinc (Adriaens et al., 1996). These studies found that a stepwise chemical dechlorination was possible.

Even though Mg/Pd has been shown to effectively dechlorinate both complex Arochlor mixtures and selected single PCB congeners, there are a number of issues that still need to be addressed to fully understand the processes of this potential remediation technology. The reaction kinetics of PCB dechlorination by Mg/Pd has been investigated in pure solvents to some extent (Agarwal et al., 2006; Halle et al., 2005) but the process is still not fully understood compared to findings reported on the kinetics of PCB dechlorination by Fe/Pd, another bimetal. Such research has not been published to date in the literature for Dioxins and PCNs. Additionally, the relative resistance of positional isomers and congener-specific dechlorination pathways were not yet identified for PCB, Dioxin, and PCN dechlorination by Mg/Pd. Not much information can be found on the identification of reaction products in other than pure solvent mixtures with high % organic solvent content (50-60%) either. Understanding the removal kinetics of chlorinated organics by Mg/Pd, the fundamentals of the dechlorination pathways of single compounds and identifying the reaction end products in pure solvents will help understand the reactions and the products formed in more complex sediment systems and therefore contribute valuable information for the development of an in-situ sediment treatment technology using the Mg/Pd bimetal. This paper discusses the newest findings on the reaction kinetics of PCB, Dioxin, and PCN dechlorination by Mg/Pd and also reports on dechlorination pathways and some byproduct identification.

Materials and Methods

Reagents

High purity, GC-grade solvents (methanol, acetone, hexane, and toluene) were used. Dioxin, PCN and PCB standards were purchased from Accustandard (New Haven, CT) and Ultrascientific (North Kingstown, RI). The purchased standards were either in dissolved (in hexane, in toluene or in methanol) or in neat form. The congeners studied included: octachlorodibenzo-p-dioxin (OCDD), 1,2,3,4-tetrachloronaphthalene (1,2,3,4-TCN), octachloronaphthalene (OCN), Arochlor 1260, biphenyl, 2,2',3,3',4,4',5-heptachlorobiphenyl (BZ 170), 4-monochlorobiphenyl (BZ 3), 2,2',3,3',4,4',5,5'-octachlorobiphenyl (BZ 194) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (BZ 204). The surrogate standard and internal standard were decachlorobiphenyl (BZ 209) and 2,4,5,6-tetrachloro-m-xylene (TCMX), respectively. The magnesium/palladium (Mg/Pd) material was obtained from the National Aeronautics and Space Administration (NASA). Figure 2.1 shows Scanning Electron Micrographs (SEMs) of the Mg/Pd bimetal. The two lower micrographs were obtained using a backscatter detector. The brighter particles are Pd on the surface of the Mg. The Mg particles were 4 μm in diameter and had 0.01% by weight

Pd coating on their surface. The Mg/Pd bimetal should be handled with extra caution due to its high reactivity that can result in an explosion hazard.

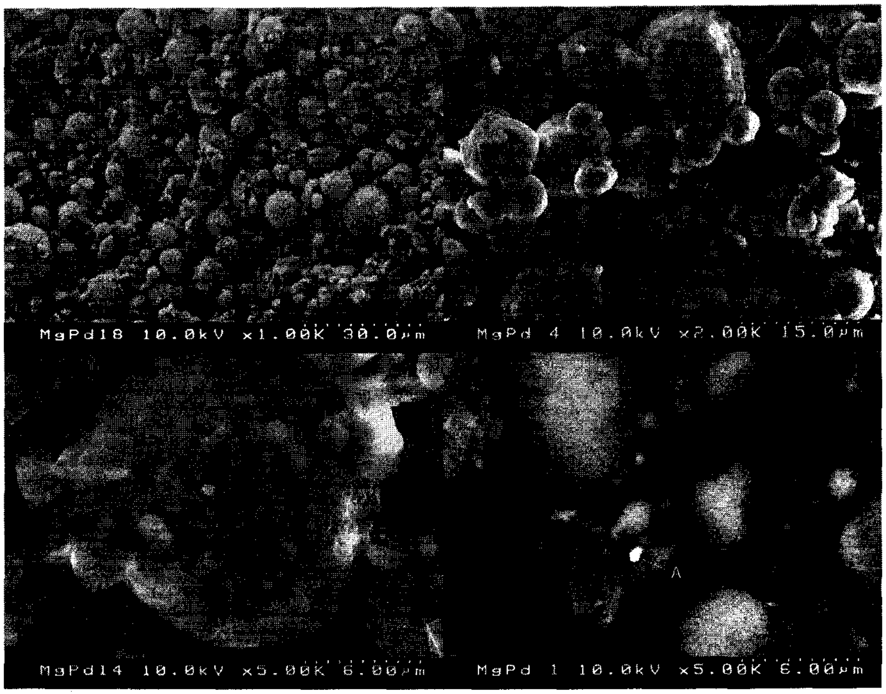


Figure 2.1 Scanning electron micrographs of the Mg/Pd powder (4 μm Mg particles coated with 0.01 % by weight Pd).

Batch Experiments

Laboratory batch experiments were conducted in a pure solvent system made up of 10 or 100 mL 10%/90% or 20%/80% (for BZ 194) (v/v) methanol/distilled water solution. Purchased standards were first dissolved in or spiked into methanol and then diluted with distilled water to make up 2 to 100 ppm batch solutions. The amount of the Mg/Pd added ranged from 0.1 to 1 g. The contaminant loading rates (LR = mass of contaminant / mass of bimetal) ranged from 0.2 mg/g to 10 mg/g in the various batches.

Note, that the LRs calculated for the Pd would be 10^4 times the previously mentioned values (in mg/g).

Experiments were conducted either in 40 mL VOA vials (10 mL batches) or in 125 mL Erlenmeyer flasks (100 mL batches). The Mg/Pd powder was added to the batch reactor either first or last. The solution was thoroughly mixed to ensure a homogeneous mixture of distilled water and Mg/Pd. Timing was started as soon as the contaminants and the bimetal were introduced. The batch reactors were shaken for a given time period by hand and/or on a rotary shaker at 170-200 rpm. Samples were taken at different time intervals, ranging from 1 minute to 2 hours. The volatile fraction of the organics was captured on activated carbon (AC) that was placed into glass columns (Supelco®) and the columns were attached to the batch reactors. The reactors were sealed in all experiments.

Sample Extraction

At given time intervals, samples were extracted into hexane or toluene (for Dioxins) either in a combined fashion or in separate phases. The reagent solution and the Mg/Pd bimetal were extracted together for samples extracted in a combined fashion using manual liquid-liquid extraction. In this method 5 mL hexane was added to 10 mL batch solution and the mixture was vigorously shaken by hand for 3x30 seconds and vented in between. Extractions performed in separate phases involved more steps. To measure the amount of contaminants adsorbed to the Mg/Pd, the bimetal was first filtered using vacuum filtration, then extracted by ultrasonic extraction using a SON-IM Sonicator® from MISONIX Inc. and finally concentrated using a TurboVap® II Concentration

Workstation from Zymark Corporation. EPA's Method 3550B "Ultrasonic Extraction" was followed. The AC was also extracted by sonication. The filtered reagent solution was extracted manually by liquid-liquid extraction. In addition, headspace extraction was also applied in some experiments. Vials used as batch reactors were placed directly into the headspace analyzers without any prior extraction step, which ensured that all volatile compounds were captured.

Gas Chromatographic Analysis

All extracts (except for the headspace experiments) were analyzed using a Varian CP3800 Gas Chromatograph (GC) / Saturn 2200 Ion Trap Mass Spectrometer (MS) with a CP8400 Auto Sampler. The chromatography column was a DB-5 type capillary column (Varian Factor Four VF-5ms), 30m long, 0.25mm ID, and 0.5μm thick. The MS uses an ion-trap detector and was operated in full scan mode (EI/MS) for PCBs and PCNs and in selected ion scan mode (MS/MS) for PCB and dioxin analyses. The column oven temperature program for PCN and dioxin analysis started at 40°C (held 2min), ramped to 180°C at a rate of 15°C/min, and then to 300°C at a rate of 8°C/min, with a final hold of 15 minutes. For PCB analysis the oven temperature program started at 40°C (held 2min), ramped to 184°C at a rate of 12°C/min, then to 280°C at a rate of 4°C/min, and finally to 300°C at a rate of 8°C/min, with a final hold of 4.5 minutes.

Dynamic headspace analysis ("purge and trap") was conducted on an Aligent 6890+ GC / Aligent 5973N MS with a Varian Archon Auto Sampler and a Tekmar-Dohrmann 3100 Sample Concentrator by Resource Laboratories LLC in Portsmouth, NH.

Samples were purged for 11 min at 60 °C. Column oven program: initial 35 °C for 4.0 min, ramped at 15 °C/min to 220 °C, with a final hold for 1.5 min. Column: Restek Rtx-502.2 fused silica capillary column, 20 m long with 0.18 mm ID and 1.0 μm film thickness. Scanned mass range: 20-300 m/z.

Results and Discussion

PCB Kinetic Studies

The dechlorination efficiency of the Mg/Pd material (0.01% by weight Pd), the degradation kinetics and the products formed during the reaction were tested in pure solvents both with Arochlor 1260 and with single PCB congeners BZ 170 and BZ 3. The degradation of biphenyl was also investigated with the bimetal. The pure solvent system consisted of 10% methanol in distilled water. All experimental batches in the kinetic studies were extracted in a combined fashion, i.e. the reagent solution and the bimetal mixed together, therefore the results are not merely showing adsorption to the Mg/Pd.

A kinetic experiment run with Arochlor 1260 indicated about 58% total PCB degradation in just 4 minutes with no significant further increase in dechlorination until the end of 1 hour (Figure 2.2). It was difficult to identify potential byproduct peaks in a PCB mixture. Therefore, further experiments were carried out using single PCB congeners. Kinetic studies conducted with single PCB congeners, BZ 170 and BZ 3 suggested rapid dechlorination in the first few minutes (Figure 2.3). More than 90% removal of BZ 170 was achieved within 10 minutes; after that time no significant degradation was observed. The degradation of BZ 3 occurred at an even faster rate. More than 90% of the initial BZ 3 was degraded in only 1 minute, which also represented the end-point of the reaction for the duration of 1 hour. The faster dechlorination of BZ 3 compared to BZ 170 confirmed that lesser chlorinated congeners dechlorinate more rapidly. Further experiments with BZ 170 revealed that PCB dechlorination decreased as the loading rate increased (Figure 2.3 inset) indicating that the amount of the available bimetal and/or the free surface area of the reducing agent influenced the extent of dechlorination. As previously mentioned, all experimental batches were extracted in a combined fashion therefore the results are not merely showing adsorption to the Mg/Pd. No byproducts were observed in these experiments, which in part may be due to the relative reaction rates of parent compound and partially dechlorinated byproducts.

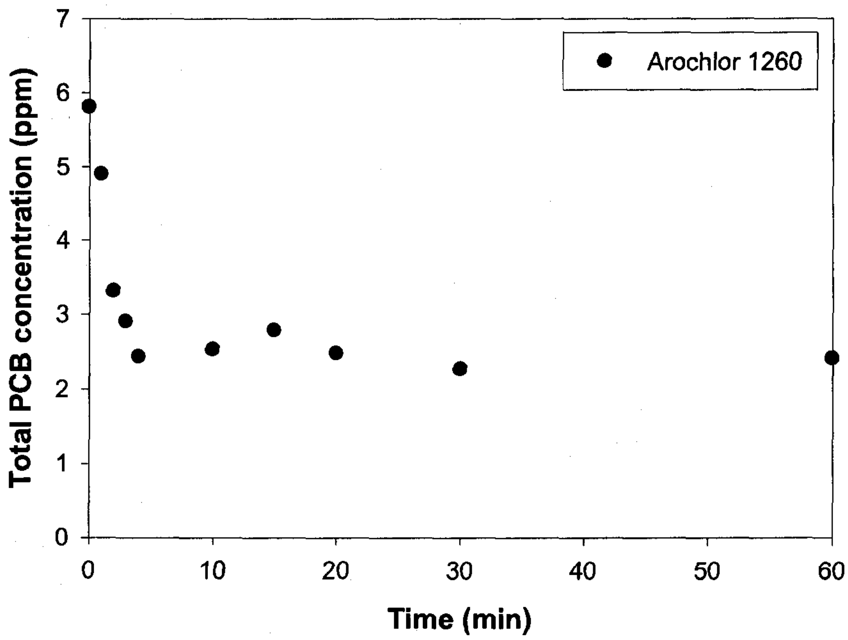


Figure 2.2 Kinetic curve showing the degradation of Arochlor 1260 by Mg/Pd in a 10% methanol-distilled water solution (LR = 0.6 mg/g).

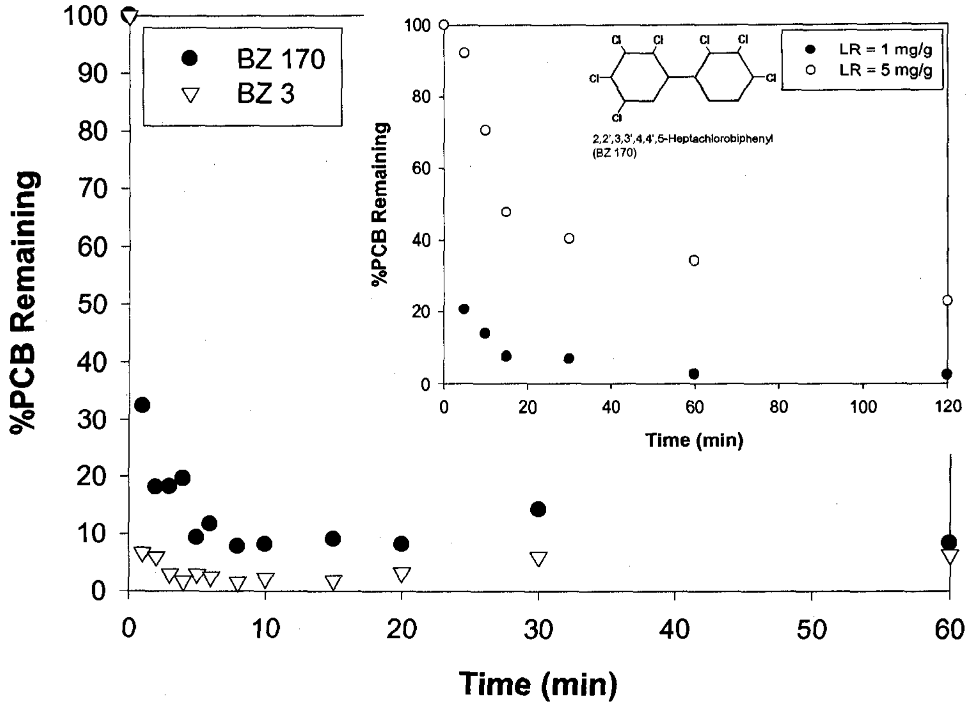


Figure 2.3 Kinetic curves of BZ 170 and BZ 3. The LR for data points on the larger plot was 0.2 mg/g. The inset shows decreased BZ 170 degradation by Mg/Pd with increased contaminant loading rate.

A logical end product for the dechlorination reaction of PCBs would be biphenyl, the hydrocarbon skeleton of a PCB molecule remaining after the removal of all the attached chlorines. However, no emerging biphenyl peaks were observed in any of the single congener experiments in pure systems. To investigate the fate of biphenyl in the present system the behavior of the compound was also tested in the same 10% methanol-distilled water pure solvent mixture. Figure 2.4 depicts the degradation (or disappearance) rate of biphenyl with the addition of 0.1, 0.5 and 1 g Mg/Pd that correspond to 10, 2, and 1 mg/g contaminant loading rates, respectively. While about 80% removal was achieved in 2 hours by adding 0.1 g Mg/Pd to the batch, the addition of higher bimetal masses resulted in almost complete reduction. Similarly to BZ 170, biphenyl degradation decreased with increased loading rates. Experiments conducted with biphenyl proved that Mg/Pd successfully degraded the compound, but the fate of the molecule still remained a question. It was hypothesized that biphenyl was volatilized, adsorbed strongly to the Mg/Pd surface or transformed into some unknown organic compound. To investigate these hypotheses and to better understand the reaction processes, experiments were conducted where the Mg/Pd material was filtered at the end of the reaction and the different phases (i.e. Mg/Pd, reagent solution, and AC that served to capture the volatile fraction) were extracted separately instead of extracting the whole batch together.

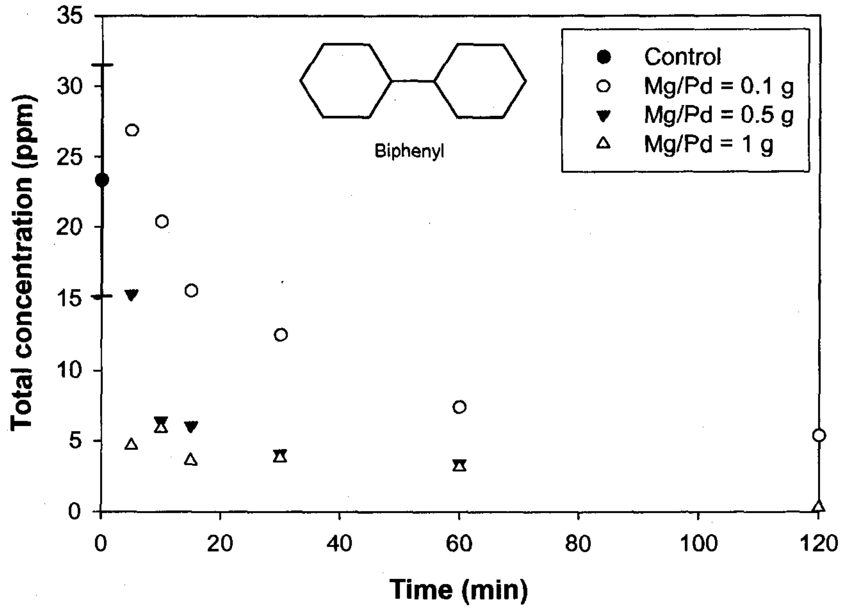


Figure 2.4 Removal of biphenyl from a 10% methanol solution with the addition of 0.1 g, 0.5 g and 1.0 g Mg/Pd (LR = 10 mg/g, 2 mg/g and 1 mg/g, respectively).

Investigating the Dechlorination Reaction in Various Phases

Studies conducted with Arochlor 1260 and biphenyl showed that volatilization was not significant in these experiments (Figure 2.5). About 48% total PCB dechlorination was achieved in experiments with Arochlor 1260 and 95 % degradation was observed in the study of biphenyl in 2 hours. A significant amount of PCBs were extracted from the filtered Mg/Pd material suggesting that PCBs adsorb strongly to the surface of the bimetal during dechlorination. Several researchers suggested that PCB dechlorination occurs while the molecules are adsorbed on the surface of Fe/Pd, another bimetal (Gu et al., 1997; Grittini et al., 1995).

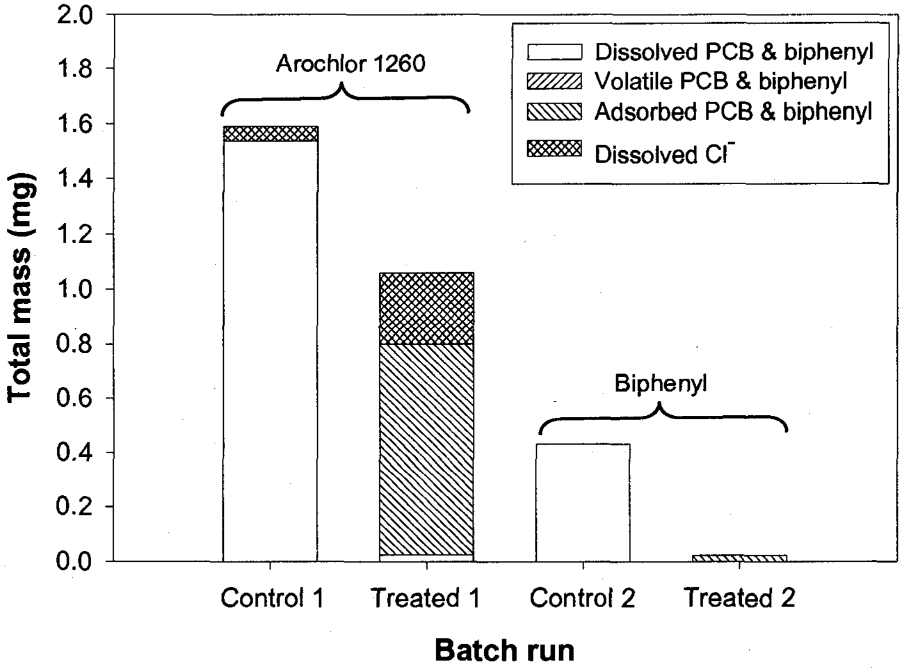


Figure 2.5 Phase distribution of Arochlor 1260 and biphenyl before and after reaction with Mg/Pd (LR = 1 mg/g and t = 2 hours).

Experiments conducted with single PCB congeners BZ 194 and BZ 204 resulted in about 36% dechlorination of BZ 194 and about 50% degradation of BZ 204 in 30 minutes (Figures 2.6 and 2.7). In both experiments, lower chlorinated PCB-congener byproduct peaks were observed in the "adsorbed" phase, i.e. in the extract of the filtered Mg/Pd. Figure 2.8 shows a diagram with the identified byproduct peaks and potential dechlorination pathways for the reaction of BZ 204. A stepwise dechlorination process is likely to have occurred. The last identified compound in the pathway was 2,2',6,6'-tetrachlorobiphenyl, or BZ 54, suggesting that ortho-chlorines were removed last. These findings are in agreement with results reported in the literature for PCB dechlorination by Fe/Pd, another bimetal. Stepwise dechlorination was suggested for Fe/Pd by many researchers (Kim et al., 2004a; Korte et al., 2002; Gu et al., 1997). Kim et al. (2004a) found that the preferential removal order for the different chlorine positions was: para > meta > ortho. Korte et al. (2002) also reported that chlorines in the meta position were more reactive than those in the ortho position.

Biphenyl was not detected in any of the samples, suggesting that it further breaks down or complexes into some unidentified organic compound. Terphenyls, quaterphenyls, cyclohexylbenzene (i.e. phenylcyclohexane) and bicyclohexyl that could form from biphenyl either through polymerization or hydrogenation reactions (Nomura et al., 2005; Kim et al., 2004b; Engelmann et al., 2003), were tested, but they were not identified in the treated samples. Headspace experiments conducted with biphenyl tentatively identified cyclohexane and phenylcyclohexane as potential by-product peaks, although in very small amounts. It was hypothesized that the reaction might proceed all the way to carbon dioxide. This hypothesis could not be quantitatively investigated due to carbon dioxide interference in the headspace instrument from the ambient air.

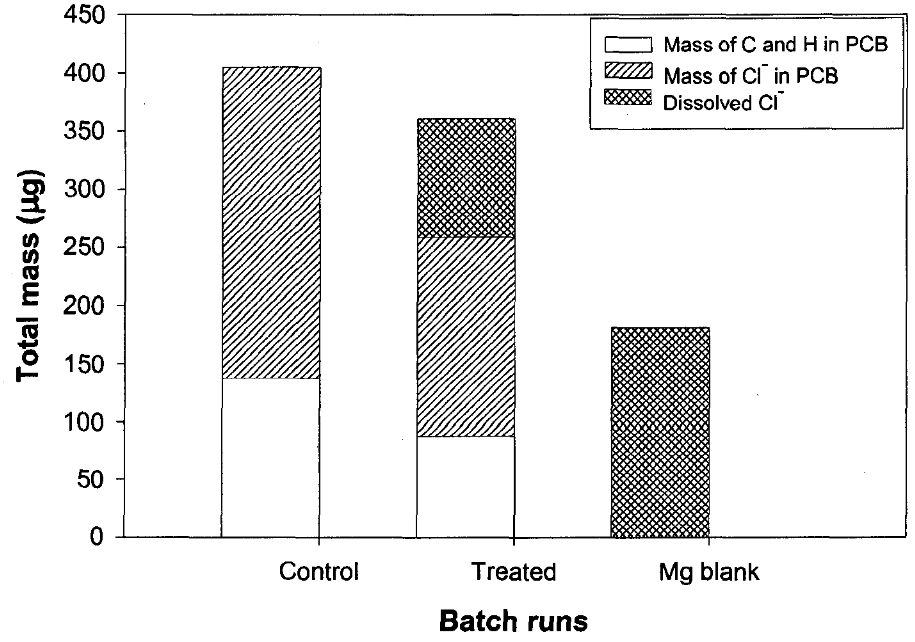


Figure 2.6 Total PCB and chloride measurements of BZ 194 after 30 min reaction with Mg/Pd (LR = 1 mg/g). "Mg blank" = Mg/Pd mixed in uncontaminated reagent solution.

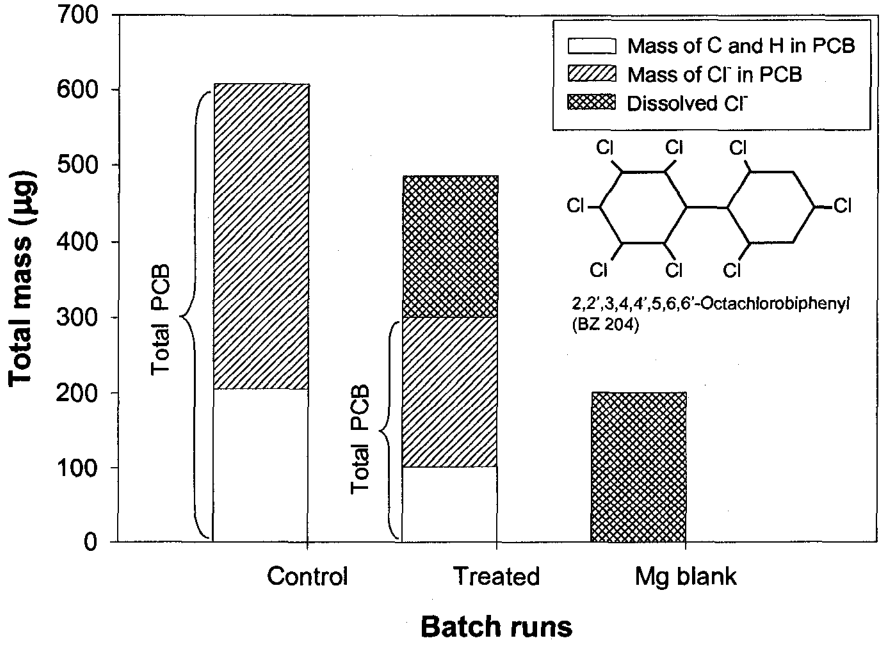


Figure 2.7 Total PCB and chloride measurements of BZ 204 after 30 min reaction with Mg/Pd (LR = 1 mg/g). "Mg blank" = Mg/Pd mixed in uncontaminated reagent solution.

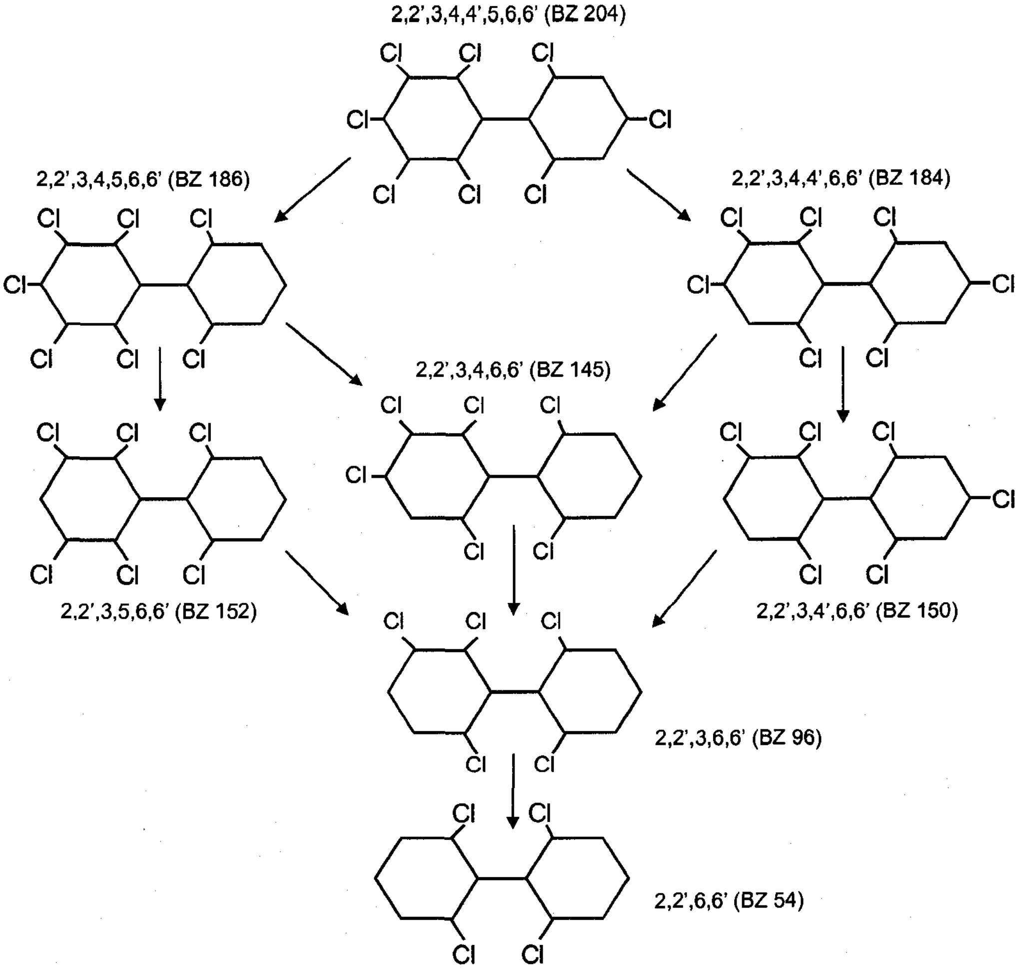


Figure 2.8 Diagram showing potential dechlorination pathways of BZ 204.

PCN and Dioxin Kinetic Studies

Experiments were conducted with single congeners of PCN and Dioxin (1,2,3,4-TCN, OCN, and OCDD) to confirm reactivity with Mg/Pd occurs similarly to that observed with PCBs. The same methods were employed for the reaction and extraction. A reduction in concentration was observed for all tested compounds. Figure 2.9 shows a GC/MS chromatogram depicting an OCDD control and a sample reacted with Mg/Pd in

10% methanol-water solution for 1 minute. Dibenzo-p-dioxin (DD), the anticipated end product, was not found at the expected retention time. A search was conducted for the most toxic Dioxin, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) to confirm it was not generated. This compound was also not found. Kinetic studies were completed for 1,2,3,4-TCN, OCN and OCDD resulting in 95%, 80%, and 69% reduction respectively after 30 minutes (Figure 2.10). As noted in most of the PCB experiments, no byproducts were observed. The loading rates for these experiments were 1 mg/g for the PCNs and 0.5 mg/g for the OCDD. If all of the loading rates were one, we might expect the OCDD curve to be even higher given the lower ratio of Mg/Pd to contaminant. This preferred reaction for PCNs over dioxins is in agreement with Adriaens et al. (1996) and Yang et al. (2006) who cited slow reactions with dioxins attributed to the stability of the ether bond.

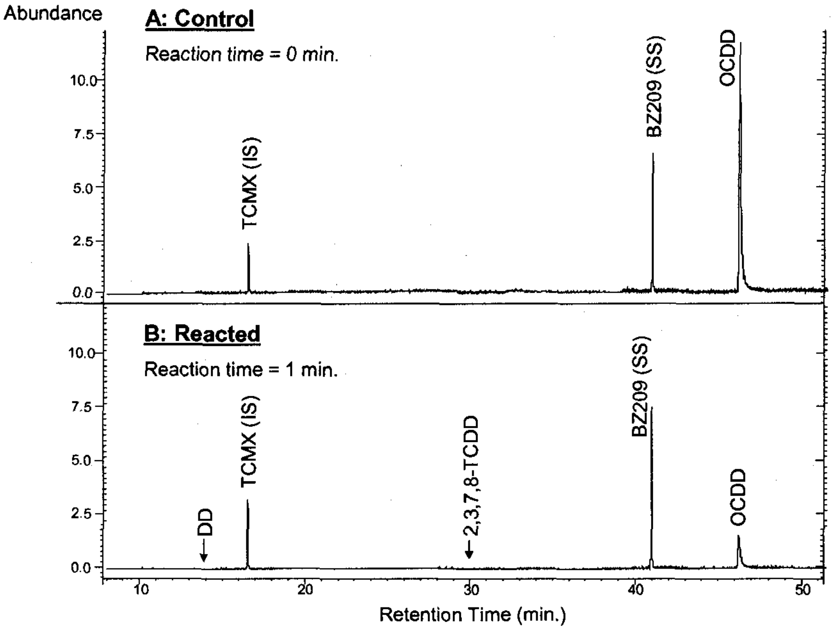


Figure 2.9 GC/MS chromatogram demonstrating that 2378-TCDD and dibenzo-p-dioxin (DD) were not the final products in the reaction of OCDD with Mg/Pd. The top (A) shows the control sample with OCDD contaminant, and TCMX and BZ 209 as the internal and surrogate standards. The bottom (B) shows 66 % removal of OCDD after 1 minute reaction and no apparent products.

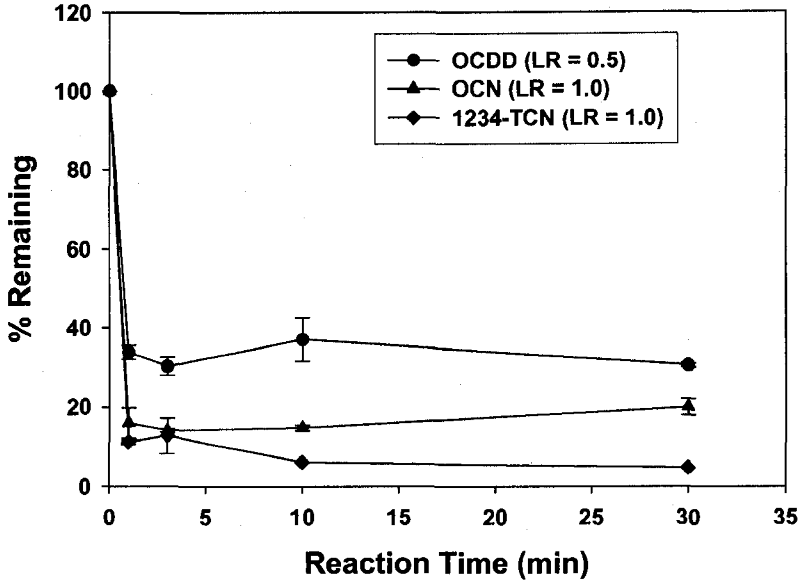


Figure 2.10 Kinetics for the reaction of OCDD, OCN, 1234-TCN with Mg/Pd in 10% MeOH/water solution [LR = loading rate (mg contaminant/g Mg/Pd)]. The reaction proceeds further for the PCNs compared to the dioxin even with a higher loading rate. The majority of removal occurs in the first minute followed by a leveling off of the curve.

Given the quick removal of the contaminant and lack of apparent byproducts, it was theorized that the starting contaminant or the products were not successfully extracted from the Mg/Pd surface. This was tested by filtering the reacted solution and extracting the dissolved phase independently of the Mg/Pd which was subjected to the more rigorous ultrasonic extraction method (Figure 2.11). The mass found adsorbed to the Mg/Pd does not account for the bulk of the contaminant mass which was not recovered after two hours reaction (88% for OCN), therefore, the observed removal rates cannot be explained my mere adsorption.

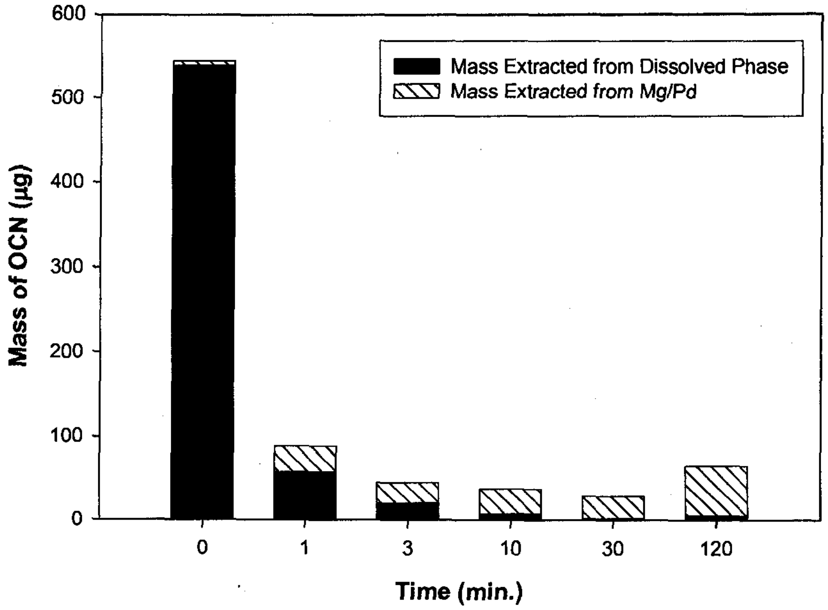


Figure 2.11 Relative mass of OCN found in the dissolved phase vs. adsorbed to Mg/Pd surface over a 120 min. reaction in 50% isopropyl alcohol/water solution. 88% mass removal of OCN was achieved. The contaminant found adsorbed to the Mg/Pd surface does not account for the overall reduction in measured OCN.

Conclusions

This work examined the efficiency of Mg/Pd to dechlorinate PCBs, Dioxins, and PCNs in pure solvent systems. The dechlorination kinetics, the reaction pathways and the products formed were also investigated. Removals greater than 90% were achieved in a matter of minutes or a few hours for each of the tested contaminants. Lower chlorinated PCB congeners were identified in some experiments run with single PCB congeners, proving that dechlorination was occurring. Pathways of a stepwise dechlorination process were suggested in which chlorines in the ortho position were removed last. A satisfactory mass balance in solvent mixtures with low % organic solvent content (10-20%) could not be achieved for PCBs because of the reaction of the biphenyl. Generally, it appears that a reaction takes place between chlorinated organics and Mg/Pd leading to a reduction in contaminant concentration and consequently overall toxicity. Furthering the understanding of this reaction could support the development of its use for treatment of contaminated sediments.

Supplemental Material to Polychlorinated Biphenyl Dechlorination Experiments Conducted in Pure Solvents

This supplemental material contains results of laboratory experiments conducted on polychlorinated biphenyl (PCB) dechlorination or biphenyl degradation by magnesium/palladium (Mg/Pd) in pure solvents that complement the findings described in Chapter 2 of this work.

PCB Dechlorination and the Effect of Relative Solvent Amount on the Extent of the Dechlorination Reaction

Dechlorination experiments were conducted in pure solvents (a 10% methanol: distilled water solution) using single PCB congers or commercially available PCB mixtures. One of the goals of these experiments was to prove that dechlorination was the removal mechanism and not adsorption. Figure 2.12 shows a set of lower chlorinated PCB congeners that were identified as dechlorination by-products of 2,2',3,4,4',5,6,6'-octachlorobiphenyl (BZ 204) when reacted with Mg/Pd for 30 min, indicating that dechlorination did occur. Figure 2.8 in Chapter 2 of this work depicts potential dechlorination pathways of the parent compound constructed from the by-product peaks shown in Figure 2.12.

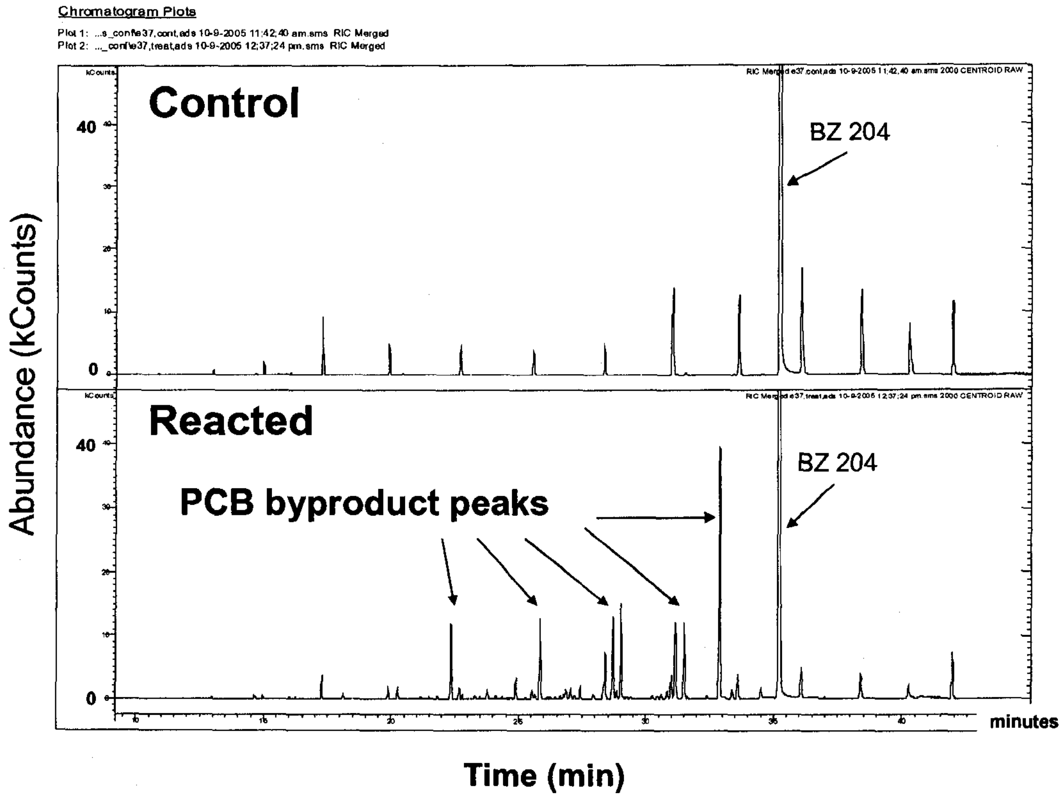


Figure 2.12 A set of lower chlorinated PCB congeners were identified as dechlorination by-products of 2,2',3,4,4',5,6,6'-octachlorobiphenyl (BZ 204) (reaction time = 30 min; LR = 1 mg/g).

Another question that was investigated was the effect of % methanol in the reaction solution on the extent of the dechlorination reaction. Figure 2.13 shows that % removals of an Arochlor 1260 solution varied depending on the composition of the reaction solution. The highest dechlorination was achieved in a 50% methanol: distilled water solution. Note, that the optimum solvent composition to achieve the highest dechlorination was not determined.

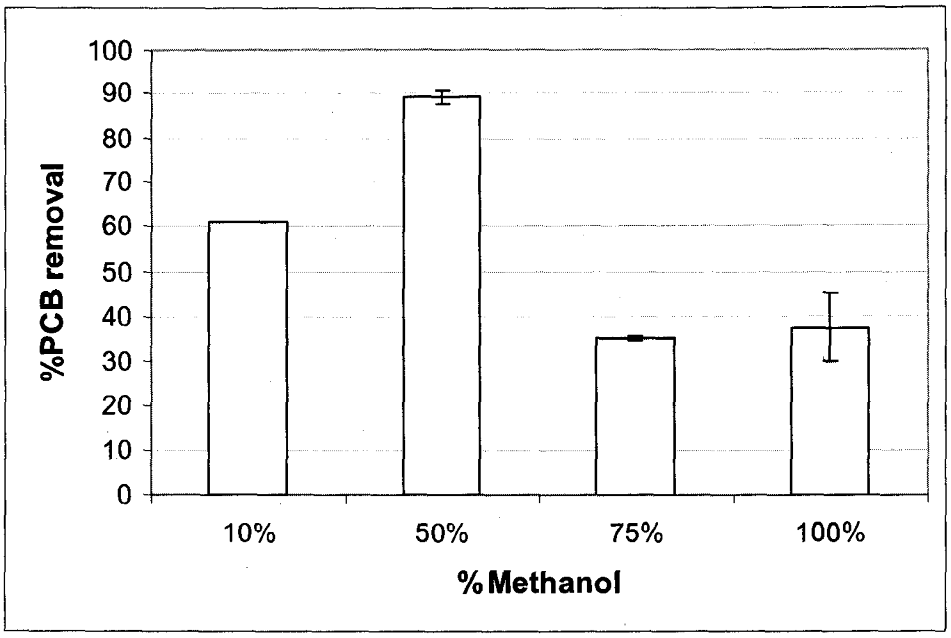


Figure 2.13 % PCB removal shown as the function of % methanol content of the reaction solution (PCBs: Arochlor 1260; reaction time = 30 min; LR = 0.6 mg/g).

Biphenyl Degradation

The Mg/Pd material did not just dechlorinate PCBs, but it also degraded biphenyl, the hydrocarbon skeleton of these compounds. Experiments were conducted with biphenyl in pure solvents to search for the reaction end-products.

Rapid reaction. The kinetics of biphenyl degradation by the Mg/Pd were described in Chapter 2 (see Figure 2.4). If enough Mg/Pd was added to the reactor relative to the amount of PCBs, rapid and complete degradation of biphenyl was observed in a 10% methanol: distilled water solution (Figure 2.14); biphenyl degradation ranged from 93% to 97% in just 4 min for loading rates of 0.4 mg/g and 0.2 mg/g, respectively.

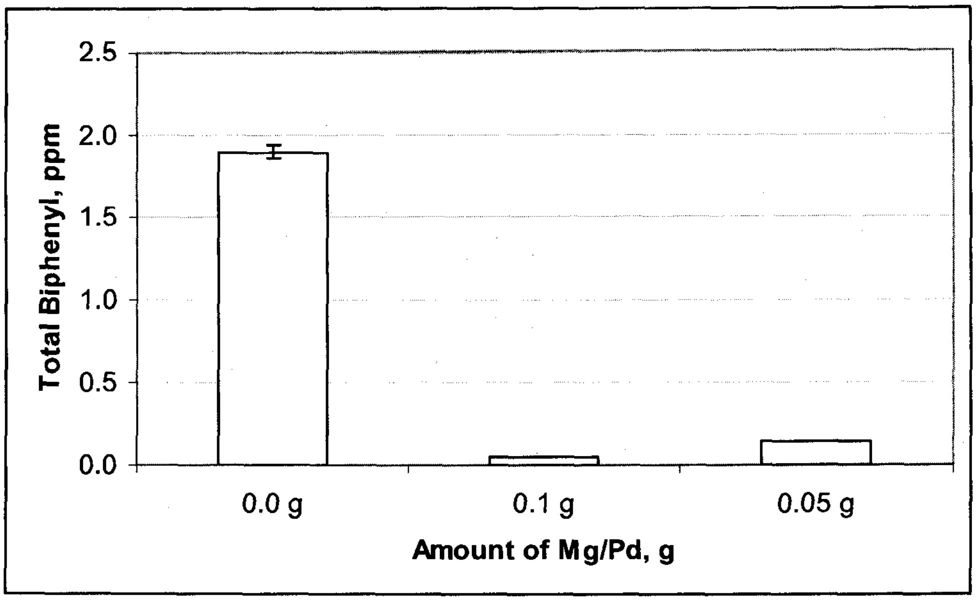


Figure 2.14 Rapid and complete degradation of biphenyl by Mg/Pd was observed in a 10% methanol: distilled water solution; biphenyl degradation ranged from 93% to 97% when adding 0.05g or 0.1 g Mg/Pd, respectively (LR = 0.4 mg/g and 0.2 mg/g; reaction time = 4 min).

Search for potential degradation by-products using headspace analysis. Headspace experiments were conducted to investigate the fate of biphenyl when reacted with Mg/Pd and to search for potential by-products of the reaction. Details of the experimental setup and the results are discussed below.

Reagents: Neat biphenyl standards were purchased from Ultrascientific (North Kingstown, RI) and from Sigma-Aldrich Co. (St. Louis, MO). Purge and trap grade methanol was purchased from Fisher Scientific (Hampton, NH). The magnesium/palladium (Mg/Pd) material was obtained from the National Aeronautics and Space Administration (NASA). The Mg particles were 4 μm in diameter and had 0.01% by weight Pd coating on their surface.

Headspace experiments: Experiments were conducted either in 40 mL VOA vials (20 mL batches) or in 20 mL headspace vials (10 mL batches). Samples sent to RL contained 0.2 g Mg/Pd mixed with 20 mL 5 mg/L biphenyl in 10%/90% (v/v) methanol/distilled water solution. Samples analyzed at UNH contained 0.1 g Mg/Pd mixed with 10 mL of saturated biphenyl solution (about 9.3 mg/L) in degassed distilled water (Photo 2.1). The samples analyzed at UNH were prepared in a controlled N_2 or N_2/O_2 environment (Photo 2.2). Vials used as batch reactors were placed directly into the headspace analyzers without any prior extraction step, which ensured that all volatile compounds were captured. The analyses were performed after 30 min to 5 hours reaction time.

Gas chromatographic analysis: Dynamic headspace analysis ("purge and trap") was conducted on an Aligent 6890+ Gas Chromatograph (GC) /Aligent 5973N Mass Spectrometer (MS) with a Varian Archon Auto Sampler and a Tekmar-Dohrmann 3100 Sample Concentrator by Resource Laboratories LLC (RL) in Portsmouth, NH. Samples were purged for 11 min at 60 °C. Column oven program: initial 35 °C for 4.0 min, ramped at 15 °C/min to 220 °C, with a final hold for 1.5 min. Column: Restek Rtx-502.2 fused silica capillary column, 20 m long with 0.18 mm ID and 1.0 μm film thickness. Scanned mass range: 20-300 m/z.

Static headspace analysis was conducted both at RL and at the University of New Hampshire (UNH). A Hewlett-Packard (Agilent) 5890 GC with a Flame Ionization Detector (FID) was used at RL applying manual injections. Samples were equilibrated at room temperature (25 °C) before analysis. Column oven program: isothermal temperature program at 70 °C for 7.5 min. Column: Restek Rt-Alumina Aluminum Oxide Porous Layer Open Tubular ("PLOT") column, 30 m long with 0.53 mm ID and 6.0 μm film thickness. At UNH, a Perkin Elmer AutoSystem XL GC with a Turbomatrix 110

Headspace Sampler and a FID was used. Samples were equilibrated at 90 °C for 20 min before analysis. Column oven program: initial 150 °C for 2.0 min, ramped at 20 °C/min to 250 °C, with a final hold for 23 min. Column: Restek Rtx-502.2 fused silica capillary column, 105 m long with 0.53 mm ID and 3.0 μm film thickness. The FID made it possible to scan for lower molecular weight compounds than the MS that could be potential by-products resulting from the degradation of the biphenyl.

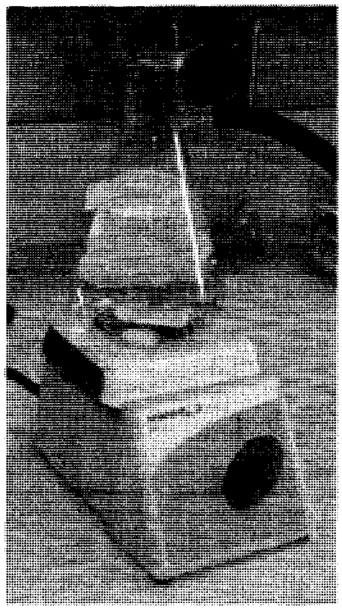


Photo 2.1 Distilled water was agitated under vacuum using a magnetic stirrer to remove CO_2 and O_2 from the solution.

Photo 2.2 Headspace experiments were conducted in a controlled environment (with N_2 or N_2/O_2 present) using a glove box that was sealed from the surroundings; a CO_2 probe within the glove box helped monitor the required conditions.

Results and discussion: Headspace experiments were conducted to identify the fate of biphenyl when reacted with Mg/Pd and to close the carbon mass balance of the system. The two main objectives were to: 1) Identify organic molecules that might form from biphenyl either through degradation or complexation, including compounds that are not detected on the GC/MS, and to 2) investigate volatilization of both biphenyl and any potential by-products.

Figure 2.15 depicts a HS-GC/MS chromatograph showing potential by-product peaks. The tentatively identified compounds were cyclohexane (RT = 6.44 min) and phenylcyclohexane (RT = 17.36 min). However, none of these peaks represented a large enough amount of the given compounds to be able to account for the missing mass in the mass balance of the system. A residual biphenyl peak was observed at 18.54 min on the same figure.

The FID made it possible to scan for lower molecular weight compounds (e.g. methane) than the MS that could be potential by-products resulting from the degradation of biphenyl. Early time results (< 1.2 min) of a HS-GC/FID chromatograph are shown in Figure 2.16. Three peaks showed up at less than 1 min in much higher amounts in the treated samples than in the 10% methanol blank and in the biphenyl control. Based on a test mix run on the same column these peaks had the same retention times as the following compounds: methane (RT = 0.78 min), ethane (RT = 0.82 min), and propane (RT = 0.94 min). However, the Mg/Pd blank contained the same peaks indicating that these compounds were not products of biphenyl degradation. Samples prepared in degassed distilled water in a controlled N_2 or N_2/O_2 environment and analyzed on the HS-GC/FID yielded similar results (Figure 2.17), i.e. peaks observed in the treated samples also showed up in the Mg/Pd blank and therefore no potential by-product peaks could be identified (note: samples were analyzed with slightly different retention times, therefore peak heights cannot be compared directly).

Overall, in headspace experiments no significant biphenyl volatilization was observed upon reaction with the Mg/Pd. A large missing mass in the mass balance still could not be accounted for and it was hypothesized that the degradation/complexation products strongly adsorbed to the Mg/Pd material and could not be recovered with sonication or headspace extraction.

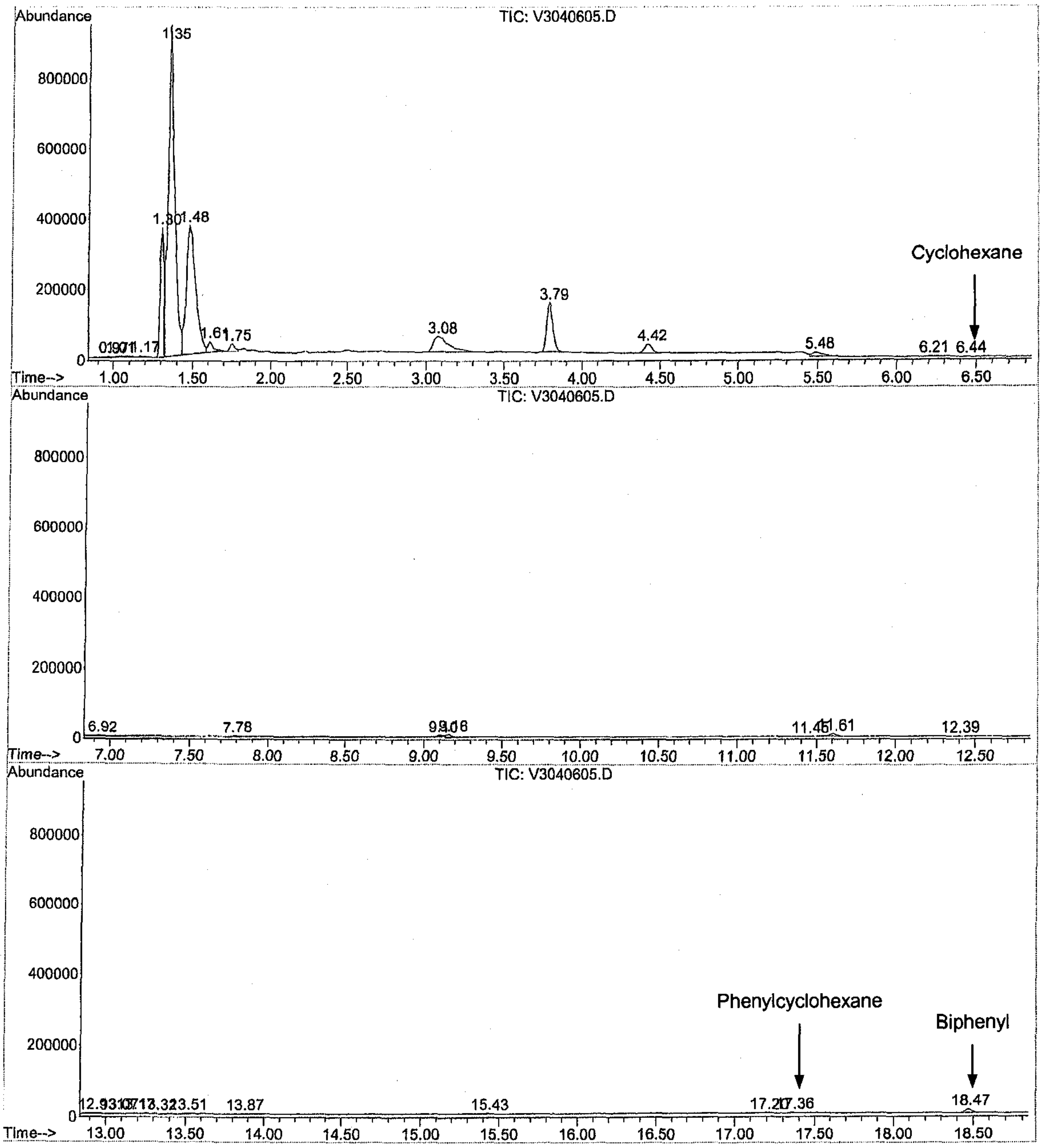


Figure 2.15 HS-GC/MS chromatograph of a 5 mg/L biphenyl solution treated with Mg/Pd showing potential by-product peaks.

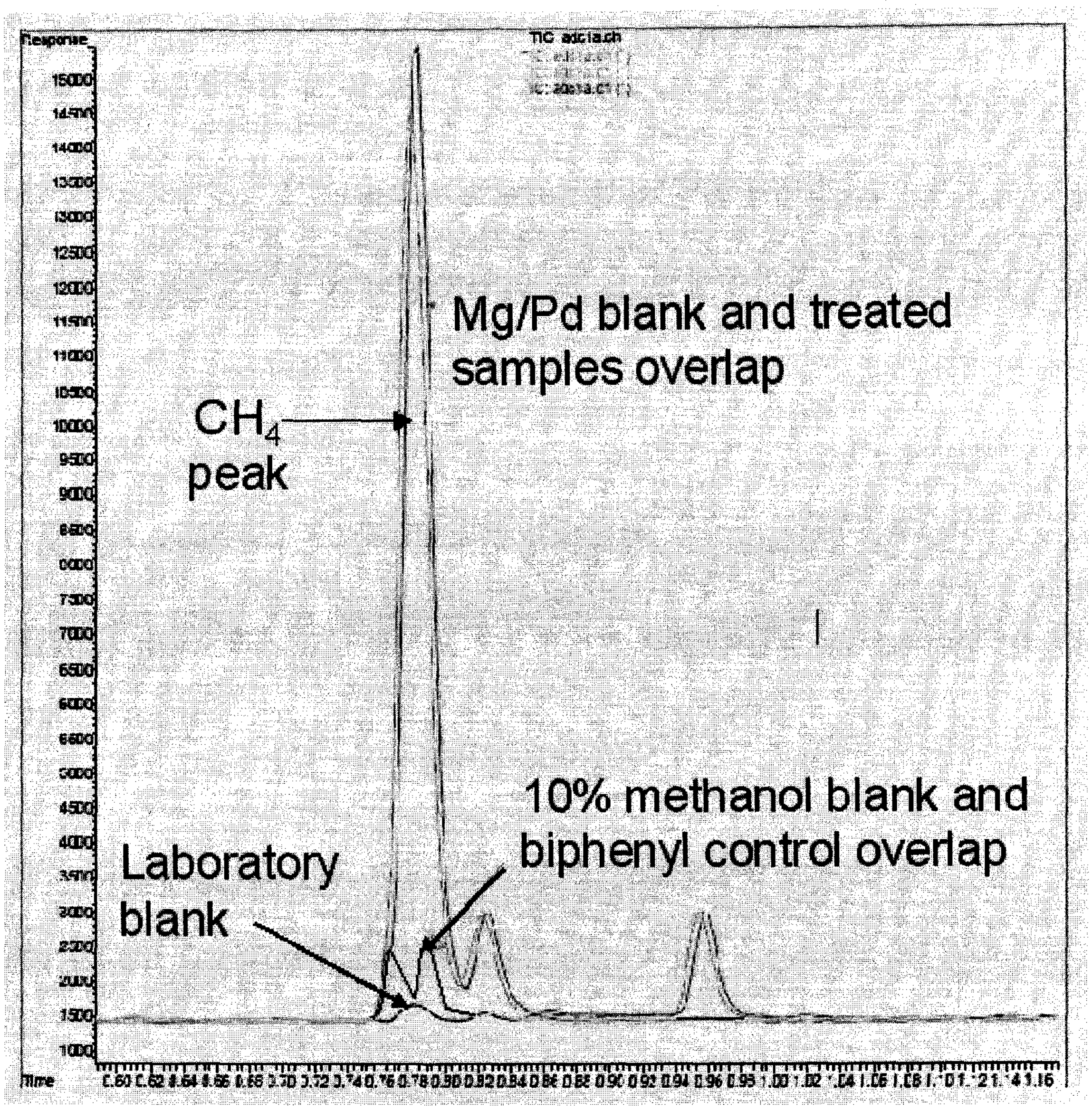


Figure 2.16 HS-GC/FID chromatographs for laboratory blank (pure water), biphenyl control (in 10% methanol), 10% methanol blank, Mg/Pd blank (Mg/Pd in 10% methanol), and treated samples.

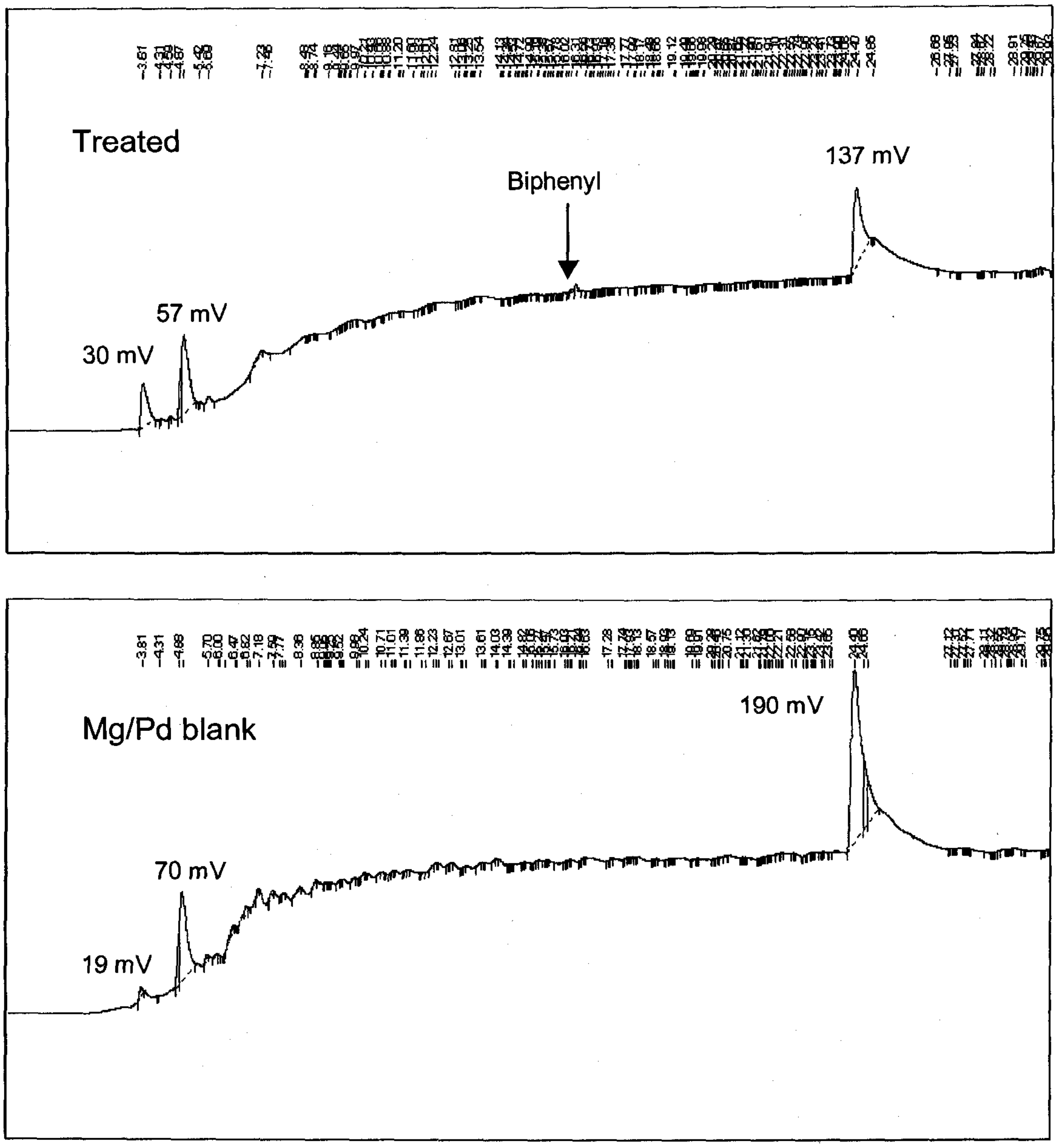


Figure 2.17 HS-GC/FID chromatographs of a treated sample and a Mg/Pd blank.

CHAPTER 3

POLYCHLORINATED BIPHENYL DECHLORINATION AND BIOAVAILABILITY IN MARINE AND FRESHWATER SEDIMENTS IN THE PRESENCE OF VARIOUS SOLVENTS

Abstract

Polychlorinated biphenyls (PCBs) are persistent and toxic pollutants found in our environment with high localized concentrations in soils and sediments. Their remediation in soils and sediments is difficult due to the variability of soil and sediment characteristics that affect PCB availability. In this work, aged PCB contaminated sediments were treated using palladized magnesium (Mg/Pd) to investigate whether significant degradation of PCB congeners represent a possible in-situ or ex-situ treatment technology. The extent of dechlorination correlated with the organic and silt/clay content of the sediments. The higher organic and silt/clay content New Bedford Harbor sediment had lower overall dechlorination than the sandy Housatonic River sediment with lower organic content; PCB desorption from the sediments did not limit dechlorination rates. Congener specific analysis demonstrated that nearly all the compounds were dechlorinated. Formation of lower chlorinated congeners could be observed in the Housatonic River sediment, mostly pentachlorobiphenyls or lesser chlorinated congeners. No co-planar congeners were formed. The most common chlorine substitution in the

lower chlorinated congeners formed was the ortho position, indicating that ortho chlorines were removed last. The average reduction in toxicity after treatment was 48.6%. The use of three polar organic solvents (methanol, ethanol and isopropanol) to enhance dechlorination by increasing contaminant solubility proved to be inefficient in both sediments when compared to water. The bioavailability of PCBs decreased by 78.0%, 59.9%, and 66.7% in the sandy Housatonic River sediment in the presence of water, ethanol and isopropanol and with associated mass removals of 48.3%, 52.2% and 17.9%, respectively, indicating that the majority of the contaminants that were not accessible for dechlorination were not bioavailable.

Introduction

Polychlorinated biphenyl (PCB) contamination in sediments remains a significant problem in many waterways and water bodies in the US and around the world. Their ubiquitous presence in the environment, recalcitrance and hydrophobicity has maintained their presence in the food chain despite the long ban on PCB manufacture and use. Current contaminated sediment management options include: dredging followed by containment or ex-situ treatment, monitored natural recovery, capping, and in-situ chemical or biological treatment. Dredging is the most common alternative used (USEPA, 2005), even though it is costly and it inherently contains several issues that need to be addressed. One of the issues is the potential for sediment resuspension that can result in the downstream transport of PCBs and in the dissolution of the contaminants into the water column, both of which can potentially worsen the problem of toxic exposure of aquatic organisms and humans. For example, Voie et al. (2002) reported that a dredging operation in contaminated marine fjord sediments was unsuccessful in terms of lowering PCB levels in biota. Even if the dredging operation is successful, the dredged sediments still need to be disposed of in a proper manner, i.e. in confined aquatic or land disposal cells. Although it might be more desirable to treat the dredged sediments with an ex-situ technology, these processes impose additional costs. On the other hand, an important benefit to both ex-situ and in-situ treatment processes is that PCBs are broken down into less harmful or harmless compounds, thus eliminating or reducing the future risk of toxic chemicals entering the food chain. Choosing the right technology for a specific site is a decision that should be based on the fine balance between many factors. Economics, contaminant mass and risk reduction and the available time for treatment are a few examples of factors that need to be considered.

Of the previously mentioned management options, in-situ treatment technologies are the most innovative and still the least common in real world applications. The major advantage of these technologies is that dredging is not involved and therefore the risk of toxic exposure maybe substantially reduced. In-situ treatments can either be biological or chemical. While processes like natural recovery or enhanced biodegradation might take several years to achieve reasonable degradation levels (Drenzek et al., 2002; Sokol et al., 1998), chemical treatment processes may achieve the same or better removals in a matter of days or hours. Chemical degradation of chlorinated organics through reductive dehalogenation using metals or bimetals is one of the alternatives that could be applied for sediment treatment in both in-situ and ex-situ conditions. PCBs have been shown to dechlorinate chemically with the addition of zero valent metals such as iron (Grittini et al., 1995). Only partial dechlorination of PCBs was achieved in water at ambient temperatures with nanoscale iron (Lowry et al., 2004). The addition of the catalyst palladium to the iron was found to increase the rate of the dechlorination (Lowry et al., 2004; Doyle et al., 1998), achieve higher dechlorination (Doyle et al., 1998), and has even been shown to dechlorinate PCBs in extracts from soils (Engelmann et al., 2003; Korte et al., 2002) and in sediment slurry supernatants (Fang et al., 2007). The dechlorination reaction is more efficient with the combination of the metal and catalyst because of the thermodynamic force associated with the metal corrosion and the catalytic hydrogenation of the palladium (Engelmann et al., 2003).

Another bimetal that has a very strong reducing potential is magnesium (E^0 = -2.022 V) coated with palladium (Doyle et al., 1998). Palladized magnesium (Mg/Pd) can achieve greater dechlorination than palladized iron (Engelmann et al., 2003) and it has been shown to effectively dechlorinate PCBs under ambient conditions in pure solvents in a matter of minutes to a few hours (Hadnagy et al., 2007; Agarwal et al., 2007; Agarwal et al., 2006; Wu et al., 2001; Engelmann et al., 2000; Doyle et al., 1998). Wu et al. (2001) showed effective dechlorination of the same contaminants in soil and sediment matrices over a period of 2 to 6 hours. More recently, Agarwal et al. (2007) reported complete dechlorination of 2-chlorobiphenyl in soil and sediment slurries over 12 hours. PCB dechlorination has been reported to yield byproducts such as biphenyl (Wu et al., 2001; Engelmann et al., 2000; Doyle et al., 1998) and other lower chlorinated congeners (Hadnagy et al., 2007). However, the formation of biphenyl and lower chlorinated congeners are not always good indicators of dechlorination because their yields can be affected by the reactivity of the dechlorination reaction, i.e. the amount of palladium and the organic solvent content (Engelmann et al., 2003).

Biodegradability of persistent organic pollutants like PCBs in soils is controlled by the rate and extent of desorption from the solid phase (Krauss et al., 2005), which relates to the compound's availability for degradation. Solvents can increase contaminant availability by increasing their solubility. Krauss et al. (2001) investigated the soil-water partitioning of PAHs and PCBs and found that contaminants became more available as the % methanol used increased. Similarly, Smith et al. (2004) reported increased DDT availability in soils in the presence of ethanol or 1-propanol. Furthermore, Lee et al. (2001) observed that ethanol enhanced PAH biodegradation in soils due to solubilization of the compounds by the solvents. Even though solvents increase PCB availability by increasing their solubility they can also decrease the dechlorination efficiency by bimetals. Korte et al. (2002) observed that as the concentration of ethanol or isopropanol increased dechlorination by palladized iron became slower in the range of 40 to 60% solvent content probably due to the decrease in hydrogen production and the increase in solubility of the PCB in the liquid phase. Similarly, Fang et al. (2007) observed slower dechlorination rates with increased methanol content (0 to 30%) when dechlorinating 2-chlorobiphenyl using palladized iron. On the other hand, Agarwal et al. (2007) found that Mg/Pd completely dechlorinated 2-chlorobiphenyl in soil and sediment slurries prepared with either pure water or a 1:1 water-acetone mixture. These studies suggest that for certain solvent and bimetal combinations it is important to find an optimum balance between the positive effect of solvents making contaminants more available and their negative effect of making the dechlorination process slower.

A key aspect of treatment performance evaluation is the assessment of contaminant bioavailability in relation to mass removal. Contaminants that remain in the sediment after treatment might be so strongly sorbed to solid particles that they might not be available to benthic organisms and therefore they would not pose bioaccumulation or toxicity risks to the food chain. Understanding how the Mg/Pd dechlorination treatment affects PCB bioaccumulation and whether the treatment contributes to toxicity to benthic organisms is important when developing a new in-situ sediment remediation technology. Conventionally, the bioavailable fraction of organic contaminants has been measured using test organisms. The notion that the bioavailable fraction of contaminants in soils and sediments can be well estimated with the pore water concentration of these compounds led to the development of various surrogate chemical methods that accumulate organic compounds in a similar way to living organisms and could be used as alternative approaches to estimate contaminant bioavailability. Examples of such chemical surrogate methods are: solid phase microextraction (You et al., 2006; Van der Wal et al., 2004; Kraaij et al., 2003), Tenax extraction (You et al., 2006; Kukkonen et al., 2004), or the use of semipermeable membrane devices (Lyytikainen et al., 2003a; Lyytikainen et al., 2003b). These chemical surrogate techniques represent a simple and cost-effective alternative for contaminant bioaccumulation assessment. The method of matrix solid phase microextraction (SPME) was used in the present study. This method uses a thin silica fiber that is coated with a microlayer of organic polymer (e.g. polydimethylsiloxane for PCBs) to mimick the bioconcentration of dissolved organic contaminants (Mayer et al., 2003). A number of studies in the literature found that using SPME fibers is a good surrogate method to using benthic organisms and they also established a relationship between contaminant bioavailability estimates by SPME fibers and concentrations found in organisms (You et al., 2006; Kraaij et al., 2003). For example, You et al. (2006) found that the uptake of PCBs in SPME fibers and in the freshwater oligochaete *Lumbriculus variegatus* compared well in spiked as well as in field-contaminated sediments.

The main goal of this research was to test the viability of PCB dechlorination by Mg/Pd as a sediment remediation technology that could be used either in an in-situ or an ex-situ scenario. Previous studies have shown PCB degradation by Mg/Pd in soil and sediment matrices (Agarwal et al., 2007; Wu et al., 2001). However, both these studies used soils/sediments that were processed prior to the reaction. The soils/sediments were dried, some ground, and sieved to smaller particle sizes, and most were spiked with PCBs, resulting in higher availability of the contaminants compared to the original wet sediment matrix. Even Wu et al. (2001) reported that as the soil/sediment particle size increased the required reaction time for total dechlorination also increased. Furthermore, the goal of that study was to convert PCBs to biphenyl for analytical purposes and an excess amount of Mg (200% based on dry soil/sediment weight) was applied that would not be economical in a remedial treatment scenario. The study by Agarwal et al. (2007) investigated the reaction as a potential remediation technology, but as previously mentioned, pre-processed sediments were used and the reaction was performed in a very dilute slurry form making the PCBs more available. The present work was the first to use aged, PCB contaminated sediments in their original form in the experiments without any pre-processing step. In these sediments PCBs were less available and reagent mixing was more challenging. It was hypothesized that sediments with higher organic and silt/clay content will exhibit lower dechlorination than the more sandy and lower organic content sediments. Congener specific analysis was conducted to look for the formation of lower chlorinated congeners in sediments as possible byproducts of the dechlorination reaction and to construct potential dechlorination pathways. The role of various solvents in increasing PCB availability and therefore potentially enhancing dechlorination and changes in PCB bioavailability due to treatment were also investigated.

Materials and Methods

Sediments

Two aged PCB contaminated sediments were collected from the following sites: New Bedford Harbor (NBH), MA; and Housatonic River (HSR), MA. The sediments presented a range of sediment characteristics and PCB concentrations (Table 3.1). The NBH sediment is composed mainly of silts and clays and has higher PCB concentration, organic content and water content than the HSR sediment. The sediments were homogenized before treatment.

Table 3.1 Sediment characteristics of one freshwater and one marine sediment.

Sediment Source	**Housatonic River**	**New Bedford Harbor**
Sediment Type	freshwater	marine
Sediment Inorganic Composition	sand	silt / clay
Organic Content		
Average	**3.18%**	**11.63%**
Maximum	3.19%	11.98%
Minimum	3.18%	10.95%
Water Content		
Average	**18.3%**	**54.5%**
Maximum	19.3%	55.5%
Minimum	17.3%	54.0%
PCB Concentration* (ppm)		
Average	**8.8**	**116.4**
Maximum	32.7	142.5
Minimum	1.6	97.2

*Based on 12 and 30 samples for the Housatonic River and New Bedford Harbor sediments, respectively.

Reagents

PCB standards in hexane were purchased from Accustandard (New Haven, CT) and Ultrascientific (North Kingstown, RI). Decachlorobiphenyl (BZ 209) was used as extraction surrogate standard. High purity, GC-grade solvents (methanol, ethanol, isopropanol, acetone, and hexane) were used. The magnesium/palladium (Mg/Pd) material was obtained from the National Aeronautics and Space Administration (NASA, Kennedy Space Center, FL). Figure 3.1 shows Scanning Electron Micrographs of the Mg/Pd bimetal. The Mg particles were 4 μm in diameter and had 0.01% by weight Pd coating on their surface. The Mg/Pd bimetal should be handled with extra caution due to its high reactivity that can result in an explosion hazard.

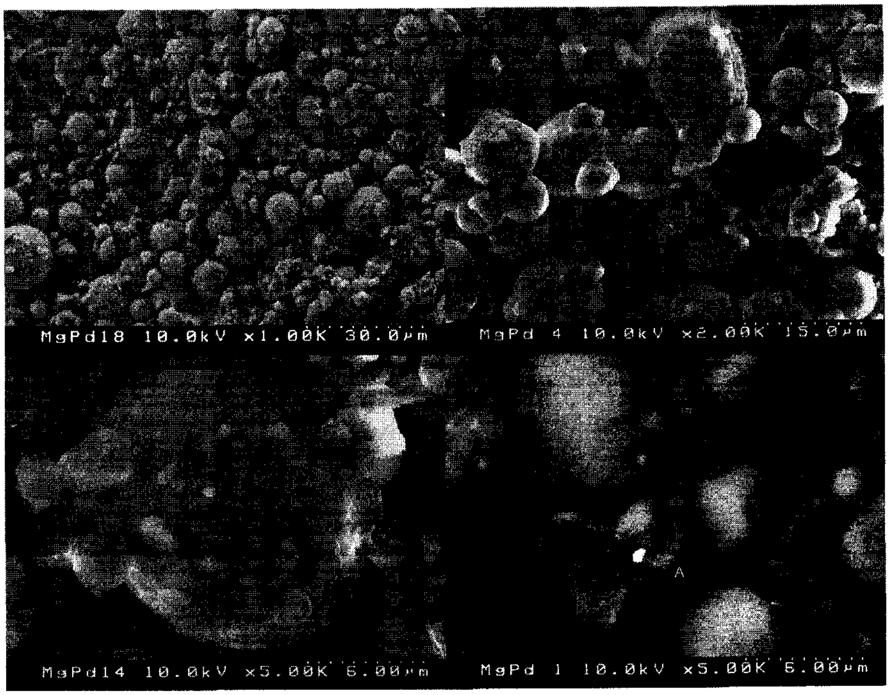


Figure 3.1 Scanning electron micrographs of the Mg/Pd powder (supplied by NASA). Bright spot, as shown by the letter "A", indicates Pd particles.

Batch Experiments

Laboratory batch experiments were conducted in 150 mL glass beakers. First, 10 g of sediment (wet weight) was placed into the reactors. The Mg/Pd was added as slurry to the sediment (0.5-10% by wet sediment weight), i.e. mixed with the appropriate solvent used (water, methanol, ethanol, isopropanol or the mixture of these alcohols and water). The sediment and the Mg/Pd slurry were mixed using a vortex shaker. Batches were prepared in two to six replicates and the reactors were shaken on a rotary shaker at

175-200 rpm for the duration of the experiments; 24 hrs for the Mg/Pd treatment experiments and 14 days for the bioavailability studies.

PCB Bioavailability

The bioavailability of PCBs was evaluated using solid phase microextraction. Polydimethylsiloxane-coated glass fibers were purchased from Fiberguide Industries (Stirling, NJ). The diameter of the fiber glass core was 210 µm and the coating thickness was 10 µm. The glass fiber was cut into 2 cm pieces that were pre-rinsed in methanol and then in distilled water for 20 min and dried at room temperature to remove any residual contamination from the coating. Five 2-cm fiber pieces were placed into stainless steel envelopes made from a 150 wire mesh purchased from TWP Inc. (Berkeley, CA). Two to three envelopes were deployed in each sediment slurry batch for 14 days. After the exposure period the envelopes were removed from the sediment and the fibers were thoroughly rinsed with distilled water. The contaminants were extracted from the fibers using the accelerated solvent extraction method (see below under "Sample extraction").

Desorption Experiments

Desorption of PCBs from the two sediments into the aqueous phase was investigated using Tenax TA® resin beads (mesh 35/60 from Scientific Instrument Services, Inc.). The Tenax beads were pre-rinsed with acetone and hexane and dried at room temperature. Triplicate batches were prepared by adding approximately 3 g dry weight sediment, 100-120 mL distilled water and 1.2 g of Tenax beads into 150 mL beakers. Batches were placed on a rotary shaker for the duration of the experiments. At 1, 2, 5, 12, 19, 26, 33, and 50 days the Tenax beads were removed from the samples and replaced with new ones. The sampled Tenax beads and the sediment after the last sampling event were extracted using the ultrasonic extraction method (see below under "Sample extraction").

Sample Extraction

Two different methods, ultrasonic extraction and accelerated solvent extraction (ASE) were used to retrieve PCBs from the sediments; all SPME fibers were extracted using the ASE method. In the first method, sediment batches were extracted into hexane by ultrasonic extraction using a SON-IM Sonicator® from MISONIX Inc. and then concentrated using a TurboVap® II Concentration Workstation from Zymark Corporation. EPA's Method 3550B "Ultrasonic Extraction" was followed. In the second method, sediment samples were first dried in a Freezone 6 Freeze Dry System from Labconco Corporation, followed by extraction on an ASE 200 Accelerated Solvent Extractor and concentration on a SE 400 Solvent Evaporator, both from Dionex Corporation. EPA's Method 3545A "Pressurized Fluid Extraction" was followed in the second method. After extraction, EPA's Method 3665A "Sulfuric Acid/Permanganate Cleanup" was used for sediment extract cleanup in order to remove the natural organic matter present in the samples.

Gas Chromatographic Analysis

All extracts were analyzed using a Varian CP3800 Gas Chromatograph (GC) / Saturn 2200 Ion Trap Mass Spectrometer (MS) with a CP8400 Autosampler. The chromatography column was a DB-5 type capillary column (Varian Factor Four VF-5ms), 30m long, 0.25mm ID, and 0.5μm thick. The MS uses an ion-trap detector and was operated in selected ion scan mode (MS/MS). The column oven temperature program started at 40°C (held 2min), ramped to 184°C at a rate of 12°C/min, then to 280°C at a rate of 4°C/min, and finally to 300°C at a rate of 8°C/min, with a final hold of 4.5 minutes. An external calibration curve was used for congener specific analysis.

Results and Discussion

Dechlorination and Desorption Experiments

Initial experiments were conducted in two different sediments, HSR and NBH to investigate if dechlorination was occurring and how the extent of the reaction was affected by the sediment characteristics. Figure 3.2 shows that higher dechlorination was achieved in the HSR than in the NBH sediment over 24 hours using 10% Mg/Pd; the total average mass removal was 48.3% and 25.7%, respectively. This indicated that PCBs were more available to the Mg/Pd in the sandy, low organic content HSR sediment than in the NBH sediment with higher silt/clay and organic content. Agarwal et al. (2007) and Wu et al. (2001) reported higher PCB dechlorination levels in contaminated sediment matrices than observed in the present study. However, both referenced studies used sediments that were processed prior to the reaction. The sediments were dried and sieved to smaller particle sizes and most were spiked with PCBs, resulting in higher availability of the contaminants compared to the original wet sediment matrix. In addition, in some cases the reaction was performed in a very dilute slurry form; 20 mL of solvent was added to 1 g sediment in the study by Agarwal et al. (2007) while the present work used only 3.5 mL solvent for 1 g of material. The present work was the first to use aged, PCB contaminated sediments in their original form in the experiments without any pre-processing step. The dechlorination reaction might have become rate-limited perhaps due to the inability of the Mg/Pd particles to reach the less labile PCBs.

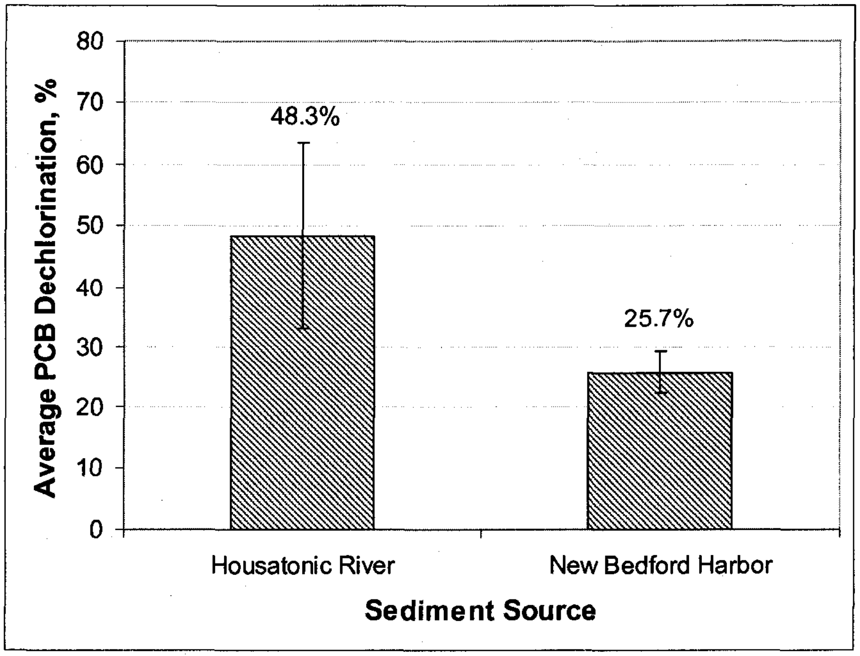


Figure 3.2 PCB dechlorination in two sediments treated with 10% Mg/Pd (by wet sediment weight) over 24 hours.

Congener-specific analysis was conducted to investigate the congener specificity of the dechlorination reaction. For Fe/Pd, dechlorination has been shown to occur stepwise where the dechlorination of highly chlorinated congeners forms lower chlorinated congeners (Korte et al., 2002). In the present study, nearly all the congeners that were present in the untreated HSR and NBH sediment controls, including lower chlorinated congeners, were dechlorinated to lower concentrations in the treated batches. Formation of lower chlorinated congeners could be observed in the HSR samples (Figure 3.3), mostly pentachlorobiphenyls or lesser chlorinated congeners. Congeners that consistently appeared in two thirds of the samples were considered to be by-products of the dechlorination reaction. None of the congeners identified this way were co-planar. The most common chlorine substitution was the ortho position, indicating that ortho chlorines were removed last. The average reduction in toxicity after treatment was 48.6% using the latest toxic equivalent factors approved by the World Health Organization (reported by Van den Berg et al., 2006). The same tendency of the consistent formation of lower chlorinated congeners could not be clearly observed in the NBH sediment (data not shown). In general, higher masses of individual congeners in treated samples compared to the controls are due to both the formation of lower chlorinated congeners from dechlorination and the variation in congener concentrations in the sediment matrix. Therefore, the exact amount of congeners formed due to dechlorination could not be determined in sediments. Furthermore, congener specific dechlorination pathways could not be identified because of the previously mentioned uncertainty and also because of co-eluting congeners. On the other hand, experiments conducted in pure solvents (10% methanol in distilled water) with 2,2',3,4,4',5,6,6'-octachlorobiphenyl (BZ 204)

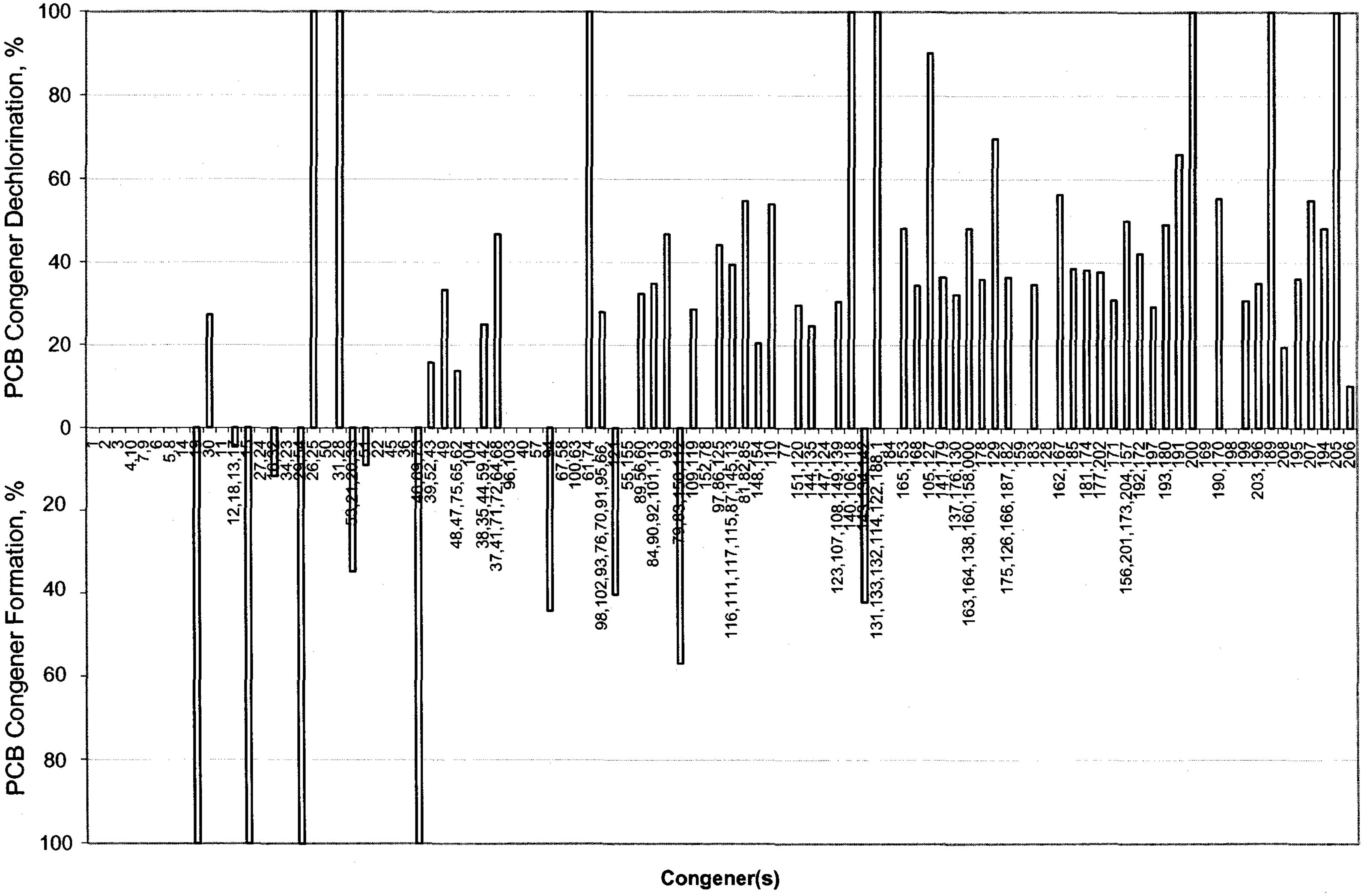


Figure 3.3 PCB congener formation and dechlorination in Housatonic River sediment treated with 10% Mg/Pd (by wet sediment weight) for 14 days.

successfully identified formation of lower chlorinated congeners by stopping the reaction in its early stages and potential dechlorination pathways were also identified (see Figures 2.8 and 2.12 in Chapter 2).

In general, the dechlorination process ceased before 24 hours, and the extent of dechlorination was observed to depend on sediment characteristics. Because of the lower removals in clayey, high organic content sediments, it was hypothesized that the strongly sorbed, and slowly desorbed, fraction of the PCBs was limiting the dechlorination observed. By comparison with desorption rates observed in separate experiments, it is clear that the reaction does not require desorption for most of the mass removal, as desorption rates for these sediments are extremely slow; for example, only 6% of total PCBs from NBH sediments were desorbed over 50 days using Tenax beads in a completely mixed system (Figure 3.4). However, there is likely some fraction of PCBs that are not available for direct contact with the bimetal as indicated by the incomplete dechlorination levels in treated sediments and this fraction may require desorption prior to reaction with Mg/Pd. To address this issue, various solvents were tested for their ability to increase PCB availability in sediments to the Mg/Pd by increasing contaminant solubility.

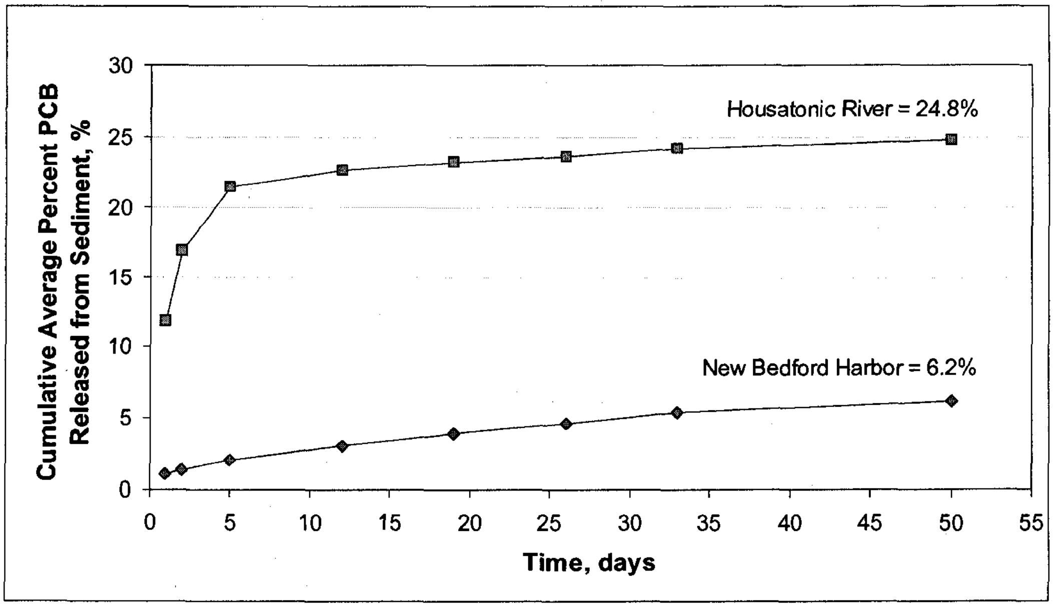


Figure 3.4 Cumulative average percent PCB desorption from two sediments.

Solvent Enhanced Dechlorination

Polar organic solvents methanol, ethanol and 1-propanol were shown to increase the availability of organic contaminants in soils (Smith et al., 2004; Krauss et al., 2001; Lee et al., 2001). Furthermore, due to polar solvents' ability to interact with the mineral sites and dissolve within the soil or sediment organic matter (Chiou, 2002) polar organic solvents were hypothesized to be effective at increasing PCB availability to the Mg/Pd surface. In the present study, experiments were conducted to see if the addition of ethanol, isopropanol and methanol improved dechlorination. Reaction batches were made up of 10 g wet sediment and an additional 10 mL of solvent or solvent-water mixture containing the Mg/Pd bimetal. The natural amount of the sediment water content was also taken into account when calculating the % solvent added to the batch. The addition of methanol, ethanol, and isopropanol did not enhance PCB dechlorination in the HSR

(Figure 3.5) or NBH sediment (Figure 3.6) when compared to water. Lower dechlorination values were observed for methanol and isopropanol in the HSR (Figure 3.5) and ethanol and isopropanol in the NBH sediment (Figure 3.6) indicating that PCBs might have preferably stayed in the solvent phase in those cases preventing sufficient contact with the Mg/Pd. The inhibitory effect was stronger in the NBH sediment, which also had the higher % solvent content, than in the HSR. Dissimilarities in sediment characteristics (i.e., gradation, organic content) might have also contributed to differences in the inhibitory effect for the two matrices. The slowing down of the dechlorination reaction was also observed by Korte et al. (2002) with increased ethanol and isopropanol content (between 40-60%, a similar range to the present study) and by Fang et al. (2007) with increasing methanol concentrations in the case of palladized iron.

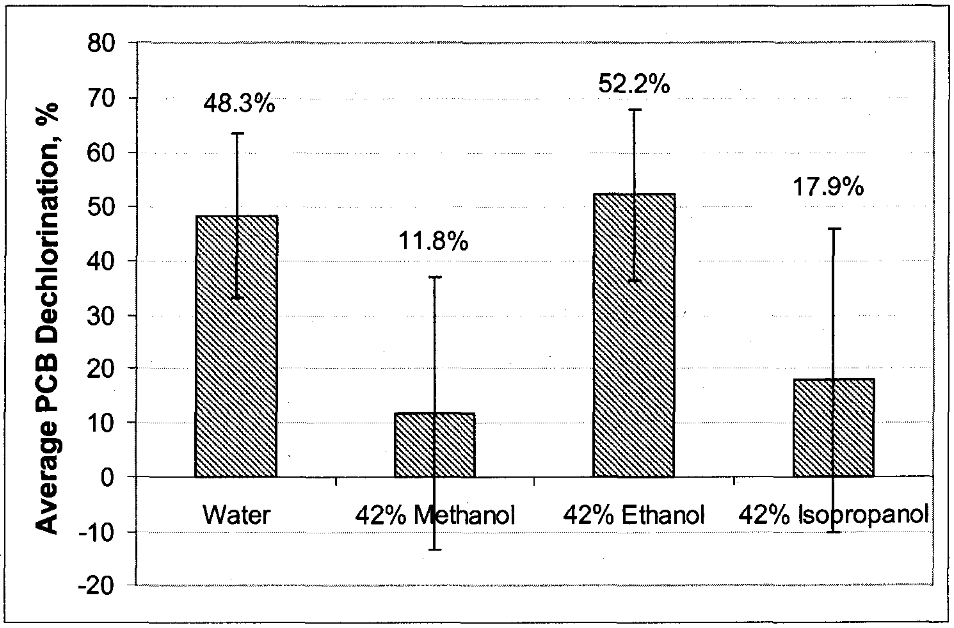


Figure 3.5 PCB dechlorination in Housatonic River sediment with 10% Mg/Pd (by wet sediment weight) in the presence of different polar solvents after 24 hours.

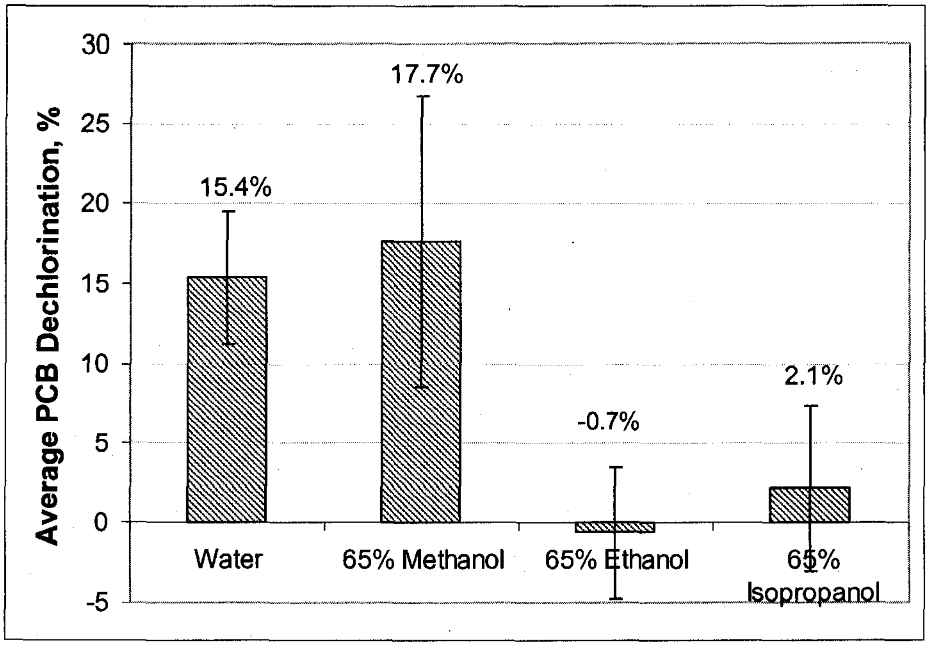


Figure 3.6 PCB dechlorination in New Bedford Harbor sediment with 1% Mg/Pd (by wet sediment weight) in the presence of different polar solvents after 24 hours.

The Effect of Treatment on PCB Bioavailability

The ultimate goal of any remediation technology is to eliminate or reduce the risk of exposure to toxic contaminants, i.e. to reduce the bioavailability of these compounds. Therefore, changes in contaminant bioavailability due to treatment and mass removal should be evaluated simultaneously. In the present study, experiments were conducted to investigate the effect of the Mg/Pd treatment on PCB bioavailability using solid phase microextraction (SPME) fibers that were placed directly into the sediment slurry. A PCB mass removal of 48.3% was related to 78% decrease in bioavailability after 14 days exposure in the Housatonic River sediment in the presence of water (Figure 3.7), indicating that the majority of the contaminants that were not accessible for dechlorination were not bioavailable. Likewise, 52.2% dechlorination for ethanol and

17.9% for isopropanol was associated with 59.9% and 66.7% reduction in bioavailability in the same sediment, respectively.

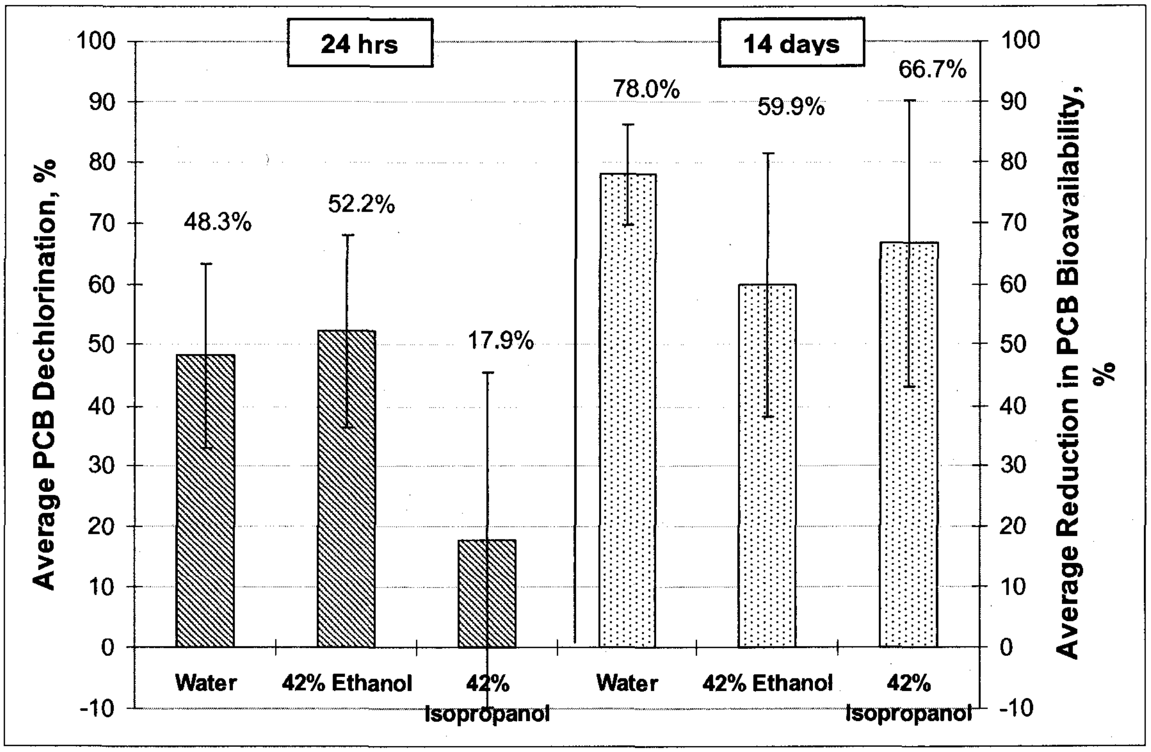


Figure 3.7 Graph showing the PCB dechlorination values in Housatonic River sediment with 10% Mg/Pd (by wet sediment weight) in the presence of various polar solvents after 24 hours and the matching average reduction in PCB bioavailability for each solvent after 14 days.

Conclusions

In this study, aged PCB contaminated sediments were treated using palladized magnesium (Mg/Pd) to investigate whether significant degradation of PCB congeners represent a possible in-situ or ex-situ treatment technology. The role of various solvents in increasing PCB availability and therefore potentially enhancing dechlorination and changes in contaminant bioavailability due to treatment were also investigated.

The extent of dechlorination correlated with the organic and silt/clay contents of the sediments, i.e. the higher the organic and silt/clay content the lower the overall dechlorination was. Congener specific analysis demonstrated that most of the compounds were dechlorinated. Formation of lower chlorinated congeners could be observed in the Housatonic River sediment, mostly pentachlorobiphenyls or lesser chlorinated congeners, indicating that dechlorination was occurring, even though clear dechlorination pathways could not be identified due to co-eluting congeners and variation in congener concentrations in the sediment matrix. No co-planar congeners were formed. The most common chlorine substitution in the lower chlorinated congeners formed was the ortho position, indicating that ortho chlorines were removed last. The average reduction in toxicity after treatment was 48.6%. Even though contaminant desorption from the sediments did not limit dechlorination rates, three polar organic solvents were tested for their potential to enhance dechlorination by increasing contaminant solubility. Neither methanol, ethanol or isopropanol proved to be efficient in increasing dechlorination when compared to water. A major finding of the study was that the average reduction in PCB bioavailability was always higher than the associated contaminant mass removal, e.g. 78.0% decrease in PCB bioavailability for 48.3% PCB dechlorination in the sandy Housatonic River sediment. The idea that contaminants that are not accessible for dechlorination are not bioavailable either presents a new alternative for treatment technology evaluation besides the traditional mass removal-based approach with the ultimate notion that technologies with less than complete contaminant removals might be viable options if the treatment led to high reduction in bioavailability. New regulatory standards favoring the bioavailability-based approach would encourage the use of this alternative. Overall, PCB dechlorination by Mg/Pd is a promising option for an in-situ or ex-situ sediment remediation technology in sandy sediments and in situations when reduction in contaminant bioavailability is the main treatment performance criterion. Further work is needed to evaluate ways to deliver and mix the reagent into sediments in-situ and to assess Mg/Pd toxicity.

Supplemental Material to Polychlorinated Biphenyl Dechlorination and Bioavailability Experiments Conducted in Sediments

This supplemental material contains results of laboratory experiments conducted on polychlorinated biphenyl (PCB) dechlorination and bioavailability by magnesium/palladium (Mg/Pd) in aged contaminated sediments that complement the findings described in Chapter 3 of this work.

Initial PCB Dechlorination Experiments with No Individual Control Batches

Initial dechlorination experiments were conducted using PCB contaminated sediments from three sites: New Bedford Harbor (NBH), MA; Hunter's Point (HP), CA; and Housatonic River (HSR), MA. The NBH and the HP sediments were clayey, while the HSR sediment was sandy. The water content of the HP sediment was 38% (see additional information in Table 3.1). For each experiment, enough sediment was taken from a 5 gal bucket previously homogenized and this batch was thoroughly mixed again prior to taking 10 g samples for control and treated batch runs. Experiments were carried out in a slurry form by adding 5-10 mL distilled water or a solvent/water mixture to the sediment. Despite all the effort made to homogenize the sediments prior to the experiments, in some cases the results indicated negative dechlorination (not shown on the graphs) that was believed to be due to inhomogeneity in contaminant concentrations in the sediments. Therefore, later experiments were run using "individual controls" when 20 g of sediment was split into a control and a treated batch to reduce the effect of sediment inhomogeneity on the results. This method significantly increased the number of samples and therefore the processing time per experiment. Results of the experiments using individual controls are described in the subsequent sections.

This section describes results of preliminary experiments run without "individual controls". First, experiments were conducted in the clayey sediments. Figure 3.8 shows 22% PCB dechlorination in New Bedford Harbor sediment over 4 days by 2% Mg/Pd. Somewhat lower dechlorination values were observed in Hunter's Point sediment over the same time period (2 to 4 days) and using similar amounts of Mg/Pd (1-5%) (Figure 3.9). In this experiment, for samples named "prewet" the Mg/Pd was mixed with distilled water and the mixture was set aside for 20-30 min prior to its addition to the sediment, while in batches labeled "direct" the dry Mg/Pd powder was added to the sediment followed by the addition of water. Results indicated that "prewetting" of the Mg/Pd did not have an effect on the extent of dechlorination.

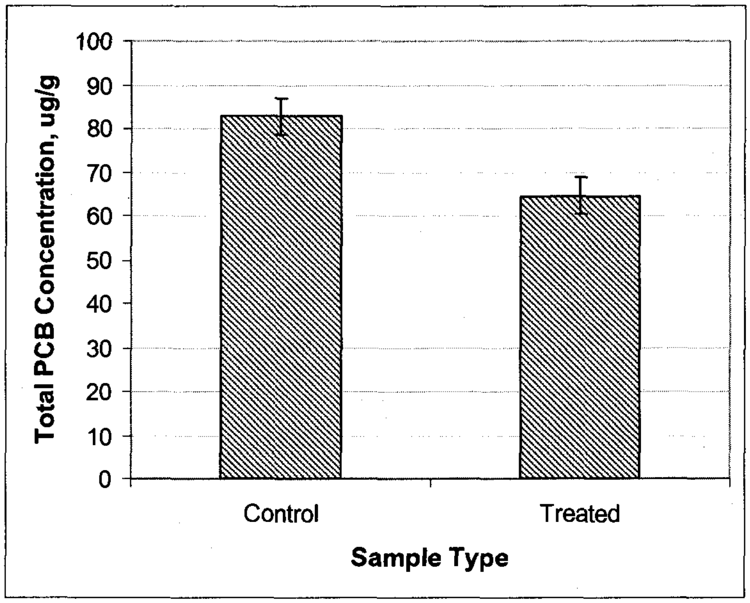


Figure 3.8 Graph showing 22% PCB dechlorination in New Bedford Harbor sediment over 4 days by 2% Mg/Pd (by wet sediment weight) [Control = no Mg/Pd].

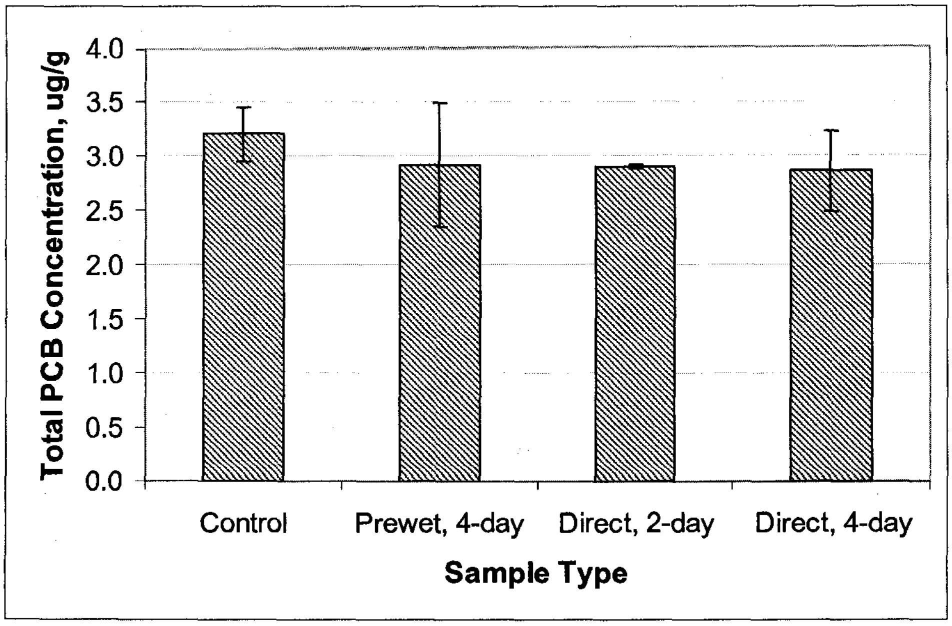


Figure 3.9 Graph showing 14% (prewet, 2-day), 9.2% (direct, 2-day), and 14.1% (direct, 4-day) PCB dechlorination in Hunter's Point sediment over 2-4 days by 1-5% Mg/Pd (by wet sediment weight) [Control = no Mg/Pd; Prewet = Mg/Pd mixed with distilled water prior to addition to sediment; Direct = dry Mg/Pd powder added to sediment].

Experiments conducted in the sandy HSR sediment yielded higher dechlorination values compared to the clayey NBH and HP materials (Figures 3.10 and 3.11) indicating that PCBs were either more available (Figure 3.10) or their availability was increased by the use of solvents in the HSR sediment (Figure 3.11). Figure 3.10 shows average 99% dechlorination in HSR sediment over 5 days using 5% Mg/Pd. Some of the samples of this experiment were extracted at the University of New Hampshire (UNH) and some were sent to Analytics Environmental Laboratory LLC (Portsmouth, NH) for quality assurance purposes. Ultrasonic extraction was used at UNH and accelerated solvent extraction at the independent laboratory. As seen from the graph, the results of the two extractions compared well to each other suggesting that the type of extraction method used did not affect the results of the dechlorination experiments.

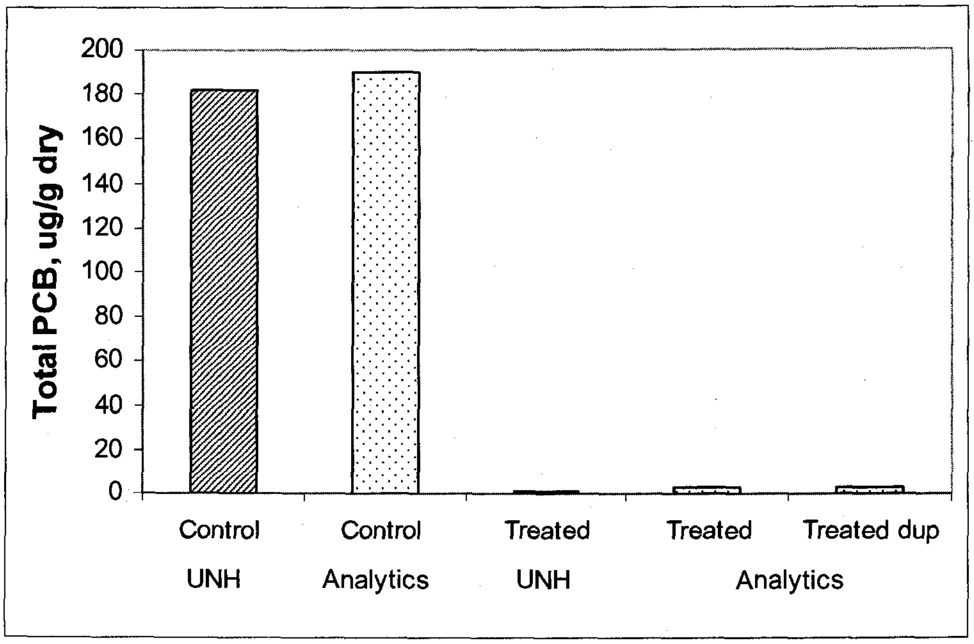


Figure 3.10 Graph showing an average of 99% PCB dechlorination in Housatonic River sediment over 5 days by 5% Mg/Pd (by wet sediment weight) [Control = no Mg/Pd]. Some samples were extracted at the University of New Hampshire = UNH and some were sent to Analytics Environmental Laboratory LLC for quality assurance purposes.

Dechlorination in the same sediment was also tested in the presence of various solvents to examine if the solvents enhanced the reaction by making the PCBs more available and to see how the effect of the different solvents compared to each other. Dechlorination values were 66.7%, 52.8%, 17%, and 34% for 10% hexane, 10% methylene chloride, 10% methanol, and 10% isopropyl alcohol, respectively (Figure 3.11). These values were all lower than the 99% dechlorination achieved with only water (Figure 3.10). However, note that the initial PCB concentrations were very high in the water only experiment; close to 200 ppm as opposed to the average 8.8 ppm for the HSR sediment (see Table 3.1). On the other hand, initial concentrations in the solvent experiment were only 1-2 ppm. Concentrations observed in the water only experiment can be considered a "hotspot" and high initial concentrations could have resulted in the exceptionally high % removals.

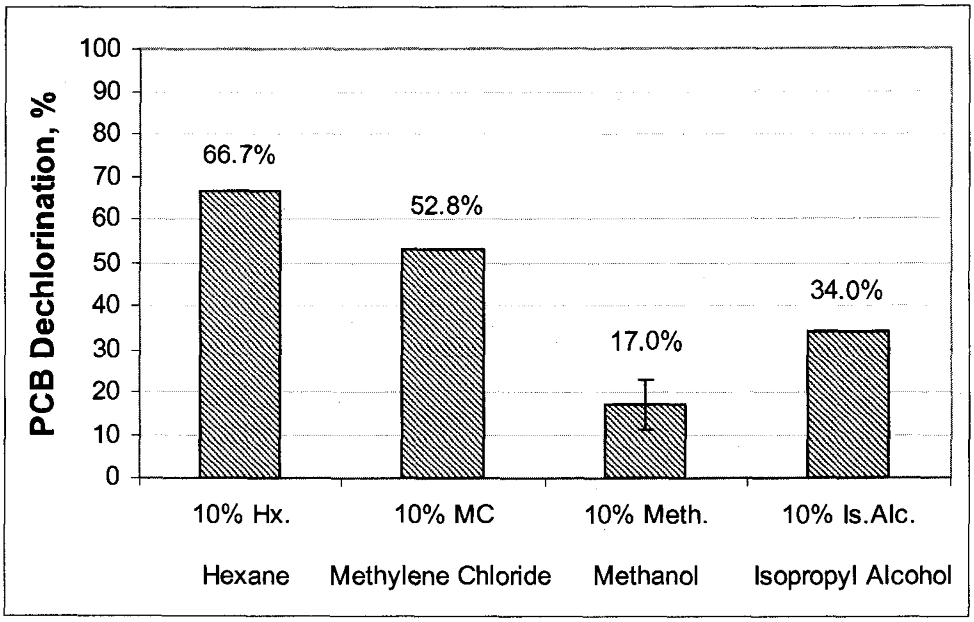


Figure 3.11 PCB dechlorination in Housatonic River sediment with 5% Mg/Pd (by wet sediment weight) and different percent solvent addition after 5 days.

The Effect of Temperature and Microwave Irradiation on PCB Dechlorination

The effect of temperature and microwave irradiation on PCB dechlorination in New Bedford Harbor sediment was investigated and the results are described in this section. Slightly elevated temperatures could enhance contaminant desorption from the sediment matrix and therefore make PCBs more available (a process termed thermal desorption). Microwave irradiation had been shown to aid PCB decomposition when contaminants were adsorbed on granular activated carbon (Liu et al., 2006). Since it was suggested that PCBs were dechlorinated by Mg/Pd while they were adsorbed on the surface of the bimetal (Hadnagy et al., 2007), the potential for microwave energy aiding the reaction was investigated in the present work.

First, PCB dechlorination was tested at 22°C, 70°C and 90°C where 22°C represented reaction at room temperature. Elevated temperatures were maintained by placing the batch reactors into a hot water bath (70°C) or an oven (90°C). The sediment was pre-heated to the reaction temperature prior to the addition of Mg/Pd. Figure 3.12 shows the effect of the three different temperatures on PCB dechlorination. Dechlorination at 90°C was higher than at room temperature, an effect expected due to low temperature thermal desorption. On the other hand, dechlorination at 70°C was lower than at 22°C indicating that thermal desorption might not had an effect at this temperature.

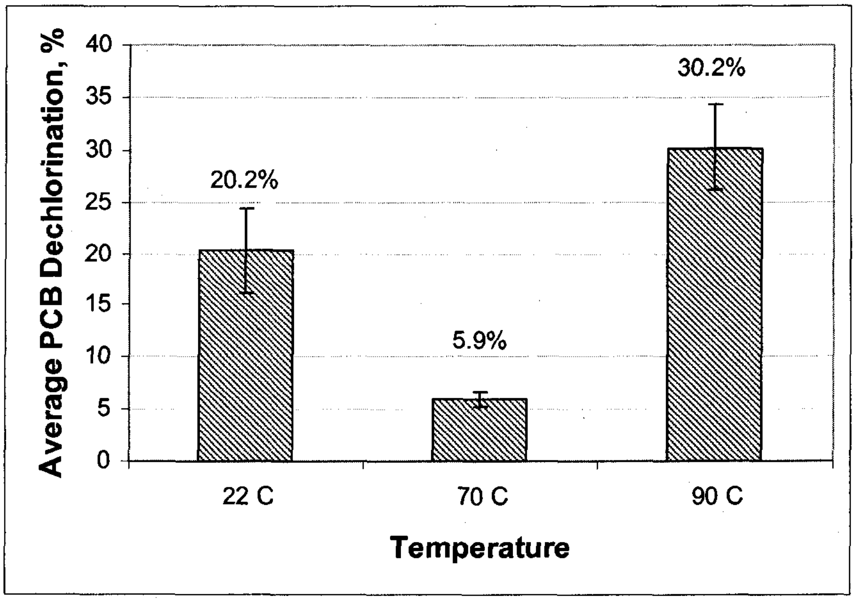


Figure 3.12 PCB dechlorination in New Bedford Harbor sediment with 0.5% Mg/Pd (by wet sediment weight) and different temperatures after 24 hours.

To investigate the effect of microwave irradiation on PCB dechlorination, batch experiments were carried out in a MARS 5 microwave digester (CEM Corporation, Matthews, NC). New Bedford Harbor sediment was mixed with distilled water and Mg/Pd and this mixture was heated to 90°C and irradiated with 600W microwave energy for 1 hour. Microwave irradiation under these conditions did not enhance PCB dechlorination when compared to dechlorination at 90°C in an oven (Figure 3.13). However, it has to be noted that there were differences in the experimental conditions for the two experiments that might be of importance when comparing the results. The experiment with microwave irradiation had a shorter reaction time (2 hours vs. 24 hours), more Mg/Pd (1% vs. 0.5%) and more water (50 mL vs. 20 mL to 10 g sediment). The effect of these differences is not known.

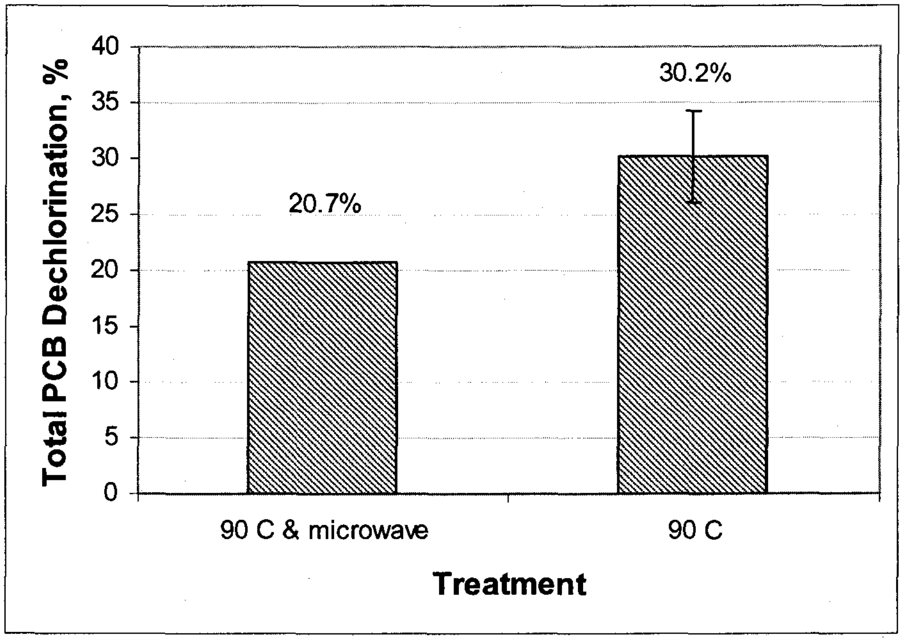


Figure 3.13 PCB dechlorination in New Bedford Harbor sediment with 0.5-1% Mg/Pd (by wet sediment weight) and 90°C after 24 hours; with or without microwave irradiation. Microwave irradiation was applied to the first sample for 1 hour at 600W.

PCB Bioavailability

Changes in PCB bioavailability due to treatment with Mg/Pd were discussed earlier in this chapter. The two graphs included in this section show either negative "reduction" in PCB bioavailability (i.e., no reduction, see Figure 3.14) or too much variation in the average reduction in PCB bioavailability (Figure 3.15), and therefore they were not included in the earlier discussion.

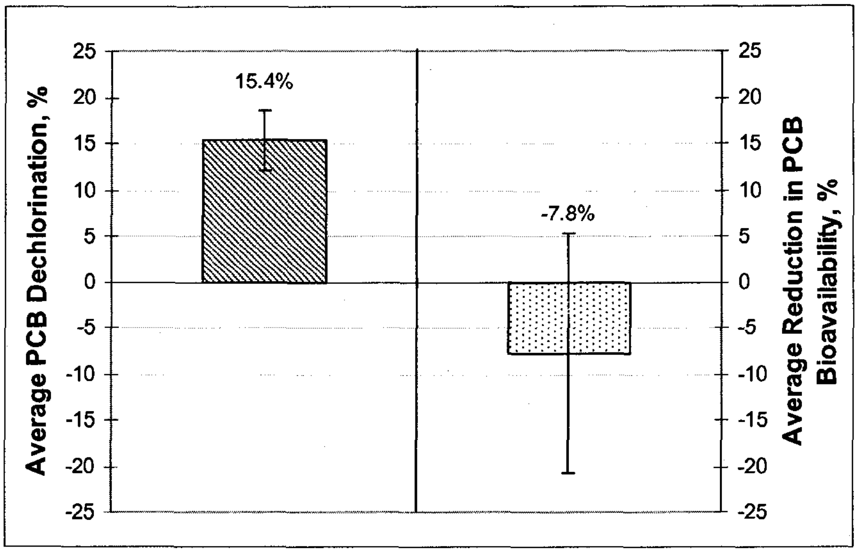


Figure 3.14 PCB dechlorination in New Bedford Harbor sediment with 1% Mg/Pd (by wet sediment weight) after 24 hours and the matching PCB bioavailability reduction after 28 days.

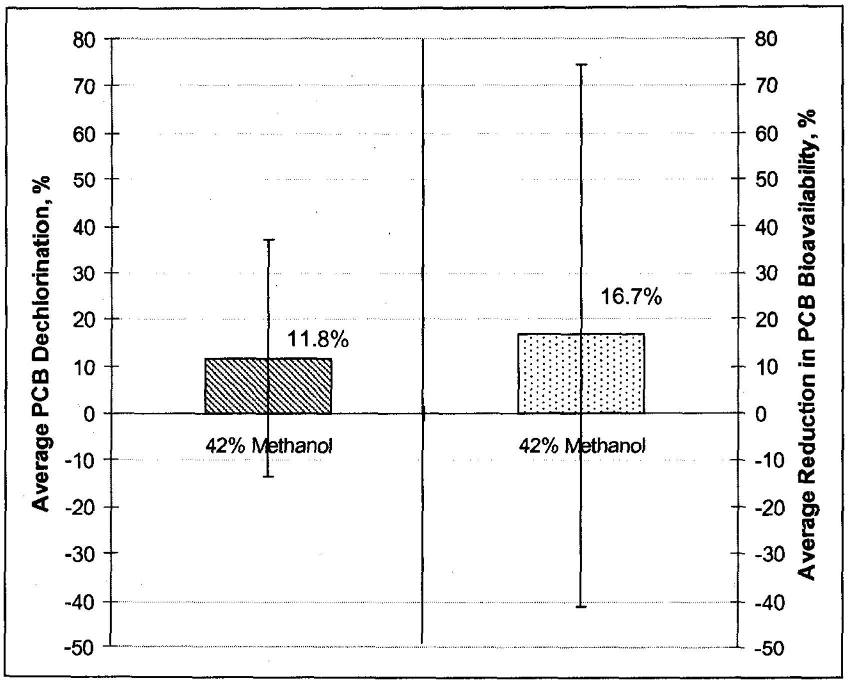


Figure 3.15 PCB dechlorination in Housatonic River sediment with 10% Mg/Pd (by wet sediment weight) in the presence of methanol after 24 hours and the matching PCB bioavailability reduction after 14 days.

Erroneously High PCB Dechlorination Values in Some Cases of Ultrasonic Extraction?

A group of experiments yielded much higher dechlorination values than the ones obtained when control batches were independent samples and not split portions of the treated sediment, i.e. they were not "individual controls". Originally, it was hypothesized that the introduction of "individual controls" and better mixing of the Mg/Pd (the bimetal was added in a slurry form as opposed to the dry powder, and the sediment batch was placed on a vortex shaker for initial mixing instead of using a spatula and manual mixing) were the reasons for increased dechlorination. However, later experiments conducted with "individual controls" and the same mixing conditions also showed less PCB removal. Closer investigation revealed that slight differences in the extraction methods used correlated well with dissimilarities observed in the dechlorination values.

Three extraction methods were used: accelerated solvent extraction (ASE) and "original" and "modified" ultrasonic extraction. The ASE method is a more novel and effective technique than sonication and it became the sole extraction method used after the purchase of a new ASE instrument. Prior to that, the "original" ultrasonic extraction technique was successfully verified against the ASE procedure by sending the samples to an independent laboratory (Figure 3.10).

The two sonication techniques only differed in the way the initial PCB concentrations were determined. In the "original" ultrasonic extraction method "true" controls were used, i.e. a control sample went through the same procedure from batch preparation through reaction, extraction and analysis as a treated sample with the exception that no Mg/Pd was added to the controls. On the other hand, in the "modified" ultrasonic extraction method initial PCB concentrations were determined from sediment samples that were extracted as they were without preparing a batch slurry and exposing it to shaking for a given time period. The difference in terms of sample processing for these two approaches was in the amount of drying powder required to dry the sediment prior to extraction; less drying powder was added to the "initial concentration" samples than to "true" controls. This also meant that the amount of drying powder was not the same in the control and treated samples for the "modified" sonication method, whereas for the "original" technique it was. Furthermore, treated samples in the "modified" method received nearly twice as much drying powder compared to treated samples in the "original" procedure due to higher volumes of solvent added, which determined the amount of drying powder needed for complete dewatering of the sediment slurry. Differences in the amount of drying powder could have led to inconsistent extractions for the control and treated samples, which in turn would have directly affected the results since the % PCB dechlorination was calculated based on the difference of these two samples. It has to be noted, that differences in the amount of drying powder were not considered to be a problem when the experiments were carried out. In extractions with higher amounts of drying powder the ultrasonic energy was expected to pass through the solid particles and strip off the contaminants as effectively in the deeper layers as with smaller solid amounts, even if the particles were not stirred up.

To investigate if in fact differences in the amount of drying powder could have affected the dechlorination results an experiment was conducted comparing the two ultrasonic extraction methods. In addition, identically prepared treated and control batches were also extracted using ASE. The comparison of the three extraction methods in terms of PCB dechlorination is shown in Figure 3.16. The total PCB dechlorination was 17.2%, 98.1%, and 17.6% for ASE, "modified" ultrasonic extraction, and "original" ultrasonic extraction, respectively, indicating that the choice of extraction method significantly influenced the results. Results obtained with the ASE method and the "original" sonication technique were similar to each other, while the "modified" ultrasonic extraction method yielded much higher dechlorination values.

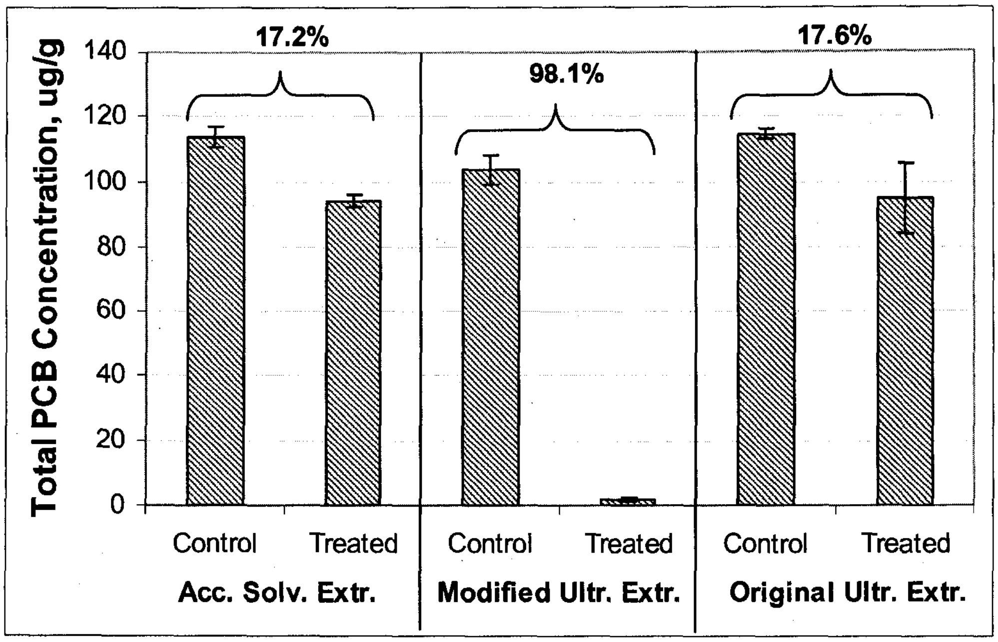


Figure 3.16 PCB dechlorination results in New Bedford Harbor sediment with 1% Mg/Pd (by wet sediment weight) and methanol after 24 hours when using accelerated solvent extraction, modified ultrasonic extraction, or original ultrasonic extraction.

The striking difference in the performance of the extraction techniques could also be observed by looking at the color of the extracts, which was an indicator of the natural organic matter content and that proved to be directly related to PCB levels in this experiment. Photo 3.1 shows the extracts for the ASE and the "modified" ultrasonic extraction methods. While all control samples were of the same color, treated extracts looked different for the two extraction methods: dark for ASE and light for "modified" sonication that was associated with high and low PCB levels, respectively. These visual observations together with the PCB concentration and dechlorination values shown in Figure 3.16 led to the conclusion that the extraction efficiency of the treated samples in the "modified" sonication method was compromised due to the high amount of drying powder added to the samples. On the other hand, controls had similar PCB concentrations for all extraction methods (Figure 3.16), indicating that all techniques worked well for these samples. Control samples also contained less drying powder, which further confirmed that high amounts of drying powder were the cause of lower extraction efficiencies.

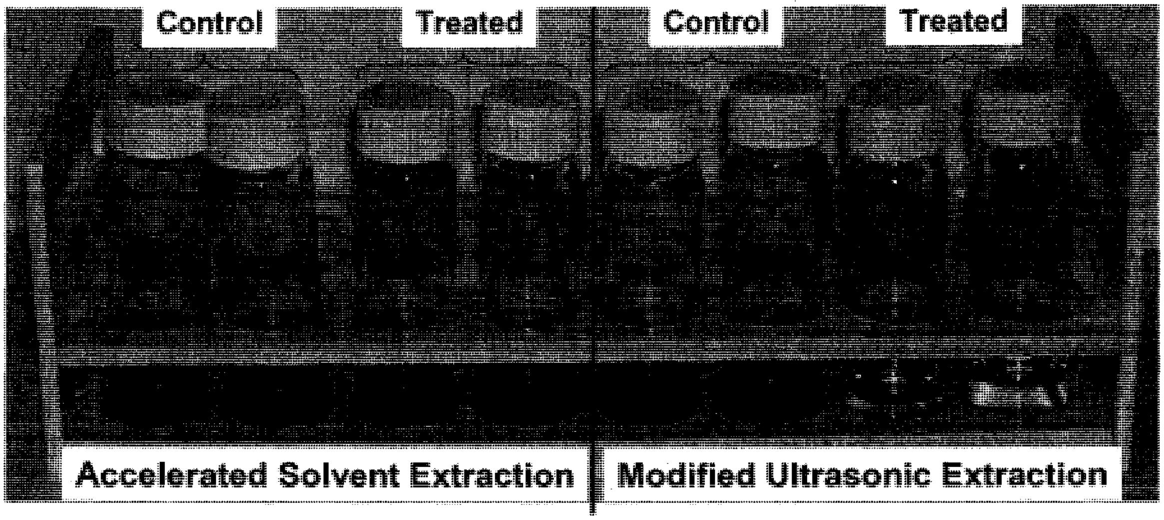


Photo 3.1 Experimental vials for some of the results presented in Figure 3.16. The order of the vials follows the sequence of the first 4 bars on the plot; each bar is represented by two vials (i.e. a duplicate run).

A summary of the experiments that used the "modified" ultrasonic extraction and therefore have questionable results is presented in the remainder of this section. The effect of various solvents and temperature on the dechlorination reaction was investigated in these experiments. First, the effect of three polar protic solvents, methanol, ethanol and isopropanol was tested. During a 24-hour reaction time and using 1% Mg/Pd (by wet sediment weight) in New Bedford Harbor sediment the average dechlorination was 86.3% for methanol, 71.3% for ethanol, 63% for isopropanol, and 37.5% for water (Figure 3.17). The dechlorination achieved with all three solvents was significantly higher at 90% confidence than water, but only ethanol was not significantly different from methanol. It was hypothesized that the successful performance of methanol and the other two polar protic solvents, ethanol and isopropanol, was the result of their polarity and low vapor pressure, which allowed them to remain in solution and interact with the PCBs in the sediment.

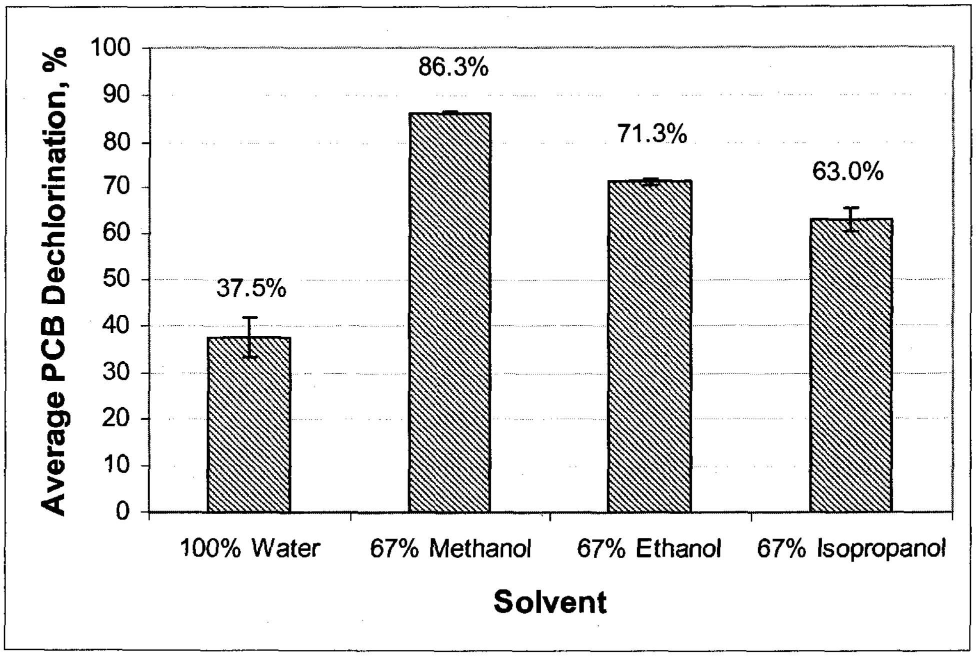


Figure 3.17 PCB dechlorination in New Bedford Harbor sediment with 1% Mg/Pd (by wet sediment weight) and different percent solvent addition after 24 hours.

The two best performing solvents, methanol and ethanol (a less hazardous solvent than methanol) were further tested in New Bedford Harbor (NBH) and Hudson River (HUR) sediments with varying solvent additions. These two sediments were from a marine and a freshwater source, respectively. Overall, the samples with the higher percent solvent addition of 65-67% had a significantly greater dechlorination in both sediments at 90% confidence than samples with only 30% solvent (Figure 3.18), indicating that the amount of solvent added will impact the extent of the dechlorination, a finding similar to observations made by Engelmann et al. (2003) in pure solvent systems.

In the present study, within the samples with 65-67% solvent addition those with methanol had greater average dechlorination (84.5% for NBH and 87.3% for HUR, Figure 3.18) than with ethanol in both sediments (70.2% for NBH and 77.0% for HUR, Figure 3.18). Although dechlorination results with ethanol were slightly lower than with methanol they were greater than previous samples with just water (37.5%, Figure 3.17). On the other hand, the samples with 30% solvent addition had similar dechlorination to water (Figures 3.17 and 3.18). The optimum % solvent content to achieve maximum dechlorination was not determined in the scope of this study.

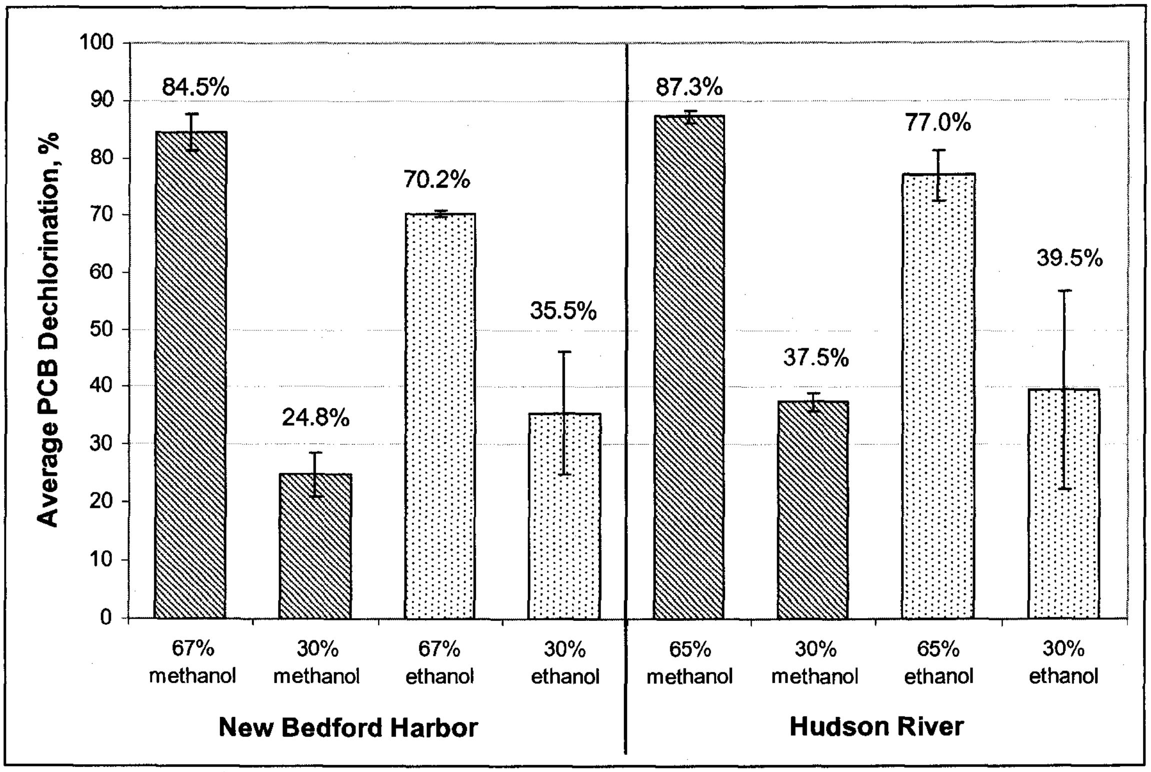


Figure 3.18 PCB dechlorination in New Bedford Harbor and Hudson River sediments with 1% Mg/Pd (by wet sediment weight) and different percent solvent addition after 24 hours.

The effect of two different temperatures, 22°C (room temperature) and 90°C, was also investigated in New Bedford Harbor sediment. Higher dechlorination was achieved with 1% Mg/Pd at 90°C than at room temperature over 24 hours (Figure 3.19), indicating that temperature did have an effect on the extent of dechlorination. The enhancing effect of the 90°C reaction temperature was probably due to low temperature thermal desorption of the PCBs.

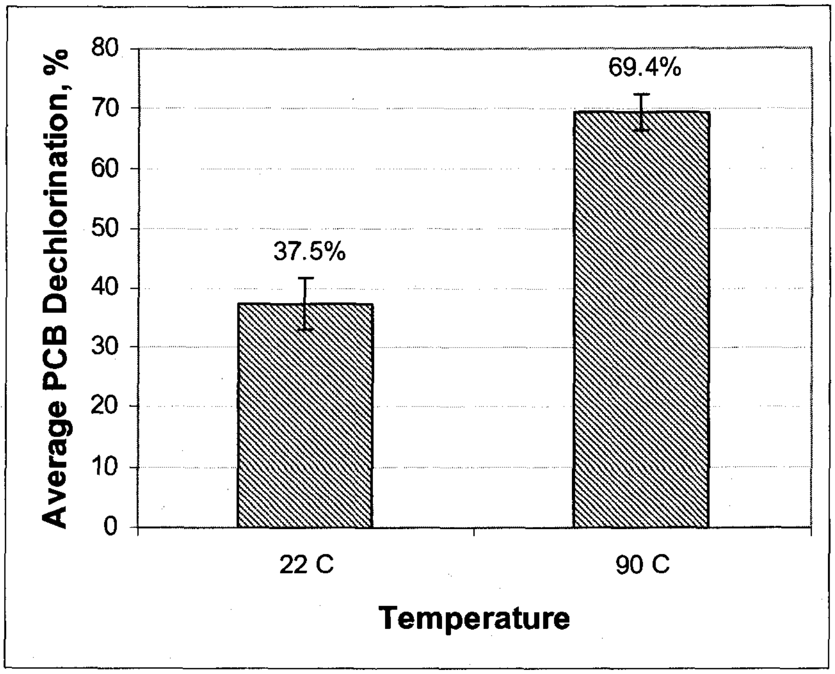


Figure 3.19 PCB dechlorination in New Bedford Harbor sediment with 1% Mg/Pd (by wet sediment weight) and two different temperatures after 24 hours. The 22°C sample represented reaction at room temperature.

Accelerated Solvent Extraction Method Development

A new extraction method was introduced for the last set of experiments of this work due to the purchase of an Accelerated Solvent Extractor from Dionex Corporation. Accelerated solvent extraction (ASE) has several advantages over sonication: 1) a smaller volume of extraction solvents is used and therefore it is less costly; 2) the extraction is performed in a completely closed and well controlled environment, making the method more reproducible; 3) it is less labor intensive due to the automated extractions. To verify the performance of the ASE method a known amount of Arochlor 1260 standard was spiked into Hudson River sediment and the spike recovery was determined after the extraction. A total of 84.7% of the spiked PCBs was recovered in three sequential extractions of the same sample (Table 3.2), indicating that the method worked well for this contaminant. The number of extraction cycles needed for sufficient recovery was determined from the % PCBs extracted in each of the three sequential cycles. More than 96% of the contaminants were extracted in the first cycle and about 99% in the first two cycles (Table 3.2), indicating that the use of two sequential extraction samples was sufficient.

Table 3.2 Table showing the extraction efficiency of an unspiked and a spiked PCB contaminated Hudson River sample.

Sample*	**All PCBs****		**Spiked Arochlor 1260, ug**		**Spike recovery, %**
	ug	% of total	Measured	Calculated	
US1	683.2	96.2			
US2	16.9	2.4			
US3	9.7	1.4			
US total	709.9				
S1	1104.2	97.4			
S2	19.6	1.7			
S3	9.4	0.8			
S total	1133.2		423.3	500.0	84.7

*US = unspiked sample; S = spiked sample (with Arochlor 1260); samples were extracted 3 times (1, 2, and 3 indicate sequential extractions of the same sample).

**Both originally present in sediment and spiked.

CHAPTER 4

PILOT SCALE EVALUATION OF AN IN-SITU AMENDMENT MIXING DEVICE IN DREDGED RIVER SEDIMENT

Abstract

Contaminated sediment management is an issue of concern in many water bodies in developed areas due to the risks associated with the persistent and toxic compounds present in these matrices. In-situ treatment technologies can be more economical alternatives than dredging and ex-situ sediment treatment and they also have the advantage of sequestering or destroying the contaminants in place, but their development and application had been hindered due to uncertainties associated with the homogeneity of amendment delivery and mixing, and the concern of contaminated sediment resuspension and amendment release into the water column. The performance of an in-situ sediment remediation system that was able to deliver and mix a chemical amendment into sub-aqueous sediment and provide enclosure for the process at the same time was evaluated in the present study. Activated carbon was used as a tracer to evaluate the efficiency of reagent delivery and mixing. When investigating the relationship between various operational variables and amendment yield, better recoveries were observed at lower added activated carbon volumes, at higher mixing speeds, at lower pump flow rates, in case of thicker mixed sediment zones, and at horizontal locations closer to the

center shaft. In general, poor amendment recoveries could be attributed to the limited capacity of the sediment pore space to accommodate the activated carbon slurry. This effect was also confirmed by the fact that most samples from outside of the mixed zone that had high activated carbon concentrations were taken from the sediment surface. Better recoveries close to the shaft might have occurred due to the fact that the amendment delivery pressure was not controlled and therefore was not constant through each reagent delivery port. No significant relationship was observed between the vertical spatial variation of activated carbon concentrations and the operational variables of the mixing device. In general, smaller vertical spatial variation was achieved if the mixed sediment layer was thicker, which might have also related to the ability to better recover the sediment cores in these cases. On the other hand, the horizontal variation in activated carbon concentrations was fairly homogeneous. Even though not all amendment was mixed successfully into the sediment the reagent stayed within the enclosure of the device, indicating that contained mixing conditions were achieved. The majority of the suspended sediment settled out fairly quickly from the overlying water column within the enclosure. The addition of a cationic polymer did not aid sediment settling.

Introduction

Despite years of on-going efforts in the field of contaminated sediment remediation, contaminated sediment management remains a pressing issue in the US and in the world. There are few water bodies in developed areas that are not affected by this problem; contaminated sediments are present in rivers, lakes, estuaries and oceans

(USEPA, 2004). Furthermore, the contaminants of most concern tend to persist in the environment and may also bioaccumulate and biomagnify through the food chain. Contaminants in sediments like PCBs or mercury are the most common reason for the 3,852 fish advisories issued by states and local authorities (USEPA, 2007), affecting 38% of the nation's lake acerage and 26% of the nation's river miles. To help mitigate this problem, the development of new cost effective technologies is needed.

Dredging is still the most commonly used contaminated sediment management technology (USEPA, 2005). The dredged material is sometimes treated ex-situ and then it is disposed of in a landfill or in a confined disposal facility. This management option typically involves many steps, each of which is costly, resulting in high overall costs. In addition, in some cases dredging can be inefficient in removing all the contaminants leaving residual contamination behind. Another significant problem is the potential for sediment resuspension during the dredging operation resulting in re-contamination of the cleanup area or contaminant transport to downgradient clean sites (USEPA, 2005; Voie et al., 2002).

Other management practices, besides dredging, recommended by regulatory agencies are monitored natural recovery and in-situ capping with an inert material (USEPA, 2005). These are in-situ management options and cause less disturbance in the environment than dredging combined with ex-situ treatment and disposal. They can also be cheaper alternatives than ex-situ treatment. Monitored natural recovery (MNR) takes advantage of naturally occurring processes to decrease unacceptable contaminant levels to concentrations that pose acceptable risks. Examples of such processes are biodegradation or abiotic transformation, sorption to the sediment particles, and burial or mixing with cleaner sediment. While the cost of MNR is very low and it does not disturb the natural habitat, this management option suffers from leaving the contaminants in place and from the process of risk reduction being very slow compared to other technologies. In-situ caps using inert materials create a clean surface over the contaminated layer thus reducing exposure due to direct contact with the contaminants. Typical concerns for this technology are issues related to cap stability, long term performance, and the potential future exposure of contaminants due to disturbances in the cap (USEPA, 2005).

In-situ capping with an inert material (e.g., sand) and MNR are considered "passive" management options because they do not introduce additives to the sediment to enhance or exhibit treatment (USEPA, 2005). Technologies that do take advantage of various amendment materials are called in-situ treatment technologies and could be more advantageous than "passive" technologies because they have the potential to significantly reduce bulk concentrations and/or the long term bioavailability of the contaminants. These technologies are often innovative and a lot of them are still in the research and development phase (USEPA, 2005).

In-situ treatment technologies utilize various amendments to either aid immobilization or destruction of the contaminants using physical, biological or chemical processes (USEPA, 2005). The processes involved in treatments that focus on immobilization of the contaminants are solidification, stabilization and sequestration, i.e. physical separation or chemical change to the contaminants so that they will be less bioavailable. Examples of amendments added to the sediment for the purpose of solidification/stabilization are Portland cement and limestone, and for contaminant sequestration different carbon forms, e.g. activated carbon (Maher et al., 2007; USEPA, 2005; Zimmerman et al., 2004). In-situ biological treatments focus on enhancing microbial degradation by introducing various amendments into the sediment such as electron acceptors, nutrients, substrates or more or different microorganisms (USEPA, 2005; Harkness et al., 1993). In-situ chemical treatment occurs through sorption/substitution or oxidation or reduction (dechlorination) processes that result in the sequestration or destruction of the contaminants, respectively, using different chemical reagents (USEPA, 2005). The above mentioned chemical treatment amendments can be deployed in the field as a component of a reactive cap or through amendment mixing into the sediment. A reactive cap prevents the contaminants migrating from the sediment from entering into the water column by sequestering or destroying them. A potential problem with this approach is that contaminants below the cap are left intact and they can get exposed to the water column if the cap is compromised. On the other hand, in-situ amendment mixing has the potential to affect a deeper sediment layer and thus limit future exposures to the contaminants. The present study focused on the issues related to in-situ amendment mixing.

While in-situ treatment can be very appealing because of its obvious advantages (it is less expensive than dredging and ex-situ treatment, causes less disturbance in the environment, and reduces contamination in place), there are also several limitations associated with in-situ technologies (USEPA, 2005). Introduction of the various amendments into the sediment in adequate levels and proper mixing to achieve homogeneous distribution throughout the contaminated zone poses many challenges. In addition, contaminated sediment resuspension and/or reagent release into the water column is of concern as well.

Devices that have been used in the field to introduce chemical amendments into sediments in-situ can be grouped into two major categories based on reagent mixing depths. Systems that can deliver reagents only into the surface layer (generally <1 ft) of sediments are of horizontal constitution and the ones that are capable of mixing deeper layers have a vertical setup. Mixing depth capabilities of a device are important because highly contaminated sediments are often located well below the sediment surface, sometimes even covered by cleaner material. The characteristics of a specific site will determine the choice of the mixing device used. A horizontal auger type system was used in a study to mix activated carbon into the top 1-ft sediment layer in a marine tidal mudflat area (Cho et al., 2007). The horizontal auger, called the "rotovator" in this technology was attached to a shallow-draft barge that was capable of sitting on the top of the sediment at low tide when the mixing occurred (i.e. with no overlying water). This technology was targeted for "shallow estuarine and coastal regions" to mix activated carbon into sediments to reduce the bioavailability of organic contaminants. Results of this study showed that activated carbon was mixed homogeneously into most of the sediment plots. In another study a horizontal rake system mounted on a barge was used for the sub aqueous introduction of a calcium nitrate solution to enhance in-situ biodegradation and to control odors (Sullivan et al., 2005 and Babin et al., 2003). Successful treatment results were achieved by injecting the amendment to about 10 cm below the sediment surface; and less then 20 cm of the top sediment layer was affected by the treatment.

Amendment delivery and mixing devices tested in the field that were capable of mixing deeper sediment layers were generally developed from well-established soil stabilization technologies. An in-situ solidification/stabilization technology to treat sediments used a rotary injection system (similar to high pressure grouting) mounted on a suction dredger (Pensaert et al., 2003). The injection system consisted of a rotating hollow shaft that had a horizontal bar with injection ports attached to its bottom. The reagent delivery/mixing system could move both in the downward and the upward direction while rotating and injecting cement slurry (or other required additives) into the sediment. This device had the capability to control the thickness of the mixed sediment layer between 0.5 and 2 m (about 1.6-6.6 ft). Greater mixing depths were achieved in another in-situ solidification/stabilization study using a device with a similar mixing tool construction (Lawson et al., 1996); the depth of the contaminated river sediments treated was about 14 ft in this case. The mixing tool contained a vertical kelly bar shaft and horizontal blades attached to it. The amendment was pumped into the sediment through the hollow center shaft and mixing blades during both the downward and upward rotation of the tool. Additional mixing was applied moving the tool up and down in the sediment column several times, with a total mixing time of 2 hours. Steel casings equipped with a seal assembly that allowed rotation of the kelly bar but no upward movement of water and sediment were used to contain the mixed sediment area. The upper 3 ft of sediment did not solidify in this study and some sediment did move up through the seal to the overlying water column within the casing. Therefore, the authors concluded that additional system refinements were needed. Another solidification/stabilization technology that used a different type of mixing device was also able to achieve greater amendment mixing depths, as deep as 10 ft in soft estuarine sediments (Maher et al., 2007). The mixing device was comprised of a triple auger system (three augers aligned adjacent to one another) attached to a barge-mounted crane. The Portland cement amendment slurry was introduced into the sediment through the hollow-stem rotating shafts of the vertical augers. The cement slurry was mixed into the sediment both during the downward and the upward movement of the augers resulting in successful stabilization/solidification. Resuspension affected a 75-ft radius zone around the mixed sediment column. Therefore, a properly designed confinement system would be needed for operation in highly contaminated sediments.

As outlined in the previous paragraphs, in-situ amendment delivery and mixing in sediments can be challenging in terms of achieving the required mixing depths and the targeted reagent yields. Another key issue is sediment resuspension and potential amendment release into the overlying water column. Although many studies addressed the need for physical separation of the mixed sediment area during operation, the devices themselves did not incorporate a solution for containment. A pilot scale in-situ sediment remediation system that provided contained conditions for amendment delivery and mixing to occur was developed by Seaway Environmental Technologies, Inc. and is described here. Confinement was achieved by using a casing that was part of the in-situ amendment mixing device. This device was a modified version of a mixing tool first reported by Chesner (2005). The device claimed to be able to: 1) deliver reagents to a specific target depth, 2) homogeneously mix amendments into the sediment, and 3) minimize sediment resuspension and therefore prevent contaminant dispersion from the site by providing containment during mixing.

The in-situ treatment system used in the present study consisted of a hydraulically operated 2x2x2 ft steel casing called the "reactor" and the mixing tool housed by this casing (Figure 4.1). This pilot-scale system was intended to represent a larger scale system appropriate for carrying out mixing operations at the full scale. The reactor was open at the bottom and closed at the top and therefore it allowed contained mixing conditions. The reactor system was supported, rotated and driven into the sediment using a DK-50 drill rig (50 HP unit) that was modified to accommodate the system design. The casing was designed to penetrate the sediment by a vertical load that pushed the reactor into the sediment. A pressure regulator on the top of the casing allowed excess air and/or hydraulic pressure to be released during descent into the sediment. The pressure release port consisted of one 1-1/2" diameter opening with a bib to attach a hose to transport and collect excess fluid generated due to excessive internal pressure.

Amendment mixing was achieved using a similar mixing tool as seen in studies reported by Lawson et al. (1996) and Pensaert et al. (2003), i.e. a hollow vertical shaft with horizontal mixing blades. The mixing tool used in the present study was deployed by a hollow stem center steel drive shaft that had free vertical (up and down through the reactor) and rotational movement at variable speeds (Figure 4.1). The device was capable of delivering amendments to sub aqueous sediments during continuous mixing in the downward or upward vertical direction. Slurried activated carbon powder was pumped through a pipe within the center shaft and was delivered and mixed into the sediment through ports located on two pipe extensions welded to the bottom of a rotating mixing tool-blade that was attached to the bottom of the shaft. Each pipe had a series of port openings (approximately 10 mm in diameter) designed to distribute the slurried

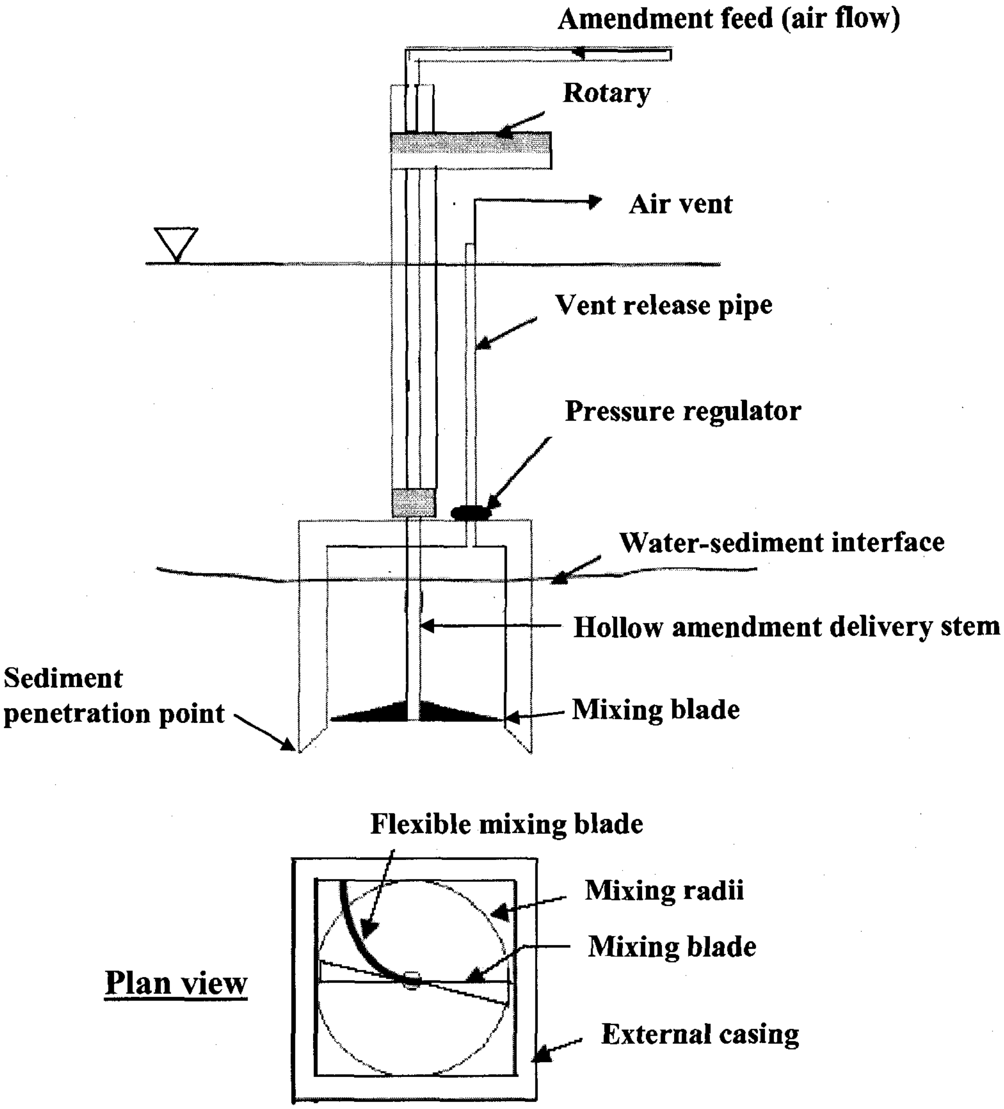


Figure 4.1 Single shaft in-situ reactor (courtesy Seaway Environmental Technologies, Inc.).

amendment into the sediment as the blade rotated through the sediment. The wing-shaped mixing blade was able to rotate through the sediment with minimal resistance and it also included a flexible blade extension made from pre-stressed steel strands designed to flex-penetrate into the squared corners of the reactor to provide for mixing of the sediment located in the potential dead corner zones. The square-shaped reactor offered one significant advantage: it minimized the field overlap problem typically encountered in in-situ solidification stabilization studies (Maher et al., 2007; Pensaert et al., 2003; Lawson et al., 1996).

The aim of the present study was to quantify and evaluate the amendment delivery and mixing efficiency of an in-situ sediment remediation system by mixing activated carbon into dredged Cocheco river sediment. The activated carbon was used as a tracer to evaluate the performance of the device in terms of reagent yield and homogeneity of the mixing. Sediment resuspension and reagent release into the water column were also investigated.

Materials and Methods

Sediment Characterization

The sediment used in this study originated from the Cocheco River in Dover, NH. The treatment demonstration took place at the City of Dover, NH's sediment disposal site. A pile of dredged sediment was set aside on the test site and left in the open for several months. All sediment used in the demonstration was pre-processed through a 3-inch bar screen to produce the final source material stockpile. The background organic content was determined by the "Loss on Ignition" method using a Stable Temp® muffle furnace from Cole-Parmer. Samples were first kept at 105°C overnight to determine the dry weight. Next, samples were heated to 550°C for 2 hours to determine the background organic content. The average background organic carbon level was 5.0 ± 3.2%. Gradation tests were performed by S.W.Cole Engineering, Inc. following the standard ASTM D2487 "Unified Soil Classification" procedure. Composition of the five samples tested ranged from 5.7 to 17.8% for gravel, 58.8 to 85.5% for sand, and 6.7 to 23.9% for fines.

Reagents

The amendment used in this study was a fine, powdered activated carbon purchased from Calgon Carbon Corporation (Pittsburgh, PA). A carbon slurry concentration of 16.7% was chosen as the design dose for the test program. The polymer added to aid sediment settling after mixing was Krysalis FC2043, a cationic acrylamide copolymer from Ciba Specialty Chemicals Corporation (Suffolk, VA).

Field Demonstration Setup

The performance of the in-situ amendment delivery and mixing device developed by Seaway Environmental Technologies, Inc. and described in the background section (see Figure 4.1 and pertinent discussion) was evaluated within specifically designed and fabricated steel test cells. Cells were open from the top and bottom, they were 4 ft high and had a cross sectional area of 3 ft by 3 ft. Six test cells were combined into one test module that had a 9 ft by 6 ft footprint. The cells were first lined with impermeable polyethylene bags. After that the compartments were filled with 2 ft of tamped and consolidated sediment. The sediment was then saturated with water. Finally, 1 ft of overlying water layer was pumped over the saturated sediment layer. This setup simulated in-situ sub aqueous mixing conditions. The test cell module provided the means to conduct consecutive test runs (i.e., one test in each individual cell).

In the demonstration the in-situ sediment treatment system was deployed from a platform elevated above the test modules that acted as a simulated marine vessel that would support the system during actual field deployment. Amendment delivery and mixing occurred within the 2x2x2 ft reactor that was submerged 18 in deep into the sediment. Activated carbon was not added to the top 1, 3 or 10 inches of sediment resulting in 17, 15 or 8 inches thick treatment zones, respectively, called the "mixed sediment layer". The purpose of the 6 in freeboard above the sediment surface within the casing was to provide expansion volume within the reactor to permit free mixing to occur and to provide sufficient space for the introduction of a slurried amendment. Variables associated with the performance of the mixer that were evaluated in each test run are summarized in Table 4.1.

Certain parameters listed in Table 4.1 were interdependent. Values for mixing depths and the amount of activated carbon added were chosen first. In a field application these values are defined by the location and the amount of the contaminants present. Next various descent/ascent-rotation ratios (called "k" values, see Table 4.1) were chosen to test at which value would most effective mixing occur. The idea behind this operational design parameter was the hypothesis that most effective mixing would happen if a given rotational or mixing speed was applied with an optimum vertical descending or ascending rate. These parameters represent a balance between minimization of sediment disturbance and therefore resuspension and the mixing required to disperse the reagent into the sediment. The amendment was mixed into the sediment during the downward rotation of the mixer for only two runs; in the rest of the tests the activated carbon was introduced during the upward mixing period. The mixing time was then defined by the ratio of the mixing depth to the vertical speed of the mixing device. The pump flow rate was calculated by dividing the required volume of the injected amendment slurry with the mixing time. This assured that the sediment layer was treated in one vertical pass.

Table 4.1 Variables associated with the performance of the mixer.

Run	v (1) in/min	Ms (2) rpm	k = Ms/v rev/in	Qp (3) gpm	Mixing depth (4) in	Mixing time min	AC added (5) %
2A	38.0	4.8	0.1	1.8	15	0.4	0.55
2B	32.0	7.5	0.2	2.4	15	0.5	0.77
3A	8.4	2.9	0.3	1.3	15	1.8	7.36
3B	6.3	5.5	0.9	2.7	15	2.4	2.33
4A	5.4	3.8	0.7	2.2	15	2.8	4.30
4B	6.3	5.5	0.9	2.7	17	2.7	1.46
5A	6.0	9.2	1.5	3.4	15	2.5	5.22
5B	7.7	9.2	1.2	3.2	15	1.9	3.81
6A	7.8	9.3	1.2	2.9	15	1.9	3.38
6B	6.8	9.2	1.4	3.1	15	2.2	4.11
7A	7.5	3.5	0.5	3.8	15	2.0	4.14
7B	4.0	6.0	1.5	2.3	8	2.0	4.02
8A	6.5	4.4	0.7	3.7	8	1.2	5.75
8B	6.0	3.7	0.6	2.5	8	1.3	3.91
9B	6.8	3.4	0.5	4.2	8	1.2	5.17
10A	6.0	2.7	0.5	2.8	8	1.3	4.88
10B	4.9	4.0	0.8	3.0	8	1.6	5.46
11A	11.4	8.0	0.7	5.0	8	0.7	4.02
11B	8.0	5.0	0.6	4.0	8	1.0	4.60
12B	10.0	5.0	0.5	4.3	15	1.5	3.99
13A	6.7	12.7	1.9	3.4	8	1.2	5.46
13B	5.9	11.8	2.0	3.5	8	1.4	5.75
14A	8.8	10.6	1.2	2.9	15	1.7	3.07
14B	10.0	10.0	1.0	3.3	15	1.5	3.07
15B	8.1	4.4	0.5	2.7	15	1.9	3.07

(1) v = vertical speed of the blade during mixing
(2) Ms = mixing speed
(3) Qp = pumping flow rate for the activated carbon
(4) Sediment mixing depth; measured from the bottom of the reactor.
(5) Activated Carbon (AC) added by dry sediment weight.

Turbidity Measurements and Total Solids Determination

Turbidity measurements were performed using a portable Hach turbidimeter. The amount of total solids was determined based on a calibration curve that was developed in the laboratory for Cocheco River sediment in the range of 0 to 199 ntu turbidity and 0 to 812 mg/L total solids: Total Solids (mg/L) = 4.0785 * Turbidity (ntu) + 5.4256 (r^2 = 0.9989).

Polymer Dosing

The actual polymer dose was determined in the field based on the amount of total solids in a given mixing cell. The following ratio was used: 1 mL of a 0.2% polymer solution was added to 830 mg total solids. The polymer was injected and mixed into the overlying water column in the reactor after amendment delivery and mixing had occurred.

Field Sediment Sampling

Grab samples were taken before mixing to determine the background carbon level. After mixing, sediment cores were taken with a Wildco® model 2424 hand corer (Wildlife Supply Company, Buffalo, NY). Sub samples from each core were analyzed to determine the amount and location of the activated carbon mixed into the sediment.

Activated Carbon Analysis

Samples were first dried at 105°C, followed by grinding and storage in a dessicator until analysis. Samples were analyzed using a TA Q600 SDT Thermogravimetric Analyzer (TA Instruments, New Castle, DE) and the % activated carbon was determined based on the weight loss measured between 400 and 625°C under high purity oxygen flow. The measured values were corrected for the background organic content in the same temperature range (1.98±0.81%). A second correction was performed using the calibration curve that was determined in the laboratory based on standards that were prepared by mixing known amounts of activated carbon into dried Cocheco River sediment: Activated Carbon measured (%) = 0.6636 * Activated Carbon added (%) + 0.577 ($r^2 = 0.9944$).

Results and Discussion

The in-situ sediment amendment delivery and mixing device developed by Seaway Environmental Technologies, Inc. was tested in the present study. The objectives of the project were: 1) to evaluate the amendment delivery and mixing efficiency of the system, and 2) to monitor and minimize sediment resuspension due to mixing. Pilot scale tests were performed in 4 ft high and 3 by 3 ft wide test cells filled with saturated dredged Cocheco River sediment with an overlying water column on top to mimic in-situ conditions for underwater amendment mixing.

Amendment delivery and mixing efficiency was evaluated by the injection and mixing of activated carbon into the sediment. Measured activated carbon concentrations, calculated amendment recoveries (i.e., measured concentrations normalized to the added amount) and standard deviations of the measured activated carbon concentrations were used as metrics to evaluate the data. Activated carbon concentrations and recoveries were related to amendment yield, while the standard deviation was used to assess the vertical and the radial distribution of the amendment. Detailed explanation of these metrics and the analyses performed is outlined in the sections below. Sediment resuspension was measured by monitoring turbidity and total solids levels in the overlying water within the reactor. A polymer was added to selected runs to evaluate its efficiency in aiding sediment settling and therefore reduce residual turbidity.

Activated Carbon Recovery and Distribution in the Mixed Sediment Zone

There was a statistically significant (at the 1% level) linear relationship between the added and the average measured activated carbon (Figure 4.2), even though most of the data points fell under the 1:1 line indicating that not all the carbon added was recovered. The amount of activated carbon added was known for each test run, while average measured percentages were calculated for each sediment core based on the sub samples taken from the core. There are a number of experimental factors that could have affected recovery rates, e.g., the accuracy of volumetric readings or settling of the activated carbon in the source container and the pumping system. However, these factors are believed to be only minor contributors to the decreased yields. A more significant effect was the limited capacity of the pore volume in the sediment to accommodate the amendment slurry (refer to Figure 4.3b and the accompanying discussion). In addition, problems associated with the sampling methodology and representativeness of the samples taken could have had a negative influence on the recoveries as well. In many cases it was difficult to properly recover the sediment cores because of the "liquid" nature of the sediment. Even when sampling was performed after a few days of sediment consolidation the recovered core lengths were shorter than the expected lengths due to compression effects of the coring procedure. The expected length was 18-20 in for the majority of the sediment cores, while the recovered lengths varied between 3 and 14 in.

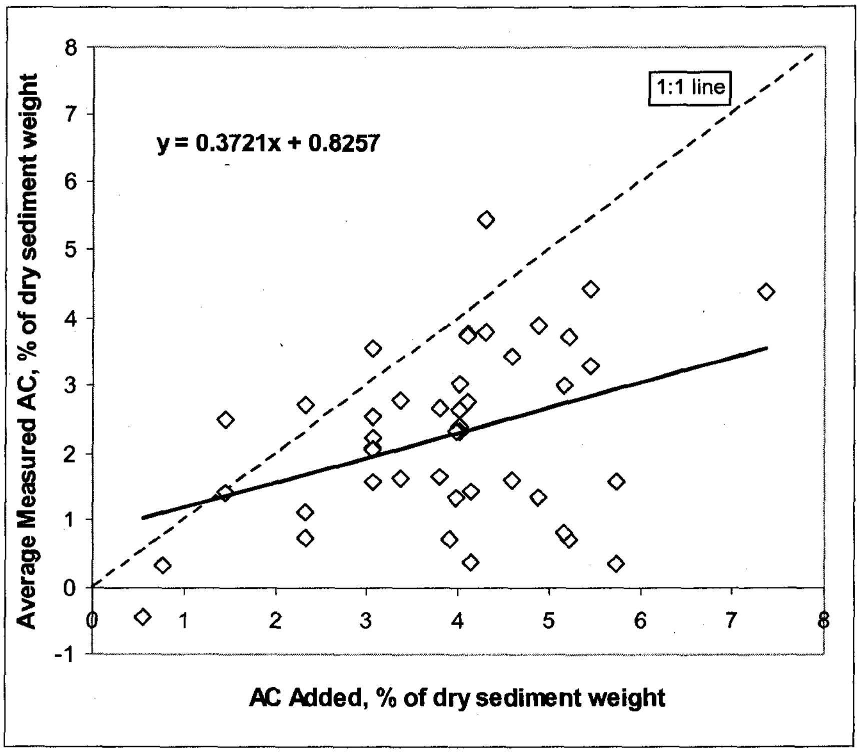


Figure 4.2 Plot showing a statistically significant linear relationship (at the 1% level, $p = 0.0089$) between the added and the average measured activated carbon (AC) for each sediment core [$n = 44$].

Besides the average measured activated carbon, the average activated carbon recovery and the standard deviation of the measured amendment concentrations were also calculated for each sediment core based on the sub samples and the values were plotted against the variables shown in Table 4.1. The average % recovery was calculated as the ratio of the average activated carbon measured for each core and the amount of amendment added in the given run and therefore it directly related to the average reagent yield, while the standard deviation served as a measure of the vertical distribution of amendment concentrations within the cores. A linear fit was applied to the data and the statistical significance of the relationship was determined between the operational variables and the average % recovery (Table 4.2) or the standard deviation (data not shown). As discussed previously, many of the variables shown in Table 4.2 were interdependent (refer to Table 4.1 and to pertaining discussion). For example, the "k" value was defined as the ratio of the vertical speed of the mixer and the rotational or mixing speed. The mixing time depended on the thickness of the mixed sediment layer and the vertical speed of the mixer, while the pump flow rate was a function of the volume of the amendment added and the mixing time.

As shown in Table 4.2, there was a statistically significant linear relationship between the average % recovery and the following variables: the % activated carbon added (at the 1% level), the pump flow rate (at the 5% level), and the mixing speed (at the 5% level). There was no evidence of a statistically significant relationship (at the 10% level) between the other variables and the average % recovery (Table 4.2) or the standard deviation (data not shown) indicating that changing the operational values of those parameters did not have a significant effect on average reagent yields and vertical amendment concentration distributions within the sediment cores.

Table 4.2 Description of the linear fit for the variables and the activated carbon (AC) recovery and the statistical significance of these linear relationships (see Table 4.1 for the definition of the variables).

Variable	**Average Recovery, %**				
	a	b	n	p-value	Significance
v (in/min)	-0.0491	60.417	48	0.8016	no at 10%
Ms (rpm)	2.0425	47.258	50	0.0316	yes at 5%
k (rev/in)	6.5718	54.663	50	0.5931	no at 10%
Qp (gpm)	-11.799	97.598	50	0.0175	yes at 5%
Mixing time (min)	18.716	28.751	50	0.3015	no at 10%
AC added (%, w/w)	-11.07	106.12	50	0.0087	yes at 1%

(a & b = slope and intercept of linear fit; n = number of samples; the p-value describes the statistical significance of a given factor, e.g. a p-value of 0.05 means that thereis a statistically significant linear relationship between the variable and the recovery at the 5% level)

Figure 4.3a indicates that as the % of activated carbon added increased the % recovery decreased. This may relate to the capacity of the pore space to accommodate the larger volumes of slurry (Figure 4.3b). The Cocheco River sediment used in this study had about 42% pore volume, which theoretically would have provided sufficient volume for the amendment added. However, the sediment was saturated when amendment delivery and mixing occurred, which meant that the activated carbon solution had to replace the water. For most runs the activated carbon slurry was first introduced at the bottom of the mixed sediment layer and after that throughout vertical mixing in the upward direction. The idea behind this approach was to allow the pore water in the upper layers to leave the sediment as it was gradually displaced by the amendment slurry.

However, not all the pore water can be displaced in such a manner. Strong attractive forces between high specific surface area silt particles and some water molecules can be difficult to break leaving water behind. Using an estimate of 50% effective void volume (i.e. pore volume that could have water displaced), in about 25% of the runs more activated carbon slurry was pumped into the cells than the available pore space.

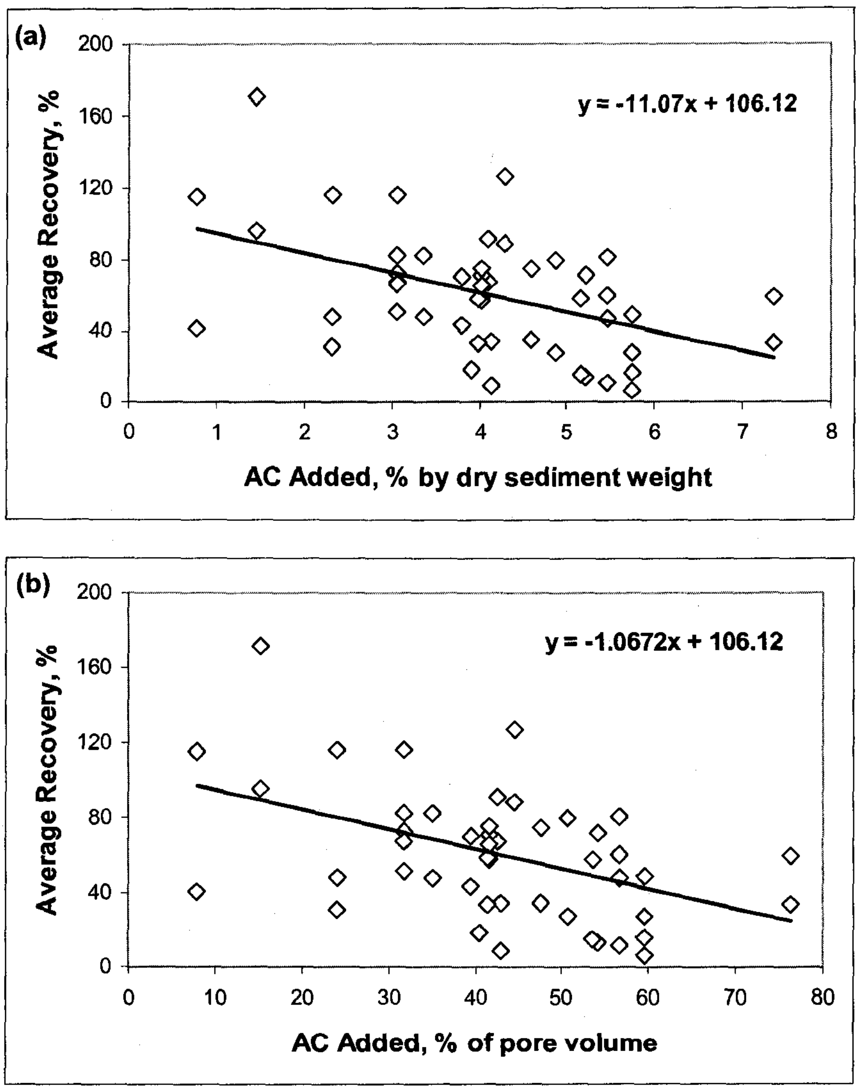


Figure 4.3 Plots showing a statistically significant linear relationship (at the 1% level, p = 0.0087) between the added activated carbon (AC) expressed as (a) % of dry sediment weight and (b) % of pore volume and the average % recovery for each sediment core [n = 50].

Figure 4.4 shows that amendment recoveries slightly improved with increased mixing speed. On the other hand, increased pump flow rates resulted in lower recoveries (Figure 4.5). Even though mixing time did not have a significant effect on amendment recoveries (Table 4.2), the interaction between pump flow rate and mixing time did (data not shown, p-value = 0.0039, significant at the 1% level). The significance of this interaction was expected because mixing time and pump flow rate are interdependent. The relationship between the two variables is described by the following equation: Pump flow rate = Volume of amendment slurry / Mixing time. Furthermore, the amount of activated carbon added expressed as % by dry sediment weight or % of pore volume (Figure 4.3a,b) and the volume of the amendment slurry added are the expression of the same variable based on weight or volume, which means that the trends shown in Figure 4.3a,b can also be related to the fit in Figure 4.5. In general better average % recoveries were achieved at lower amendment volumes, lower pump flow rates, and at higher mixing speeds.

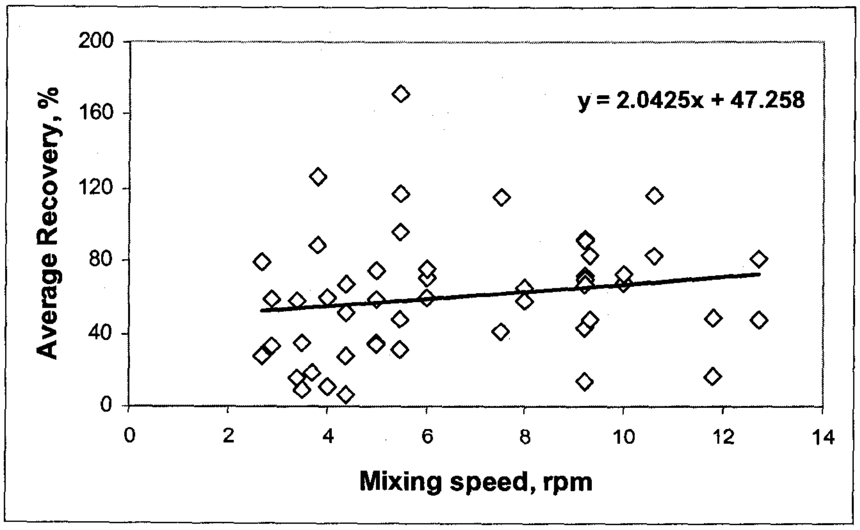


Figure 4.4 Plot showing a statistically significant linear relationship (at the 5% level, p = 0.0316) between the mixing speed and the average % recovery for each sediment core [n = 50].

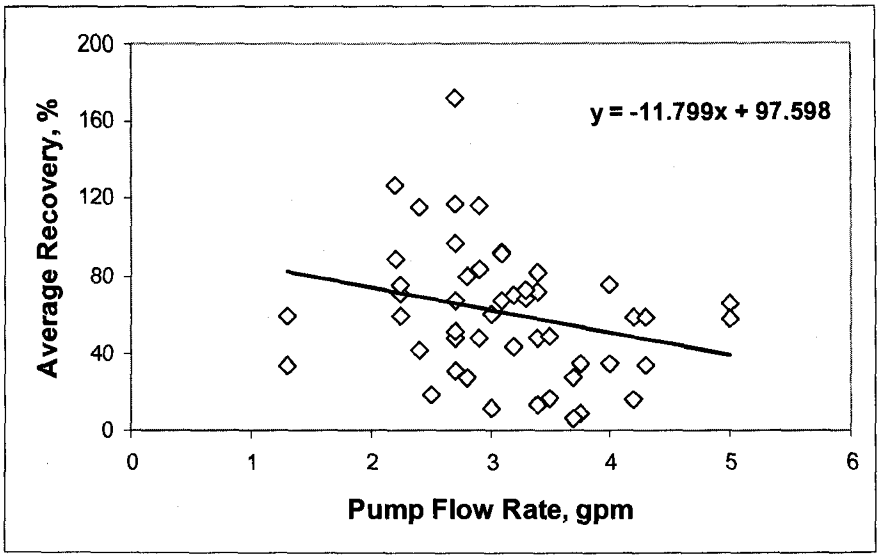


Figure 4.5 Plot showing a statistically significant linear relationship (at the 5% level, p = 0.0175) between the pump flow rate and the average % recovery for each sediment core [n = 50].

In addition to the parameters shown in Table 4.2, the effect of the thickness of the mixed sediment zone on the activated carbon recoveries and on the vertical distribution of the amendment concentrations was also investigated. In general, better amendment recoveries were achieved if the mixed sediment layer was thicker (Figure 4.6). The vertical spatial variation in activated carbon concentrations was also smaller in these cases (results not shown). These observations might have also been related to the ability to better recover the cores in these cases. Sediment condition at the time of coring varied for the different cells. Some cells were sampled the day after the test not allowing enough time for proper water drainage and sediment consolidation. In these cases cores were shorter and sometimes it was difficult to properly recover them because the sediment lacked sufficient strength. On the other hand, cores taken from cells that were allowed to drain and consolidate for a few days were generally longer and had a more solid consistency. This happened to coincide with runs with thicker mixing depths more than with thinner mixing depth tests. Furthermore, on average there was more activated carbon added to the runs with thinner mixing depths: 50.4±7.4 %, 37.3±16.2%, and 15.2 % expressed as % of the available pore space for the 8-, 15-, and 17-inch mixing depths, respectively. This might have also contributed to the lower recoveries observed in Figure 4.6 because of the limited capacity of the pore volume to accommodate larger amounts of activated carbon (see also Figure 4.3b).

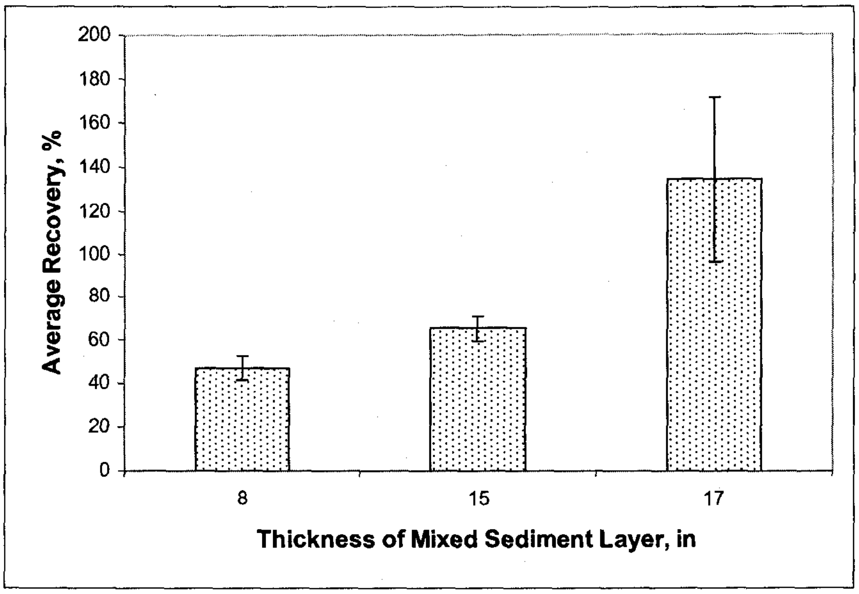


Figure 4.6 Plot showing the relationship between the thickness of the mixed sediment layer and the average % recovery for each thickness; the amount of activated carbon added (as % of pore volume) to the different mixing zones was: 50.4±7.4 % (to 8 in), 37.3±16.2% (to 15 in), and 15.2 % (to 17 in).

Besides the parameters used to evaluate the vertical distribution of the activated carbon, the horizontal distribution of the amendment was also investigated. The horizontal cross section of the mixed zone was divided into four areas shown in Figure 4.7 and the sediment cores were grouped based on their radial location. Higher recoveries were observed in the middle and the center of the mixed zone than in the edge and corner areas (Figure 4.8). This could have occurred because the pressure was not controlled and therefore it was not kept constant through each reagent delivery port on the mixing blade resulting in higher activated carbon yields closer to the center shaft. Figure 4.8 also suggests that the achieved activated carbon yields were closer to the expected values near the mixing shaft. The extent of variation in the recoveries was similar for the different zones as indicated by the error bars. Similarly, the average standard deviation of the measured activated carbon concentrations for cores in the same four horizontal mixing zones were of the same magnitude (data not shown) indicating that the variation in amendment concentrations with depth was similar in the whole mixed zone. Therefore, the activated carbon that did get mixed into the sediment was spread around fairly evenly in each zone.

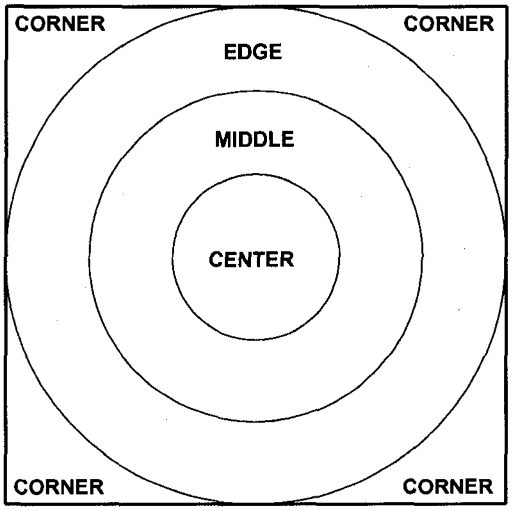


Figure 4.7 Areas defined in the horizontal cross section of the mixed zone to evaluate the radial amendment distribution.

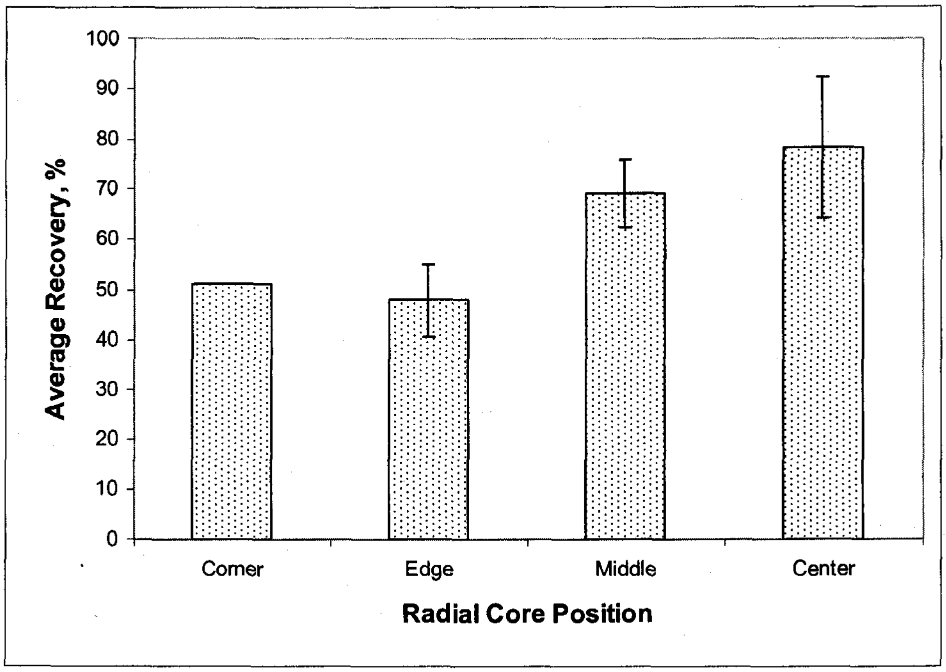


Figure 4.8 Plot showing the relationship between the radial core position and the average % recovery for each radial core position zone.

Activated Carbon Measured Outside of the Mixed Sediment Zone

Reagent mixing occurred within the 2x2x2 ft in-situ treatment reactor (Figure 4.1) that contained 18 in of sediment and 6 in of water. Amendment mixing occurred at the bottom 8, 15, or 17 in of the enclosed sediment volume leaving 10, 3, or 1 in of material intact at the surface, respectively. There were two reasons for implementing this strategy: 1) To minimize residual turbidity by preventing the sediment surface from breaking up and therefore complete mixing with the overlying water, and 2) to minimize percolation of the amendment slurry from the sediment to the overlying water. Despite this precaution some of the amendment solution did escape from the sediment in certain runs, which was attributed to the limited capacity of the pore spaces (see Figure 4.3b). It is important to note that the amendment released into the overlying water stayed within the reactor and it was observed as a thin layer of activated carbon on the top of the sediment after the reactor was removed and the water was pumped out of the cell, indicating contained mixing conditions.

Data points shown on Figure 4.9 represent individual sub samples within the cores taken from above or below the mixed sediment zone. There was one whole core taken outside of the reactor after mixing had occurred and activated carbon concentrations in sub samples of that core were equal to the background carbon level of the sediment. Data points indicated by an "x" in Figure 4.9 are sub samples taken at or close to the sediment surface (within the top 4 in). The majority of high activated carbon concentrations found outside of the mixed sediment were associated with these samples, suggesting that not all of the amendment was successfully mixed into the intended mixing zone. As mentioned earlier, the activated carbon was forced out of the sediment porewater to the overlying water inside the mixing device in those runs.

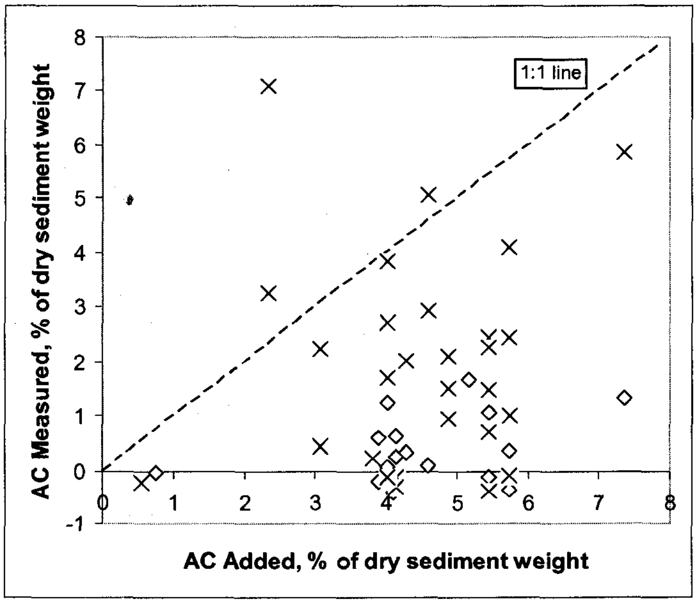


Figure 4.9 Plot of the added vs. the measured activated carbon (AC) for samples outside of the mixed zone (n = 44); samples labeled "x" were taken at or close to the sediment surface (in top 4 inches).

Sediment Resuspension Due to In-Situ Mixing

Rapid mixing speeds will induce sediment resuspension, therefore an attempt was made to maintain as low a mixing speed as possible to reduce dispersion. Laboratory results (not shown here) indicated that there was a mixing speed below which sediment resuspension and destabilization was minimized. The actual value of this mixing speed depended on the specific mixing tool. Sediment resuspension in the field was assessed in selected test cells by monitoring the level of turbidity and suspended solids generated in the water column during the sediment mixing tests. To aid sediment settling and therefore minimize post treatment dispersion, densifying-agglomerating reagents (e.g., polymer flocculants) could be introduced into the sub aqueous sediments during/post treatment. Polymeric flocculants have been used in the dredging industry to thicken and dewater sediments (Baize, 1976; Shanfelt et al., 1970), to enhance the settling characteristics of the dredged material after its disposal (Santos, et al., 2002) and to reduce solids concentrations in the effluent water of dredged sediment disposal sites (Schroeder et al., 1983).

A cationic acrylamide copolymer (Krysalis FC2043) was added to the reactor for selected test runs in the present study after the activated carbon mixing to evaluate the efficiency of the polymer in aiding sediment settling in the overlying water column and thus its ability to reduce the residual turbidity that was caused by the mixing operation. The turbidity was measured before and after amendment mixing, after the polymer addition, and at given settling times after the mixing. The data show that the polymer did not have an effect on sediment settling, i.e. the same total solids concentrations were achieved both with and without the polymer addition over 10 to 20 min. This was probably due to the high total solids concentrations at which compression settling is dominant and the polymer does not work. The same effect was observed in laboratory studies conducted with Krysalis FC2043 in Cocheco River sediment.

Conclusions

The present study evaluated the pilot-scale performance of the in-situ sediment remediation system by pumping and mixing slurried powder activated carbon under enclosed conditions into sub-aqueous sediment. The performance of the treatment system was evaluated by investigating the relationship between operational variables such as mixing speed, pump flow rate, mixing time, the vertical speed of the blade during mixing, thickness of the mixed sediment zone, and volume of the activated carbon slurry added and the amendment yield or the spatial variation of the measured reagent concentrations. Better amendment recoveries were observed at lower added activated carbon volumes, at faster mixing speeds, and at lower pump flow rates, all of which was directly or indirectly related to the availability of sufficient sediment pore space to accommodate the activated carbon slurry. For that reason, an important finding of the study was that a proper estimate of the available pore capacity to accommodate the amendment is critical in determining the amount of the reagent that can be successfully delivered into the sediment without release of the material into the overlying water column. On the other hand, no clear relationship was identified between the operational parameters and the spatial variation of the activated carbon concentrations most probably due to the poor core recoveries observed for most runs that resulted from the sediment lacking sufficient strength. Contained mixing conditions were achieved and the majority of the suspended sediment settled out fairly quickly from the overlying water column within the enclosure that was attributed to the large sand and gravel fraction of the tested sediment. Sediments containing larger silt and clay fractions are likely to behave differently in terms of sediment resuspension due to amendment mixing and therefore careful risk considerations should be implemented when applying the remediation system in those scenarios. Overall, the in-situ sediment remediation system showed great promise in terms of successful amendment delivery and mixing into sub-aqueous sediments. This study is the first report on the performance evaluation of an in-situ sediment treatment technology in which the same device served as both the amendment delivery/mixing and containment tool. The design should be further tested at the field-scale to evaluate the potential for a larger scale, commercial application of the system.

Supplemental Material to the In-Situ Amendment Mixing Device Evaluation Project

This supplemental material contains results of the laboratory studies conducted in support of the pilot-scale in-situ amendment mixing device evaluation performed in dredged Cocheco River sediment in the field. Activated carbon (AC) was used as a tracer to assess amendment delivery and mixing efficiency of the device. The goal of the laboratory investigations was to characterize the sediment material, to choose the type of AC to be used in the field, and to develop the methods that supported the field evaluation as well as the analytical technique to measure the AC. Photos of the field demonstration and outputs of the statistical analyses of the data are also included.

Cocheco River Sediment Characterization

Table 4.3 Background organic content of the Cocheco River sediment samples

Sample	**Organic Content* %**	**Sample**	**Organic Content* %**
1 Cocheco (12/01/06)	3.8	1 Cocheco (12/08/06)	7.4
2 Cocheco (12/01/06)	4.9	2 Cocheco (12/08/06)	6.2
3 Cocheco (12/01/06)	6.8	3 Cocheco (12/08/06)	2.9
4 Cocheco (12/01/06)	6.2	4 Cocheco (12/08/06)	4.8
5 Cocheco (12/01/06)	7.8	5 Cocheco (12/08/06)	5.7
6 Cocheco (12/01/06)	3.6	6 Cocheco (12/08/06)	4.5
7 Cocheco (12/01/06)	4.4	7 Cocheco (12/08/06)	7.4
8 Cocheco (12/01/06)	2.7	8 Cocheco (12/08/06)	4.0
9 Cocheco (12/01/06)	4.7	9 Cocheco (12/08/06)	5.0
10 Cocheco (12/01/06)	19.3	10 Cocheco (12/08/06)	5.8
11 Cocheco (12/01/06)	2.9	11 Cocheco (12/08/06)	3.8
12 Cocheco (12/01/06)	3.8	12 Cocheco (12/08/06)	4.6
13 Cocheco (12/01/06)	3.8	13 Cocheco (12/08/06)	6.0
14 Cocheco (12/01/06)	6.3	14 Cocheco (12/08/06)	5.1
15 Cocheco (12/01/06)	0.9	15 Cocheco (12/08/06)	4.4
16 Cocheco (12/01/06)	13.5	16 Cocheco (12/08/06)	4.7
17 Cocheco (12/01/06)	2.9	17 Cocheco (12/08/06)	4.7
18 Cocheco (12/01/06)	3.3	18 Cocheco (12/08/06)	2.7
19 Cocheco (12/01/06)	5.0	19 Cocheco (12/08/06)	4.7
20 Cocheco (12/01/06)	-0.4	20 Cocheco (12/08/06)	1.2
AVERAGE	5.3	AVERAGE	4.8
STDEV	4.4	STDEV	1.5
ave+stdev ; ave-stdev	0.9 ; 9.7	ave+stdev ; ave-stdev	3.3 ; 6.3
Range	0 to 19.3	Range	1.2 to 7.4
Total AVERAGE	**5.0**	**Total STDEV**	**3.2**

*Determined by the "Loss on Ignition" method (values based on dry sediment weight).

Table 4.4 Gradation and specific gravity of the Cocheco River sediment samples (determined by S.W. Cole Engineering, Inc.)

Sample	**Gravel, %**	**Sand, %**	**Fines, %**	**Specific gravity**
Dover dredge - 1	5.7	83.2	11	2.504
Dover dredge - 2	7.9	85.5	6.7	2.551
Dover dredge - 3	5.9	80.1	14	2.592
Dover dredge - 4	17.8	58.8	23.4	2.537
Dover dredge - 5	14.1	62	23.9	2.512

Evaluation of Various AC Types and AC Measurement Method Development

The purpose of this part of the study was to determine the level of AC that can be clearly distinguished from the background carbon level in the Cocheco river sediment and to develop a method that yielded accurate and reproducible measurement of the chosen type of AC. Two types of thermal methods were used: analysis either by a muffle furnace or a Thermogravimetric Analyzer (TGA).

Muffle furnace experiments. Four types of AC were tested from Calgon Carbon Corporation (Pittsburgh, PA); one was coconut based (12x40 OLC) and the other three were coal based (Filtrasorb® 400; WPH AC; and 50x200 mesh Carbsorb™). Sediment-AC mixtures as well as pure AC were analyzed for all four materials using a muffle furnace. Thermograms were developed showing the temperature range when the AC burned off. Pure AC thermograms indicated that the coal-based AC Filtrasorb burned off between 375 and 600°C (Figure 4.10). On the other hand, the coconut based AC (OCL) was oxidized at a lower temperature range, between 300 and 500°C (Figure 4.10). When the coal based ACs were mixed with sediment, the carbon burned off between 375 and 450°C (Figure 4.11) or 375 and 500°C (Figure 4.12a,b), a much shorter range than observed for pure AC (Figure 4.10), indicating that AC mixed with sediment will not be oxidized at the same temperature levels as AC by itself.

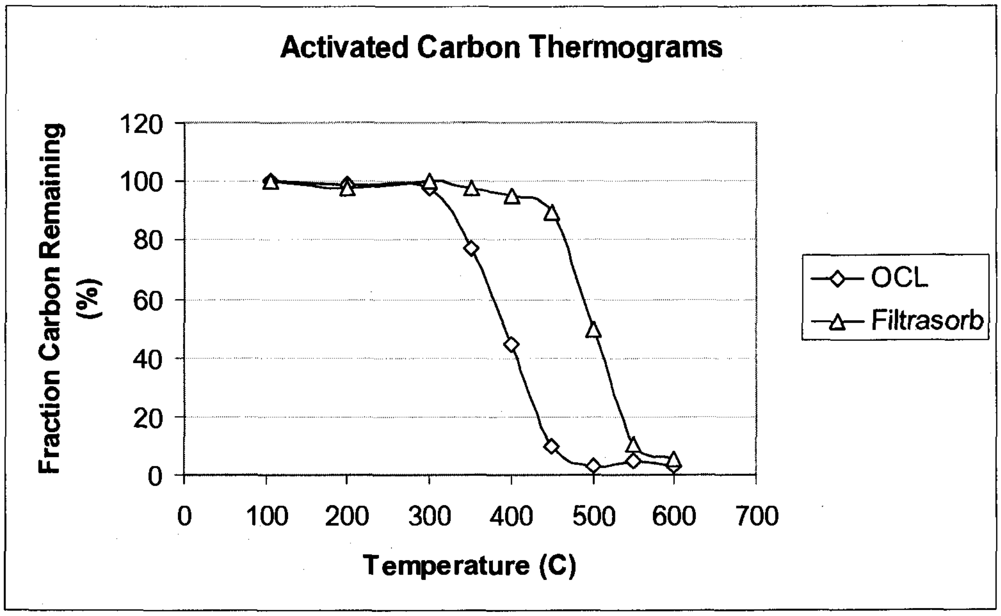


Figure 4.10 Thermographs of the OLC (coconut based) and Filtrasorb AC (coal based) show that the coal based AC burned off at a higher temperature (375-600°C) than the coconut based carbon (300-500°C).

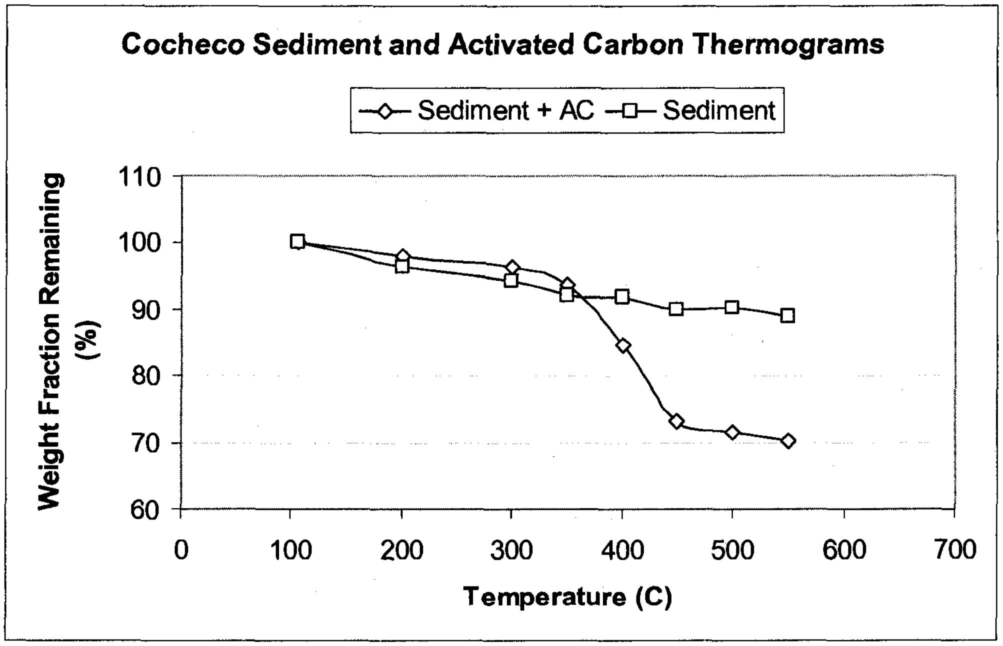


Figure 4.11 Thermographs of Cocheco River sediment mixed with or without Filtrasorb AC (coal based).

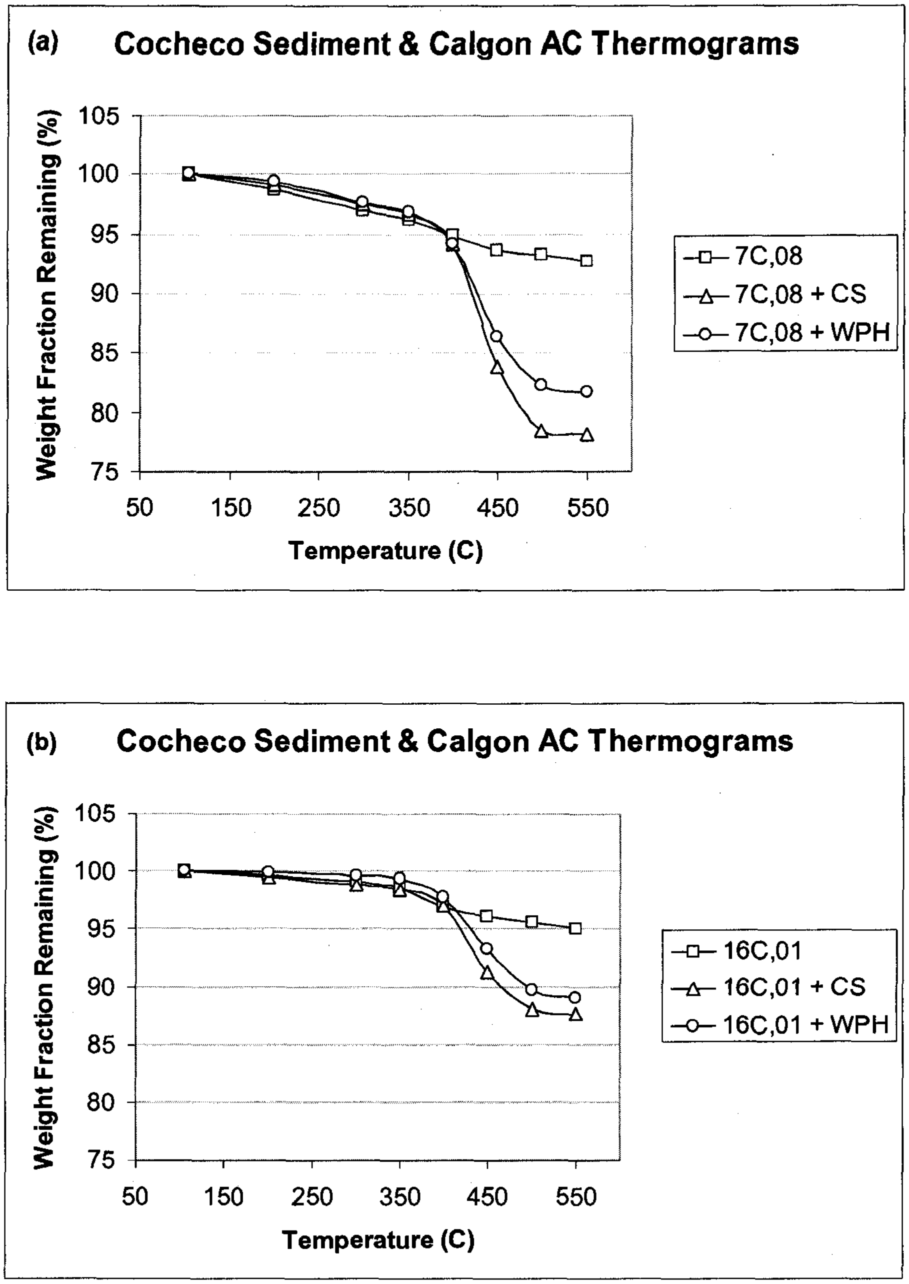


Figure 4.12 Thermographs of Cocheco River sediment samples (a) "7C,08" and (b) "16C,01" mixed with or without Carbsorb (CS) and WPH AC (both coal based). Sediment samples "7C,08" and "16C,01" were samples "7 Cocheco (12/08/06)" and "16 Cocheco (12/01/06)" shown in Table 4.3, respectively.

The amount of AC added was relatively high in these experiments (9.4 to 24.2% by dry sediment weight) therefore further investigation was performed to determine the minimum amount of carbon that can be distinguished from the background carbon content. Figure 4.13 shows thermograms for 1, 2, and 4% WPH AC (by dry sediment weight) mixed with Cocheco river sediment. Less than 2% AC content could not be clearly distinguished from the background carbon levels. The minimum amount of AC addition recommended for the in-situ amendment mixing was 4% if the muffle furnace technique was used as measurement method.

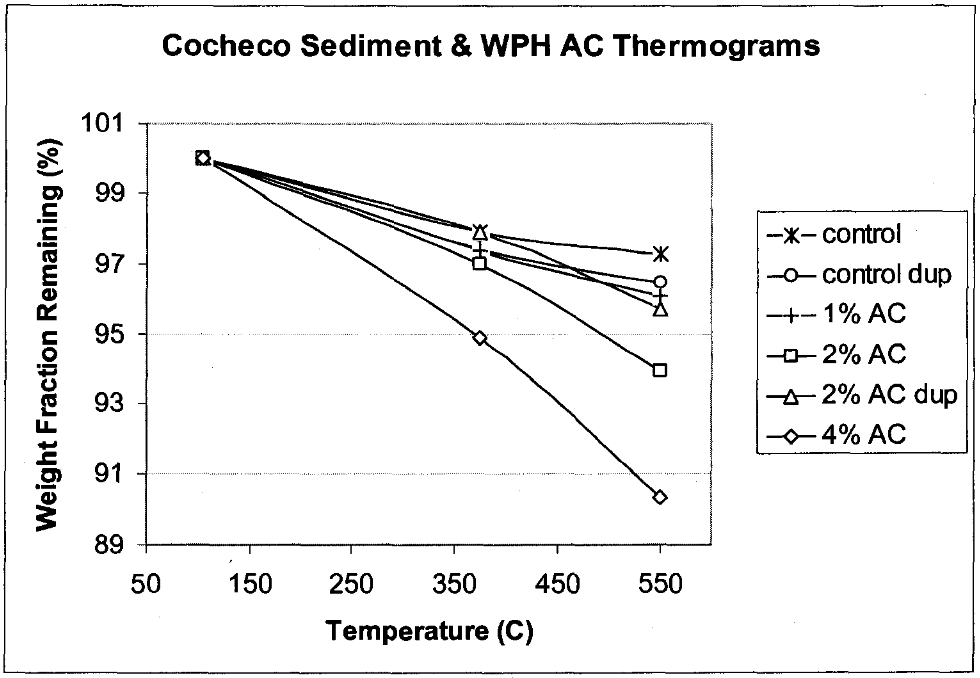


Figure 4.13 Thermographs of Cocheco River sediment mixed with or without WPH AC (coal based). The %AC added was based on dry sediment weight and the values tested were 1, 2, and 4%.

Thermogravimetric analyzer experiments. To improve the sensitivity of the AC measurements in sediment, experiment were performed using a thermogravimetric analyzer (TGA), an instrument more accurate than the muffle furnace. The goal was to develop an optimized measurement method for AC using the TGA and to establish a calibration curve using that method for the WPH AC.

The effect of various temperature programs and two different gases, high purity air and oxygen, on the AC oxidation procedure was investigated. Thermograms were prepared under both oxygen and air flow for pure AC, sediment mixed with AC and also for sediment without AC to determine the temperature levels at which the AC started to oxidize. Under air flow all the AC burned off between 475 and 675°C (Figures 4.14-4.15), and under oxygen flow between 400 and 625°C (Figures 4.16-4.17).

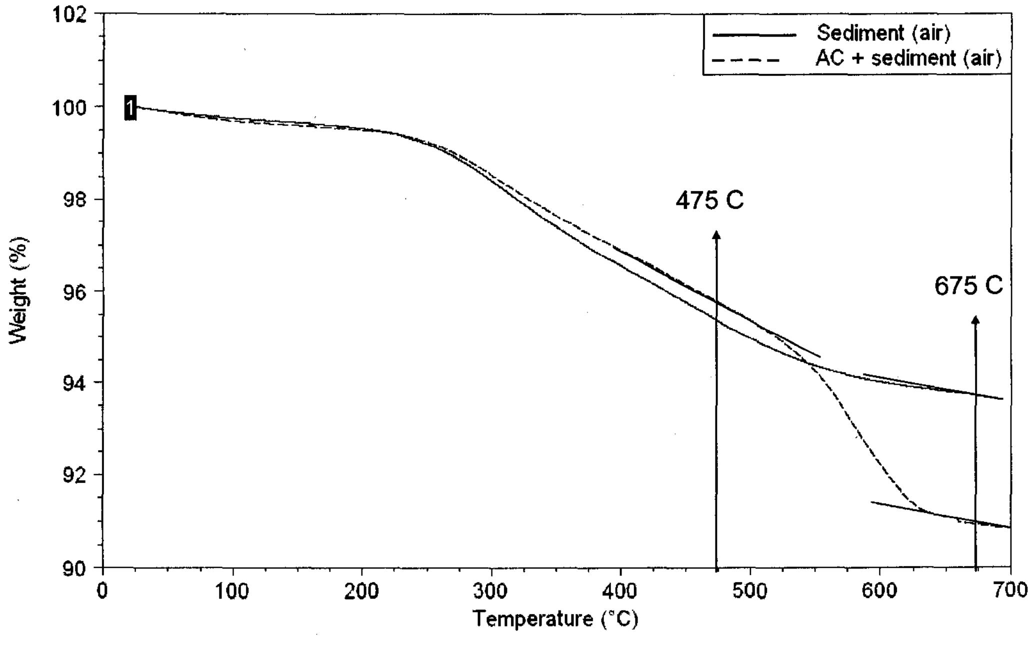


Figure 4.14 Thermograms of Cocheco River sediment with or without AC added under air flow.

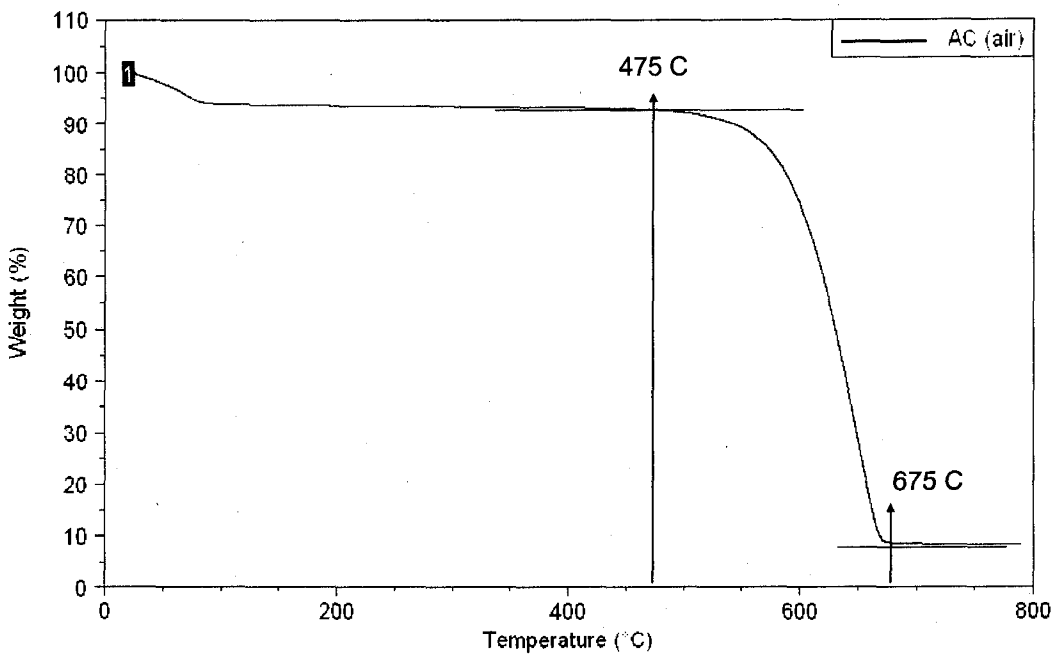


Figure 4.15 Thermogram of WPH AC under air flow.

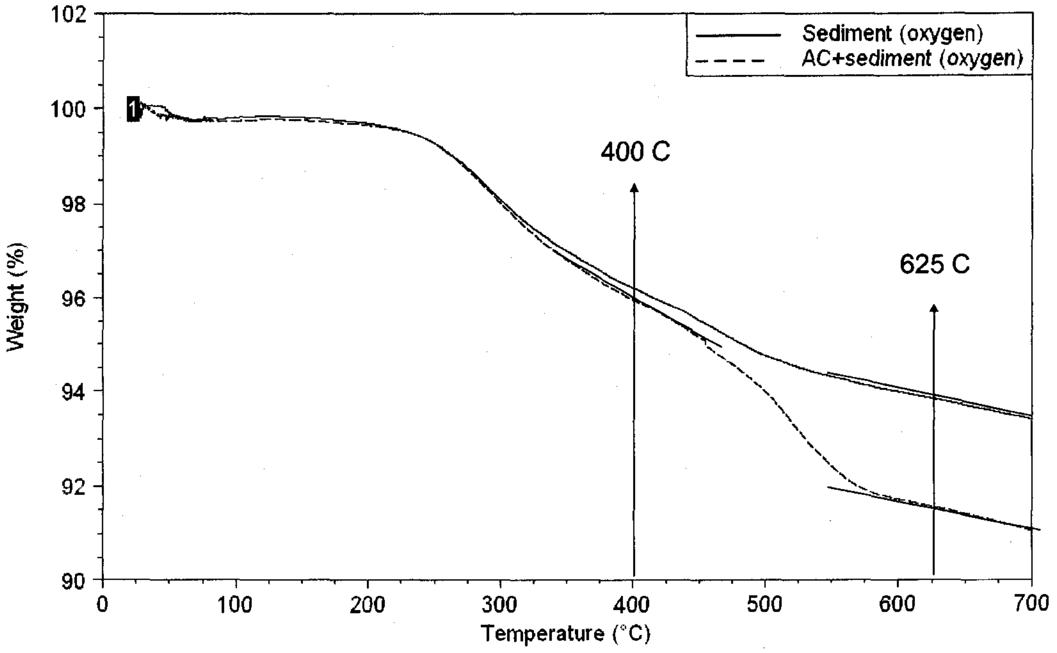


Figure 4.16 Thermograms of Cocheco River sediment with or without AC added under oxygen flow.

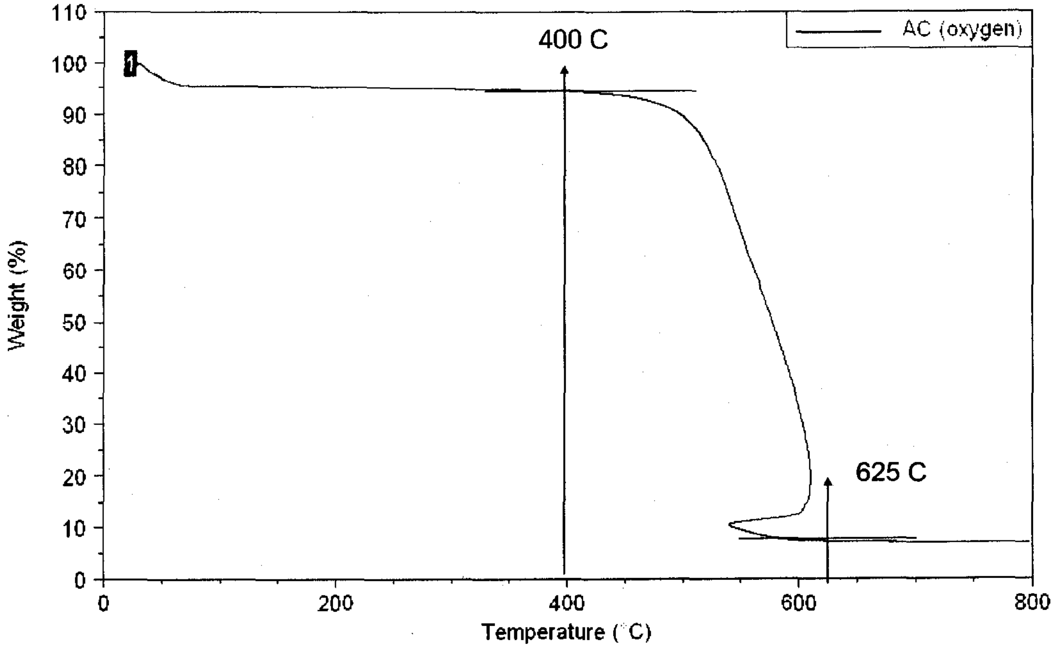


Figure 4.17 Thermogram of WPH AC under oxygen flow.

Standards were prepared to develop the calibration curve by mixing AC with dried Cocheco River sediment at different percentages, ranging from 1 to 10%. Samples were analyzed in the TGA both under high purity air and oxygen flow. The AC calibration curve developed under oxygen flow had a slightly better fit compared to air (Figure 4.18a,b), especially at the lower levels of AC where precise measurements were needed to be able to minimize the amount of AC used in the field study. The oxygen method was also slightly shorter than the air method, 65 vs. 69 min, respectively, which given the large number of samples (in the hundreds) during the field study was also an important factor. Since oxygen ensured more effective burning than air, it was chosen as the final analysis method. The calibration curve for this method was: AC measured (%) = 0.6636 * AC added (%) + 0.577 ($r^2 = 0.9944$).

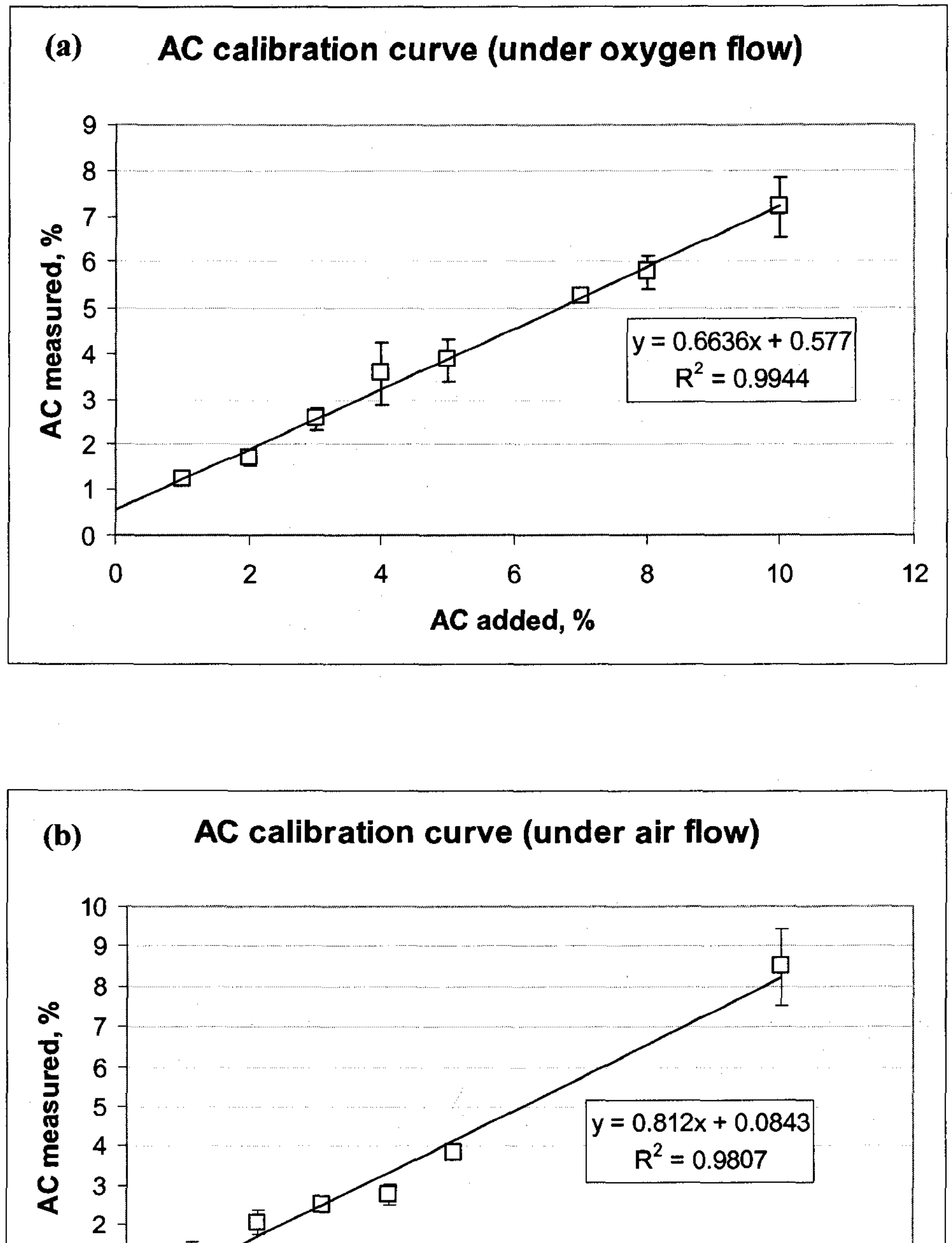


Figure 4.18 Calibration curves for WPH AC under (a) oxygen and (b) air flow.

Calculating the Concentration of Total Solids Based on Turbidity Measurements

Sediment resuspension and the potential transport of contaminated sediment material to clean sites after amendment mixing is a concern in case of in-situ treatment technologies. The amount of suspended sediment in the overlying water column after mixing was measured in the present study as turbidity in the field. The amount of total solids (TS) was determined based on a calibration curve that was established between turbidity readings and known amounts of TS in solutions prepared in the laboratory. Figure 4.19 shows a strong linear relationship between the two variables in the range of 0 to 812 mg/L TS or 0 to 199 ntu turbidity described by the following equation: TS (mg/L) = 4.0785 * Turbidity (ntu) + 5.4256 ($r^2 = 0.9989$).

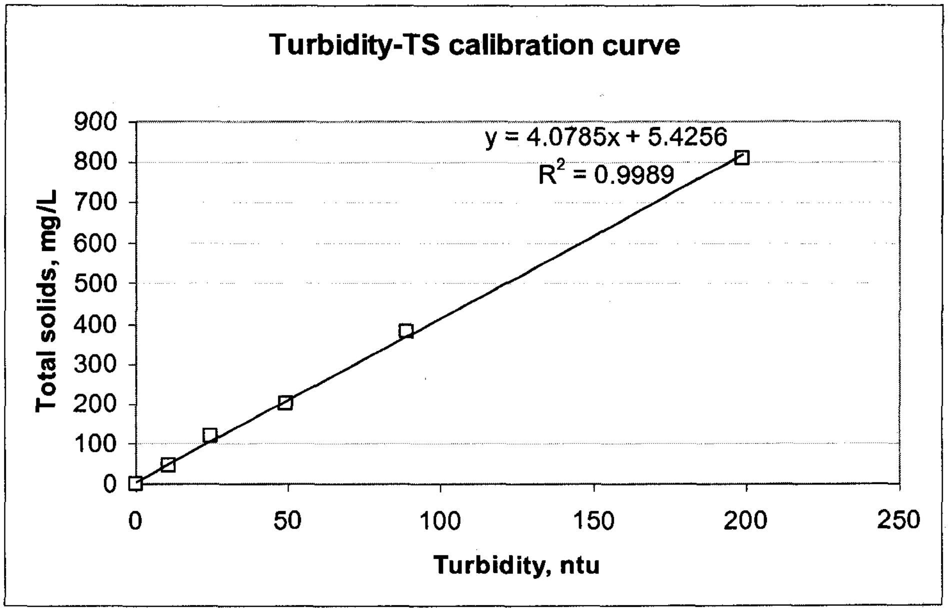


Figure 4.19 Turbidity-total solids (TS) calibration curve for Cocheco River sediment.

Sediment Settling Experiments – Polymer Testing

Settling experiments were performed to evaluate the efficiency of polymers in aiding sediment settling in the overlying water column after mixing and thus reduce the residual turbidity that was caused by the mixing operation. The type of polymer to be used, the minimum amount of sediment resuspension and an optimum polymer dose for minimum turbidity were determined. The exact polymer dose applied in the field demonstration was determined based on the concentration of TS in each mixing test. Total solids can only be measured in a laboratory, whereas turbidity can be determined in the field resulting in faster test performance. For this reason a calibration curve between turbidity and total solids (TS) in the water column was established in the laboratory (see Figure 4.19) and was subsequently used in the field to determine the polymer dose on site.

Testing different polymer types and the effect of polymer dose and solution L/S ratio on sediment settling. Two types of polymers were evaluated: Krysalis FC2043, a cationic acrylamide copolymer from Ciba Specialty Chemicals Corporation (Suffolk, VA) and the Ultrion® 7157 coagulant together with the Nalclear® 7768 flocculant from Nalco Company (Naperville, IL). Settling column tests using these two polymers revealed that Krysalis FC2043 effectively aided sediment settling and helped clear the overlying water column within minutes (Figure 4.20 and Photo 4.1), while Ultrion® 7157 / Nalclear® 7768 did not have any effect even over the period of a few hours. Therefore further experiments were only conducted with the Krysalis FC2043 polymer.

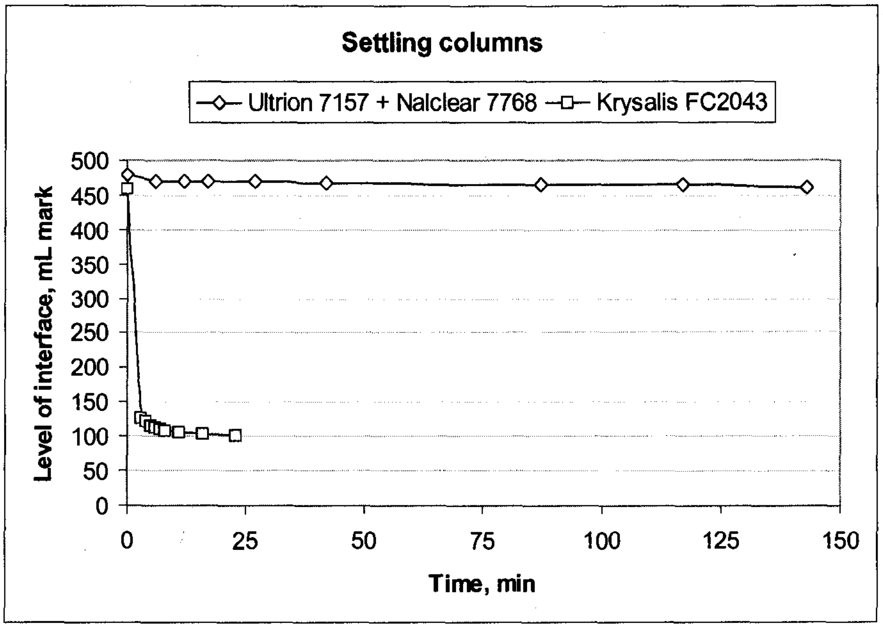
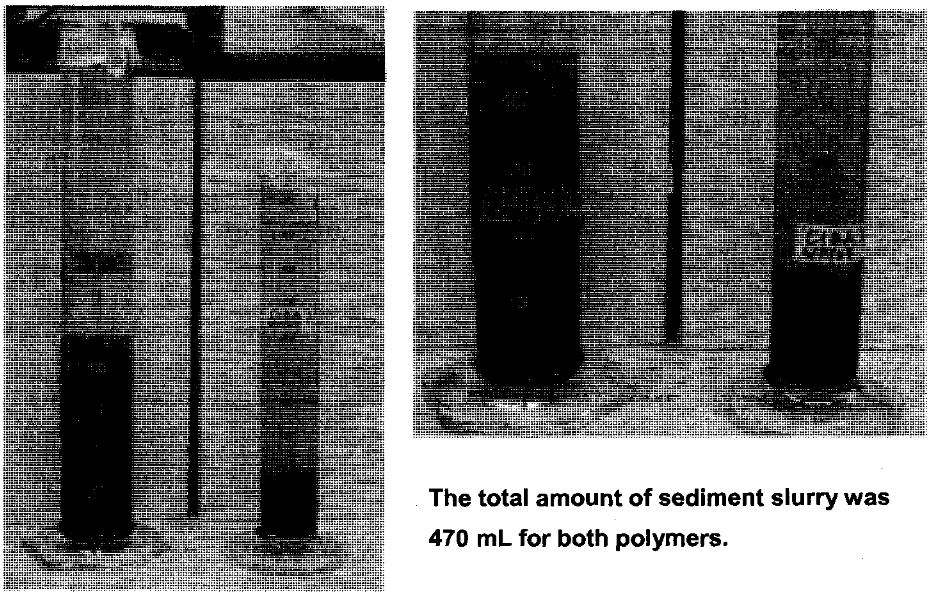


Figure 4.20 Settling column tests performed with Cocheco River sediment (L/S = 8.8) and two polymers, Krysalis FC2043 and Ultrion® 7157 / Nalclear® 7768.



The total amount of sediment slurry was 470 mL for both polymers.

Photo 4.1 Photos showing the settling column tests for Cocheco River sediment using two different polymers: Ultrion® 7157 / Nalclear® 7768 (Nalco Company) and Krysalis FC2043 (Ciba Specialty Chemicals Corporation).

A set of settling experiments was performed using different liquid to solid (L/S) ratios (ranging from 2 to 8.8) to investigate the effect of the L/S ratio on the performance of the polymer. The graphs below show that the L/S ratio did affect the effectiveness of the polymer to aid sediment settling (Figure 4.21). Below L/S 3 no floc formation and sweep settling was observed, which means that the polymer had no affect on sediment settling.

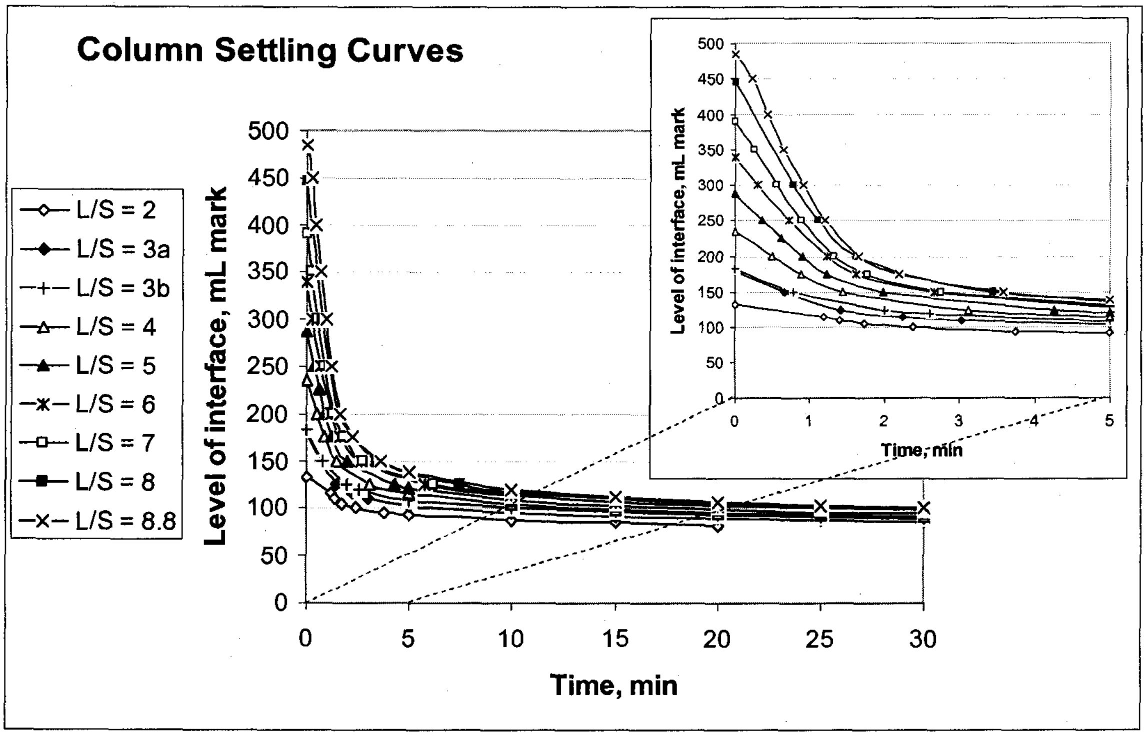


Figure 4.21 Column settling curves of Cocheco River sediment using different L/S ratios (polymer type: Krysalis FC2043; polymer dose = 0.4 lbs/DT).

Settling tests were also performed at a very low L/S ratio (L/S = 1.6) using different polymer doses to investigate the effect of polymer dose in the compression settling phase. As shown in Figure 4.22 none of the doses applied aided sediment settling successfully under compression settling conditions that suggested that using polymers to reduce residual turbidity after amendment mixing into the sediment is only reasonable in the overlying water column.

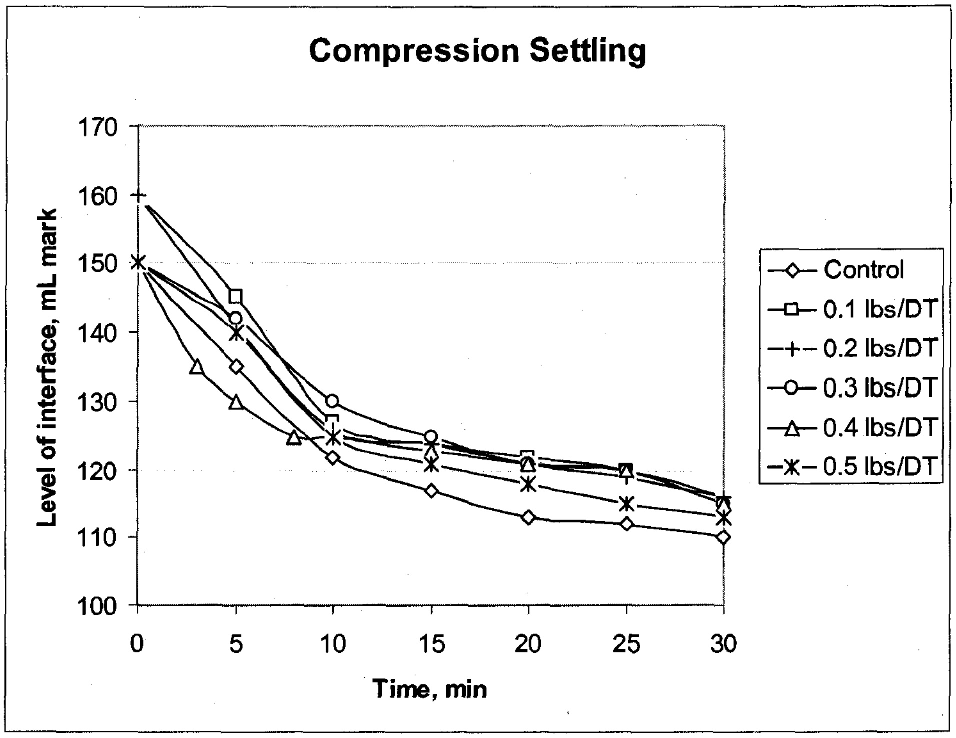


Figure 4.22 Compression settling curves of the Cocheco River sediment (L/S = 1.6) using different polymer doses (polymer type: Krysalis FC2043; control = no polymer).

Estimating the amount of minimum turbidity due to mixing. Sediment mixing experiments were performed in the laboratory to estimate the minimum amount of sediment that will be suspended in the water column within the casing of the mixer in the field. A beaker setup was used to simulate field conditions. Sediment and water layer proportions were kept similar to the planned pilot-scale runs; 150 mL wet sediment with 40% water content was added into 300 mL tall beakers and then 50 mL tap water (i.e. 75% sediment and 25% water by volume). The beakers were set aside until the water column cleared; mixing was performed only after this was achieved. An overhead mixer with a flat mixing blade (50 mm x 15 mm x 1 mm) was used to perform the mixing. The top layer of the sediment (~ 1 cm) was not mixed to minimize resuspension. Mixing speeds in the range of 14-30 rpm caused minimal resuspension in the laboratory with TS concentrations ranging between 7,000 and 8,300 mg/L. This means that even with 30 rpm mixing speed less than 1% of the total sediment volume got resuspended in the laboratory experiments. Based on the findings the goal in the field was to keep the mixing speed as low as possible to prevent complete mixing of the sediment and the overlying water column, which would result in very high TS concentrations and thus no effect of the polymer on sediment settling.

Optimal polymer dose to treat the estimated minimum turbidity. Experiments were carried out to determine the optimum polymer dose that enhanced settling of the previously determined minimum suspended sediment amount. A set of solutions was prepared with L/S = 120, which was equivalent to 8,333 mg/L TS, the upper end of the range for the minimum suspended sediment amount. The solution was then treated with various doses of the Krysalis FC2043 polymer and the optimum dose for minimum turbidity was determined.

Figure 4.23 shows the diluted turbidity of the solution after the polymer addition. Based on this graph the optimum polymer dose for minimum turbidity was 1 mL of the 0.2% stock solution into 100 mL of the 8,333 mg/L sediment solution. The TS concentration of this sample was 7,595.3 mg/L before and 1,050 mg/L after treatment, an 86% decrease in TS due to the polymer addition.

The optimum polymer dose in the field was determined for each run based on the amount of TS in the water column. It is important to note, that the above conditions only applied when resuspension was minimized during mixing in the field. The critical step was to avoid the breaking up of the sediment surface during stirring that caused complete mixing of the sediment and the overlying water. In that case the water was completely incorporated into the sediment and no polymer addition was able to aid settling (i.e., compression settling conditions).

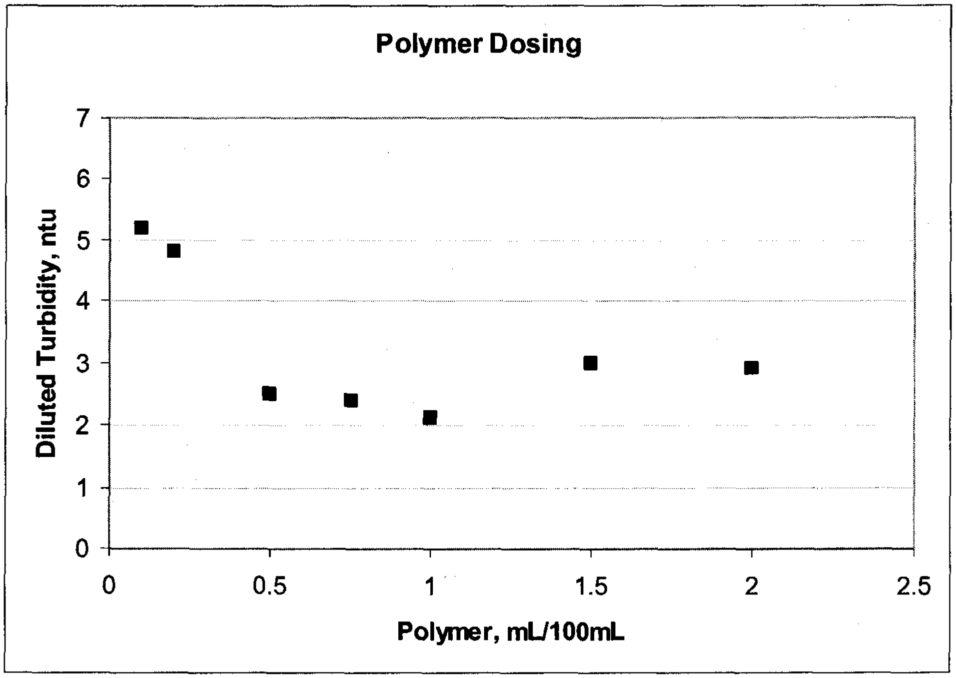


Figure 4.23 Graph showing the relationship between polymer dose and turbidity after settling in a Cocheco River sediment solution with a L/S ratio of 120 (polymer type: Krysalis FC2043).

Field Demonstration Photos

This section shows photos of the in-situ sediment remediation system pilot-scale performance evaluation tests conducted in the fall of 2007 in Dover, NH. Photos 4.2-4.4, 4.6-4.7, 4.10, 4.12, and 4.14-4.15 were obtained from Warren H. Chesner at Seaway Environmental Technologies, Inc.

Photo 4.2 Screening the sediment to remove rocks and other large objects.

Photo 4.3 The screened sediment stockpile.

Photo 4.4 Overview of the setup with the in-situ remediation system in the background and the two test cell modules in the front.

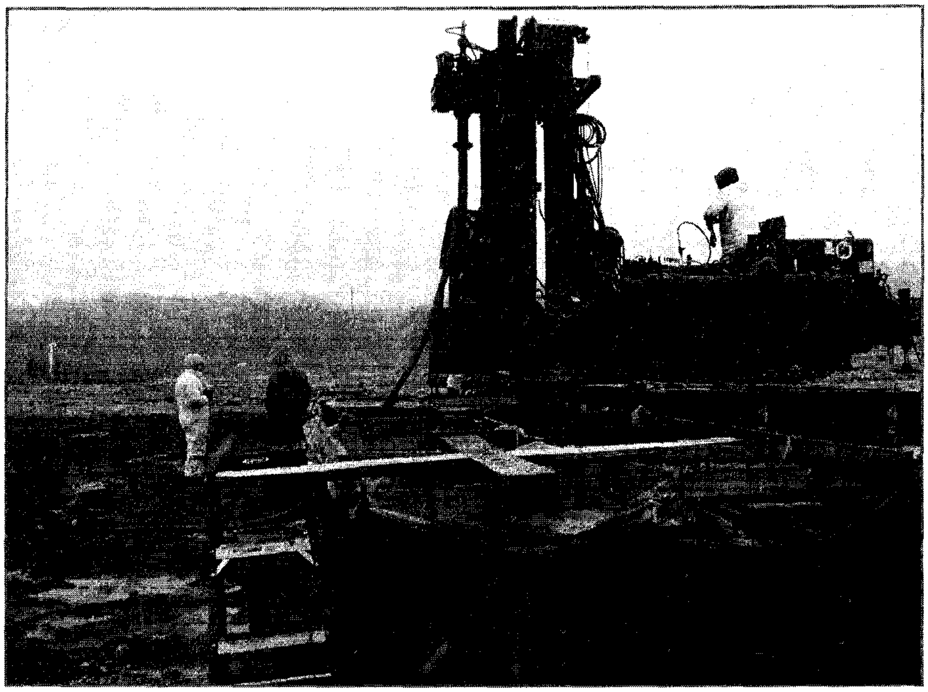


Photo 4.5 The in-situ remediation system with the test cell modules in front of it.

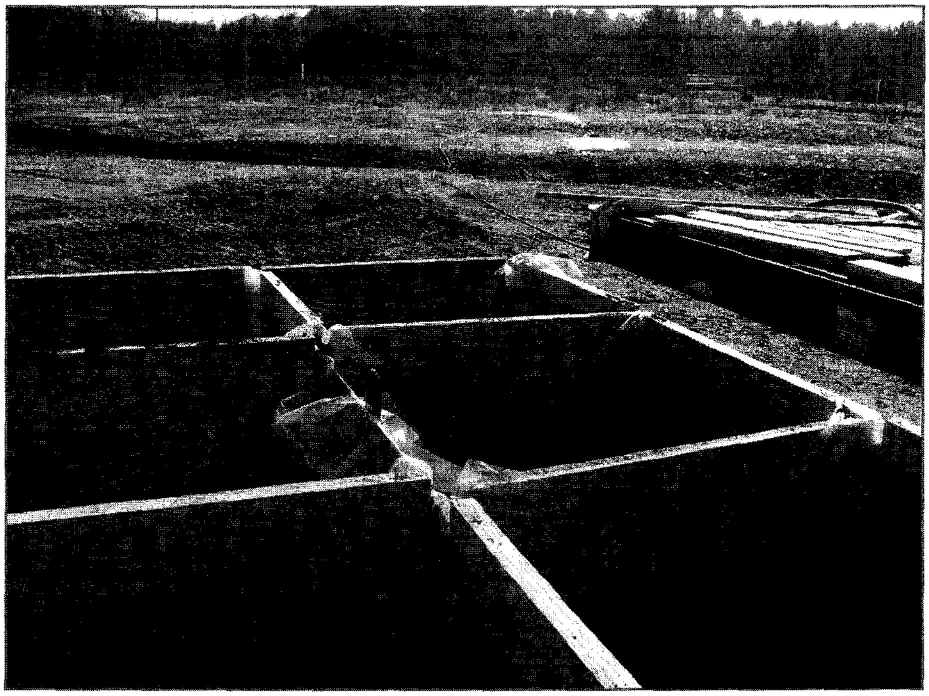


Photo 4.6 Plastic liners installed in the test cell module.

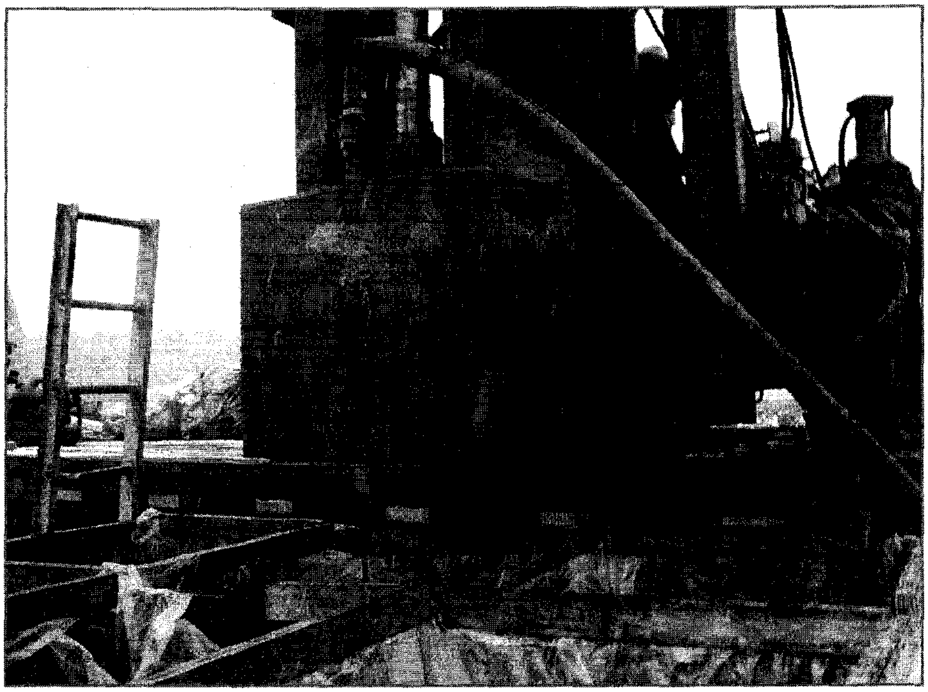


Photo 4.7 The in-situ remediation system mixing reactor positioned above the test cells.

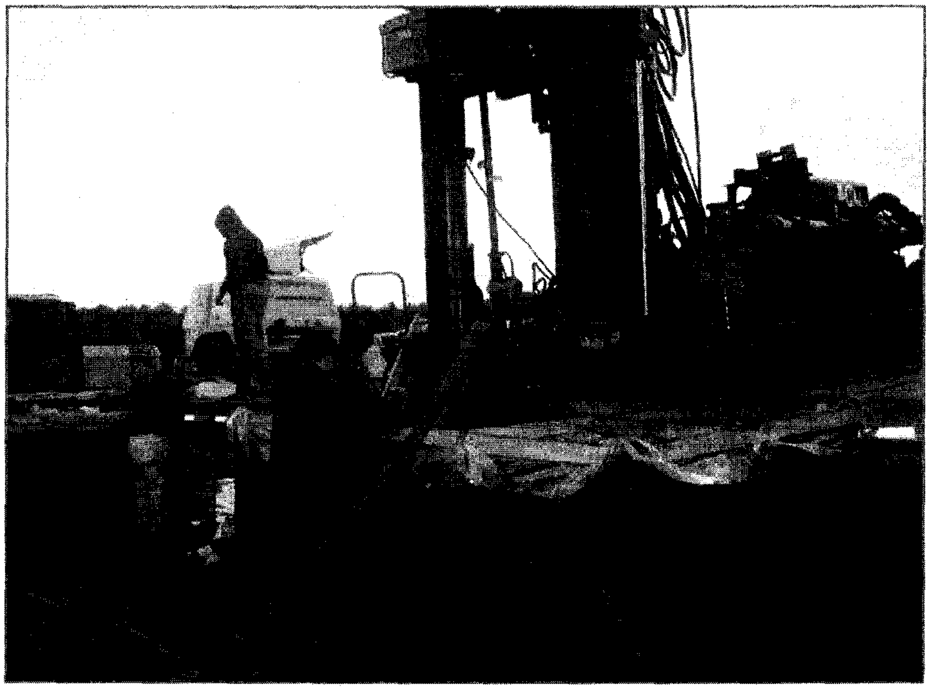


Photo 4.8 The in-situ remediation system mixing reactor lowered into the sediment. Sampling for turbidity measurements.

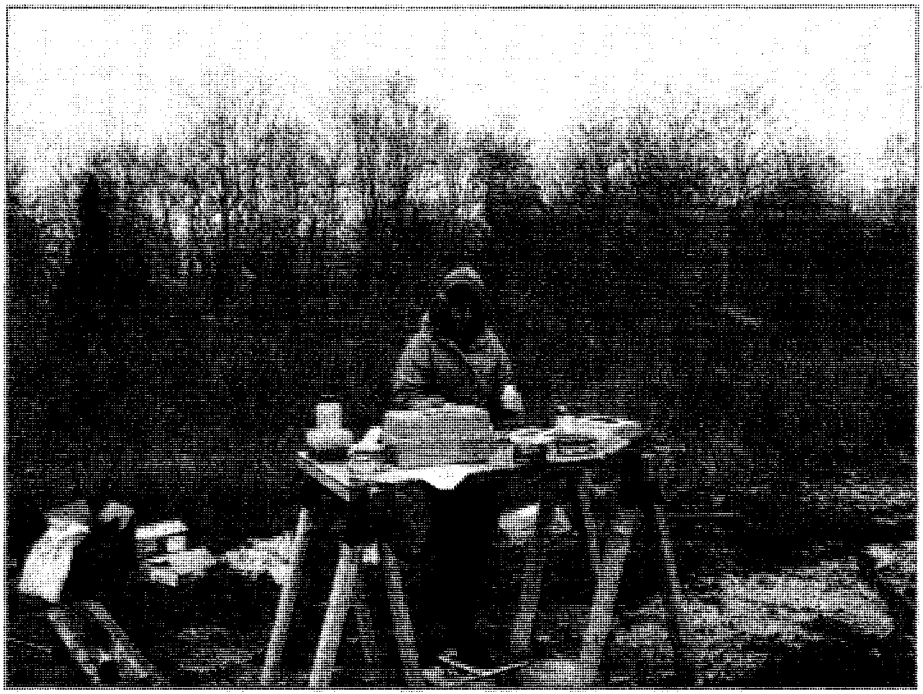


Photo 4.9 Measuring the turbidity of the overlying water column using a field turbidimeter.

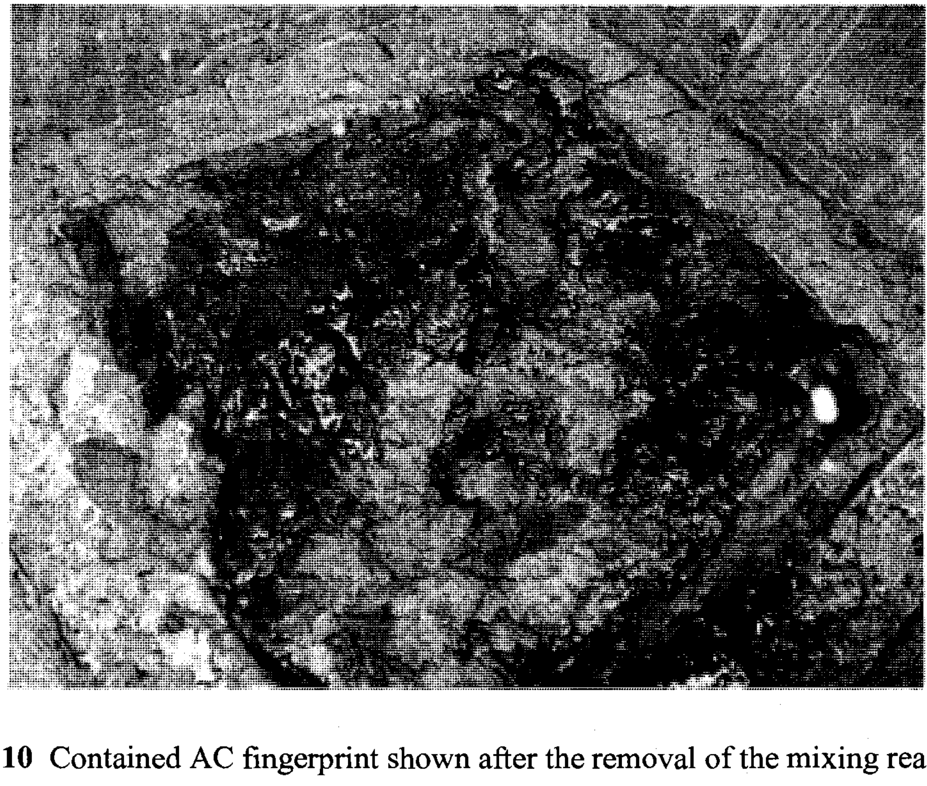


Photo 4.10 Contained AC fingerprint shown after the removal of the mixing reactor.

Photo 4.11 Taking a sediment core using a hand coring device.

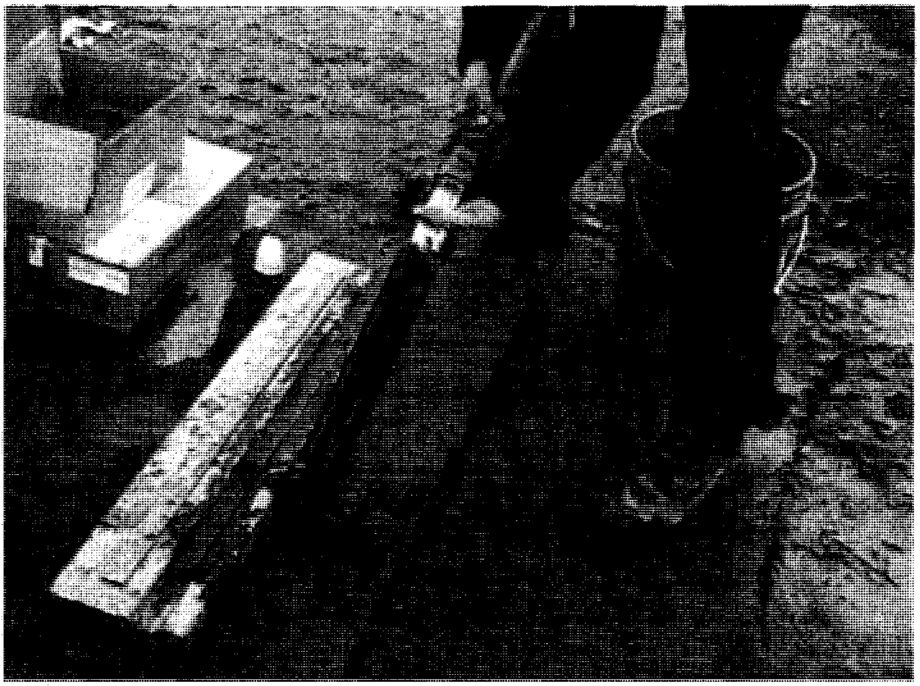


Photo 4.12 Opening the hand coring device to retrieve the sediment core.

Photo 4.13 Placing the sediment core on the measuring board.

Photo 4.14 Picture of a sediment core with somewhat "liquid" consistency.

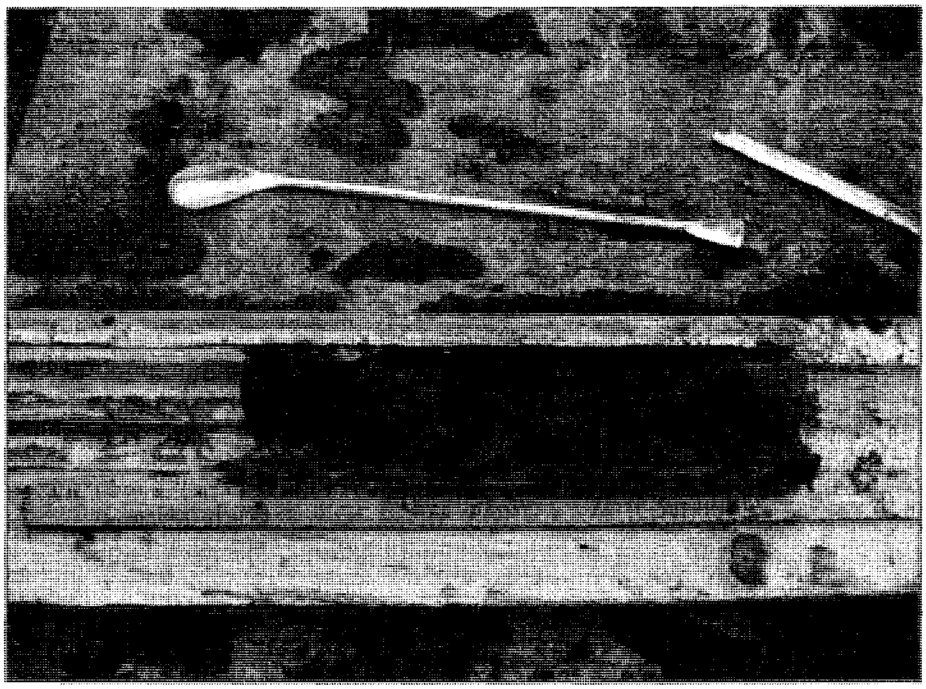


Photo 4.15 Picture of a sediment core containing a lot of AC.

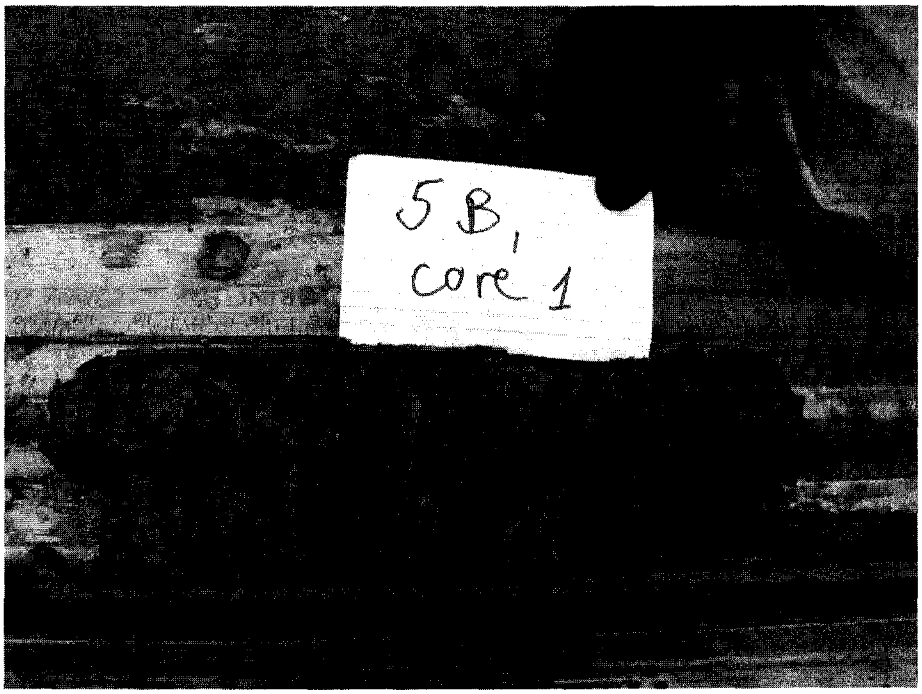


Photo 4.16 Sediment core cut into half. The darker zones are AC.

Photo 4.17 Test module lifted up at the end of the run to clean out the cells.

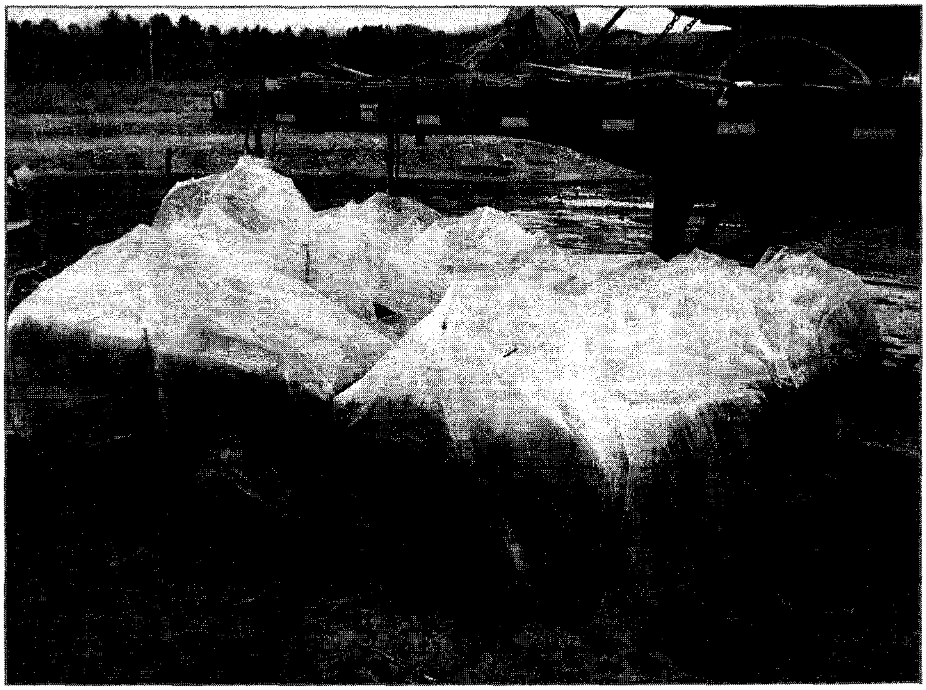


Photo 4.18 Lined, consolidated sediment cubes when the test module was removed few days after the mixing tests.

Photo 4.19 Taking a cross section of the consolidated sediment cube.

Photo 4.20 Cross section of a consolidated sediment cube. The darker zones are higher in AC.

Field Demonstration Raw Data

The measured AC concentrations for the samples taken from the sediment cores are presented in this section. Data for samples taken in and outside of the mixed sediment zone are summarized in Table 4.5 and Table 4.6, respectively. The average and the standard deviation of the measured AC concentrations and the average AC recovery are also reported for each core.

Table 4.5 Measured AC concentrations of samples taken in the mixed sediment zone.

Run	Core	Sample	Sample depth in from surface	Added AC %	Measured AC %	In mixing zone		
						Average, %	SD, %	Recovery, %
2A	c1	s1	6	0.55	-0.08	-0.43	0.50	-78.6
		s2	18		-0.79			
2B	c1	s1	18	0.77	0.48	0.32	0.42	41.3
		s2	8		-0.16			
		s3	5		0.63			
	c2	s5	4		0.88			115.3
3A	c1	s2	11	7.36	2.47			33.5
	c2	s1	18		3.49	4.37	1.25	59.4
		s2	9		5.25			
3B	c1	s1	18	2.33	0.55	1.12	0.51	47.8
		s2	10		1.26			
		s3	3		1.53			
	c2	s1	18		0.79	0.73	0.10	31.1
		s2	9		0.66			
	c3	s1	18		2.80	2.72	0.11	116.8
		s2	10		2.65			
4A	c1	s1	13.5 to 15.8	4.30	1.34	5.44	5.81	126.7
		s2	6.8 to 9		9.55			
	c2	s1	5		27.50	10.97	14.36	255.2
		s2	9		3.81			
		s3	13.5 to 15.8		1.59			
	c3	s1	4		6.55	3.80	2.77	88.5
		s2	9		3.85			
		s3	13 to 14		1.01			
4B	c1	s1	4	1.46	0.94	2.51	1.35	171.6
		s2	9		3.34			
		s3	15		3.24			
	c2	s1	3.8 to 4.7		2.11	1.41	0.70	96.3
		s2	9		0.70			
		s3	14		1.41			
5A	c1	s1	4	5.22	1.17	0.70	0.53	13.5
		s2	6		0.13			
		s3	12		0.81			
	c2	s1	5		3.45	3.74	3.73	71.6
		s2	8		7.61			
		s3	12		0.16			
5B	c1	s1	4	3.81	3.96	2.67	1.19	70.1
		s2	9		2.44			
		s3	15.3 to 16.2		1.61			
	c2	s2	7		1.77	1.65	0.17	43.4
		s3	15		1.53			

Table 4.5 Measured AC concentrations of samples taken in the mixed sediment zone. (continued)

Run	Core	Sample	Sample depth in from surface	Added AC %	Measured AC %	In mixing zone		
						Average, %	SD, %	Recovery, %
6A	c1	s1	3	3.38	6.29	2.79	2.53	82.8
		s2	7		1.35			
		s3	11.8 to 12.5		2.93			
		s4	16		0.60			
	c2	s1	3		2.04	1.62	1.58	48.1
		s2	8		2.95			
		s3	14		-0.13			
6B	c1	s1	3	4.11	4.29	2.76	2.38	67.2
		s2	8		0.03			
		s3	12		3.97			
	c2	s1	3		6.96	3.77	2.79	91.7
		s2	6		2.57			
		s3	11		1.79			
	c3	s1	3		2.99	3.76	3.17	91.5
		s2	7 to 7.8		7.24			
		s3	13		1.05			
7A	c1	s2	8	4.14	2.06	1.43	0.88	34.6
		s3	14		0.81			
	c2	s1	7		0.81	0.37	0.39	9.0
		s2	11		0.25			
		s3	17		0.06			
7B	c1	s2	13	4.02	2.86			71.1
	c2	s3	13		3.66	2.40	1.78	59.7
		s4	17		1.14			
	c3	s1	9		1.07	3.02	2.77	75.2
		s2	14.5 to 15.4		4.98			
8A	c1	s2	10	5.75	0.34	0.36	0.02	6.2
		s3	16		0.37			
	c2	s2	9		0.87	1.58	1.00	27.4
		s3	16		2.29			
8B	c1	s1	9	3.91	4.55	8.57	5.69	219.3
		s2	13		12.59			
	c2	s2	11		0.73	0.72	0.02	18.4
		s3	15 to 16.25		0.70			
9B	c1	s2	11	5.17	-0.05	0.80	1.20	15.5
		s3	17		1.65			
	c2	s1	8		6.78	3.01	3.28	58.2
		s2	12		0.75			
		s3	16		1.50			
10A	c1	s1	18	4.88	0.79	1.34	0.77	27.4
		s2	12		1.88			
	c2	s1	15		2.66	3.89	1.74	79.7
		s2	8		5.12			
10B	c1	s1	15	5.46	0.63			11.5
	c2	s1	13		1.17	3.29	2.99	60.2
		s2	11		5.41			

Table 4.5 Measured AC concentrations of samples taken in the mixed sediment zone. (continued)

Run	Core	Sample	Sample depth in from surface	Added AC %	Measured AC %	In mixing zone		
						Average, %	SD, %	Recovery, %
11A	c1	s1	12.7 to 13.3	4.02	0.70	2.65	2.75	65.8
		s2	8.7 to 9.3		4.59			
	c2	s1	15		0.54	2.32	2.21	57.7
		s2	12		1.64			
		s3	10		4.79			
11B	c1	s1	15	4.60	2.50	1.60	1.27	34.8
		s2	11		0.70			
	c2	s1	15		1.08	3.45	2.21	75.0
		s2	11		5.47			
		s3	7.4 to 8.2		3.79			
12B	c1	s1	15	3.99	0.22	1.35	1.09	33.8
		s2	9.5 to 11.4		1.41			
		s3	4		2.41			
	c2	s1	13.2 to 13.9		1.38	2.34	2.08	58.6
		s2	8.8 to 9.5		4.73			
		s3	3		0.90			
13A	c1	s1	11	5.46	3.17	4.44	1.76	81.3
		s2	10		6.45			
		s3	7		3.69			
	c2	s1	10.3 to 11.2		2.60			47.7
13B	c1	s1	13	5.75	0.94			16.4
	c2	s1	14.2 to 15		2.80			48.7
14A	c1	s1	16	3.07	5.99	3.57	3.07	116.2
		s2	14		4.59			
		s3	6		0.12			
	c2	s1	17		5.41	2.54	4.05	82.8
		s2	8		-0.32			
14B	c1	s1	15.5 to 16.4	3.07	3.49	2.08	1.32	67.9
		s2	12		1.88			
		s3	3.4 to 4.3		0.88			
	c2	s1	16.2 to 16.9		2.09	2.23	1.92	72.5
		s2	13.1 to 13.8		3.36			
		s3	9.2 to 10		-0.43			
		s4	4		3.88			
15B	c1	s1	14	3.07	1.61	2.06	1.26	67.1
		s2	13		2.92			
		s3	9		0.49			
		s4	7		3.22			
	c2	s1	12.6 to 13.3		2.26	1.57	1.87	51.2
		s2	10		3.01			
		s3	4		-0.55			

Table 4.6 Measured AC concentrations of samples taken outside of the mixed sediment zone.

Run	Core	Sample	Sample depth in from surface	Added AC %	Measured AC %	Outside of mixing zone		
						Average, %	SD, %	Recovery, %
2A	surface grab			0.55	-0.23			
2B	c2	s4	18	0.77	-0.03			
3A	c1	s1	21	7.36	1.34			
	c2	s3	2		5.87			
3B	c2	s3	2	2.33	3.24			
	c3	s3	2		7.09			
4A	c1	s3	0	4.30	2.01			
	c3	s4	20		0.33			
5A	surface grab			5.22	22.49			
5B	c2	s1	3	3.81	0.24			
	surface grab				24.33			
6B	c1	s4	19	4.11	-0.41			
7A	c1	s1	2	4.14	-0.11			
	c3	s1	2.9 to 4.3		-0.31	0.19	0.47	4.6
		s2	10		0.63			
		s3	17		0.25			
7B	c1	s1	4	4.02	2.71			
	c2	s1	3		1.70	1.47	0.32	36.6
		s2	8		1.25			
	c3	s3	18		0.06			
8A	c1	s1	4	5.75	4.11			
	c2	s1	3		1.01			
8B	c1	s3	17.1 to 18.6	3.91	-0.20			
	c2	s1	6		0.60			
9B	c1	s1	6	5.17	1.68			
10A	c1	s3	4	4.88	0.96	1.52	0.80	31.2
		s4	0		2.09			
	c2	s3	3		1.50			
10B	c1	s2	7.5 to 8.8	5.46	-0.11	0.68	1.12	12.5
		s3	0		1.47			
	c2	s3	4.7 to 5.3		2.44	2.35	0.12	43.1
		s4	1.3		2.27			
11A	c1	s3	4 to 4.7	4.02	3.84			
	c2	s4	3		-0.13			
11B	c1	s3	5	4.60	0.09	1.50	2.00	32.7
		s4	0.8		2.92			
	c2	s4	0.8 to 1.6		5.06			
13A	c1	s4	2	5.46	-0.38			
	c2	s2	9		1.07	0.89	0.25	16.3
		s3	4		0.72			
13B	c1	s2	7	5.75	0.36	1.40	1.48	24.4
		s3	4		2.45			
	c2	s2	8		-0.37	-0.22	0.20	-3.9
		s3	0 to 0.8		-0.08			
14A	c2	s3	2.9 to 4.4	3.07	0.45			
15B	c2	s4	0.7	3.07	2.23			

Statistical Analyses of the Field Demonstration Data

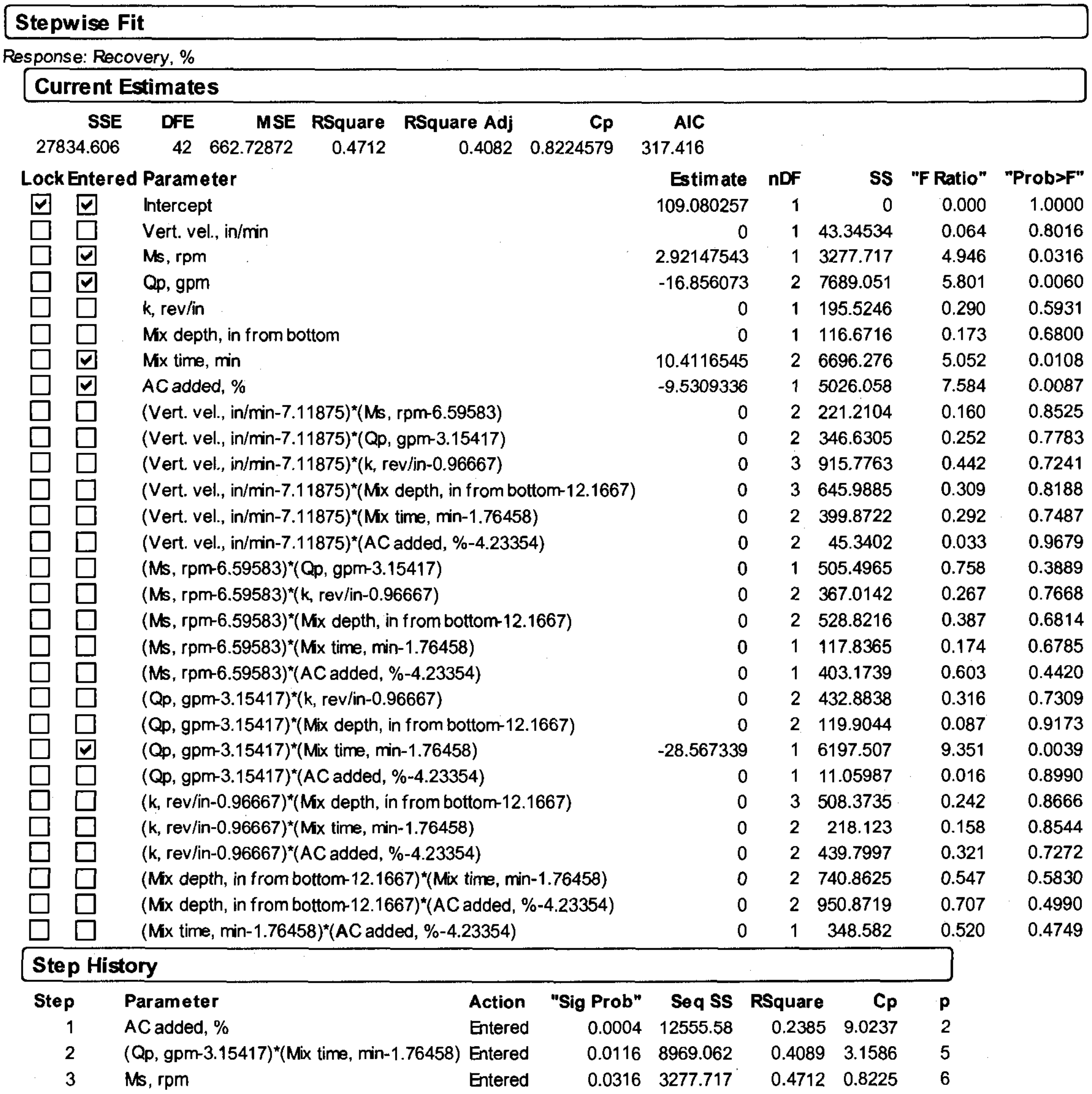
The statistical significance of the relationships between the following variables was investigated using the JMP® 7.0.1 software: 1) the added and the average measured AC concentration for each core; 2) the average AC recovery for each core and the operational variables shown in Table 4.1 earlier in this chapter; and 3) the standard deviation of the measured AC concentrations for each core and the operational variables shown in Table 4.1. First, bivariate plots were generated under the "Fit Y by X" platform for the above described three scenarios. However, this analysis did not allow for the evaluation of factor interactions. Therefore, the "Fit model" platform was used next to determine the statistical significance of the variables and their interactions. The initial model consisted of the 7 variables shown in Table 4.1 and all 2-way interactions of these terms. The "stepwise" function was used to determine the final model. The significance of the linear relationship was determined from the p-values calculated by the F-test. The summary of the linear fits and their significance is presented in Table 4.7.

Table 4.7 Description of the linear fit for the variables and the activated carbon (AC) recovery or standard deviation and the statistical significance of these linear relationships (see Table 4.1 for the definition of the variables).

Variable	**Average Recovery, %**					**Standard Deviation, %**				
	a	b	n	p-value	Significance	a	b	n	p-value	Significance
v (in/min)	-0.0491	60.417	48	0.8016	no at 10%	-0.0365	2.127	43	0.7689	no at 10%
Ms (rpm)	2.0425	47.258	50	0.0316	yes at 5%	0.0694	1.3624	45	0.3737	no at 10%
k (rev/in)	6.5718	54.663	50	0.5931	no at 10%	0.7451	1.1601	45	0.1688	no at 10%
Qp (gpm)	-11.799	97.598	50	0.0175	yes at 5%	-0.0381	1.9187	45	0.8738	no at 10%
Mixing time (min)	18.716	28.751	50	0.3015	no at 10%	0.2569	1.3566	45	0.4459	no at 10%
AC added (%, w/w)	-11.07	106.12	50	0.0087	yes at 1%	0.1998	1.0241	45	0.1972	no at 10%

(a & b = slope and intercept of linear fit; n = number of samples; the p-value describes the statistical significance of a given factor, e.g. a p-value of 0.05 means that there is a statistically significant linear relationship between the variable and the recovery or the standard deviation at the 5% level)

The final model for the amendment recovery was determined using the "stepwise" function under the "Fit model" platform:



Stepwise Fit

Response: Recovery, %

Current Estimates

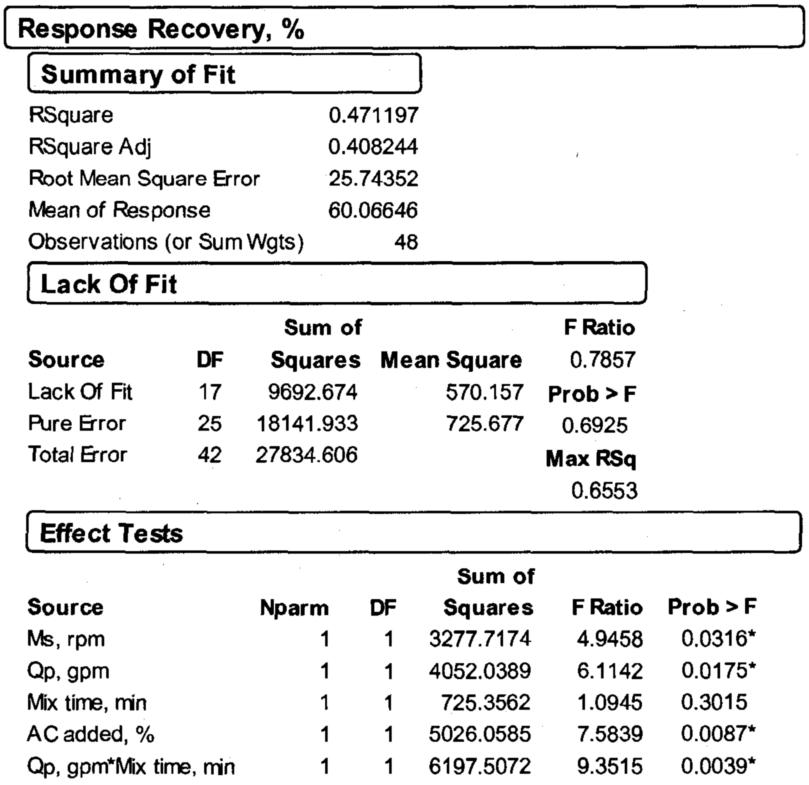
SSE	DFE	MSE	RSquare	RSquare Adj	Cp	AIC
27834.606	42	662.72872	0.4712	0.4082	0.8224579	317.416

Lock	Entered	Parameter	Estimate	nDF	SS	"F Ratio"	"Prob>F"
☑	☑	Intercept	109.080257	1	0	0.000	1.0000
☐	☐	Vert. vel., in/min	0	1	43.34534	0.064	0.8016
☐	☑	Ms, rpm	2.92147543	1	3277.717	4.946	0.0316
☐	☑	Qp, gpm	-16.856073	2	7689.051	5.801	0.0060
☐	☐	k, rev/in	0	1	195.5246	0.290	0.5931
☐	☐	Mix depth, in from bottom	0	1	116.6716	0.173	0.6800
☐	☑	Mix time, min	10.4116545	2	6696.276	5.052	0.0108
☐	☑	AC added, %	-9.5309336	1	5026.058	7.584	0.0087
☐	☐	(Vert. vel., in/min-7.11875)*(Ms, rpm-6.59583)	0	2	221.2104	0.160	0.8525
☐	☐	(Vert. vel., in/min-7.11875)*(Qp, gpm-3.15417)	0	2	346.6305	0.252	0.7783
☐	☐	(Vert. vel., in/min-7.11875)*(k, rev/in-0.96667)	0	3	915.7763	0.442	0.7241
☐	☐	(Vert. vel., in/min-7.11875)*(Mix depth, in from bottom-12.1667)	0	3	645.9885	0.309	0.8188
☐	☐	(Vert. vel., in/min-7.11875)*(Mix time, min-1.76458)	0	2	399.8722	0.292	0.7487
☐	☐	(Vert. vel., in/min-7.11875)*(AC added, %-4.23354)	0	2	45.3402	0.033	0.9679
☐	☐	(Ms, rpm-6.59583)*(Qp, gpm-3.15417)	0	1	505.4965	0.758	0.3889
☐	☐	(Ms, rpm-6.59583)*(k, rev/in-0.96667)	0	2	367.0142	0.267	0.7668
☐	☐	(Ms, rpm-6.59583)*(Mix depth, in from bottom-12.1667)	0	2	528.8216	0.387	0.6814
☐	☐	(Ms, rpm-6.59583)*(Mix time, min-1.76458)	0	1	117.8365	0.174	0.6785
☐	☐	(Ms, rpm-6.59583)*(AC added, %-4.23354)	0	1	403.1739	0.603	0.4420
☐	☐	(Qp, gpm-3.15417)*(k, rev/in-0.96667)	0	2	432.8838	0.316	0.7309
☐	☐	(Qp, gpm-3.15417)*(Mix depth, in from bottom-12.1667)	0	2	119.9044	0.087	0.9173
☐	☑	(Qp, gpm-3.15417)*(Mix time, min-1.76458)	-28.567339	1	6197.507	9.351	0.0039
☐	☐	(Qp, gpm-3.15417)*(AC added, %-4.23354)	0	1	11.05987	0.016	0.8990
☐	☐	(k, rev/in-0.96667)*(Mix depth, in from bottom-12.1667)	0	3	508.3735	0.242	0.8666
☐	☐	(k, rev/in-0.96667)*(Mix time, min-1.76458)	0	2	218.123	0.158	0.8544
☐	☐	(k, rev/in-0.96667)*(AC added, %-4.23354)	0	2	439.7997	0.321	0.7272
☐	☐	(Mix depth, in from bottom-12.1667)*(Mix time, min-1.76458)	0	2	740.8625	0.547	0.5830
☐	☐	(Mix depth, in from bottom-12.1667)*(AC added, %-4.23354)	0	2	950.8719	0.707	0.4990
☐	☐	(Mix time, min-1.76458)*(AC added, %-4.23354)	0	1	348.582	0.520	0.4749

Step History

Step	Parameter	Action	"Sig Prob"	Seq SS	RSquare	Cp	p
1	AC added, %	Entered	0.0004	12555.58	0.2385	9.0237	2
2	(Qp, gpm-3.15417)*(Mix time, min-1.76458)	Entered	0.0116	8969.062	0.4089	3.1586	5
3	Ms, rpm	Entered	0.0316	3277.717	0.4712	0.8225	6

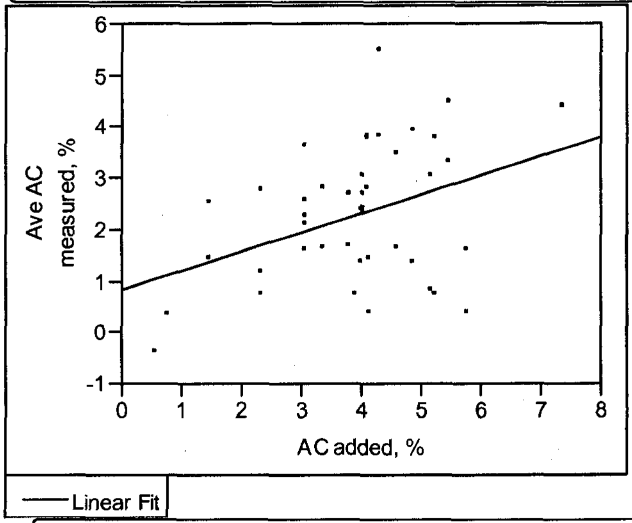
Summary of the final model fit for amendment recovery and F-tests showing the significance of the factors. All factors except mixing time were significant at least at the 5% level:



```
Response Recovery, %
  Summary of Fit
  RSquare                          0.471197
  RSquare Adj                      0.408244
  Root Mean Square Error           25.74352
  Mean of Response                 60.06646
  Observations (or Sum Wgts)             48
  Lack Of Fit
                          Sum of                   F Ratio
  Source         DF      Squares  Mean Square       0.7857
  Lack Of Fit    17     9692.674      570.157     Prob > F
  Pure Error     25    18141.933      725.677       0.6925
  Total Error    42    27834.606                 Max RSq
                                                    0.6553
  Effect Tests
                                              Sum of
  Source                   Nparm   DF        Squares   F Ratio   Prob > F
  Ms, rpm                      1    1      3277.7174    4.9458    0.0316*
  Qp, gpm                      1    1      4052.0389    6.1142    0.0175*
  Mix time, min                1    1       725.3562    1.0945    0.3015
  AC added, %                  1    1      5026.0585    7.5839    0.0087*
  Qp, gpm*Mix time, min        1    1      6197.5072    9.3515    0.0039*
```

Bivariate fit showing a significant relationship between the added and the average measured AC concentration for each core at the 1% level:

Bivariate Fit of Ave AC measured, % By AC added, %



Linear Fit

Ave AC measured, % = 0.8275395 + 0.3716292*AC added, %

Summary of Fit

RSquare	0.152032
RSquare Adj	0.131842
Root Mean Square Error	1.203184
Mean of Response	2.269545
Observations (or Sum Wgts)	44

Lack Of Fit

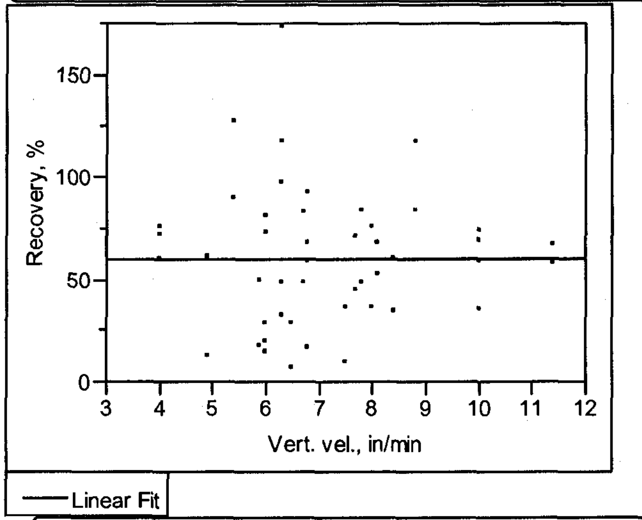
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio** 2.1707
Lack Of Fit	18	37.665626	2.09253	**Prob > F**
Pure Error	24	23.135725	0.96399	0.0385*
Total Error	42	60.801351		**Max RSq**
				0.6773

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	1	10.901040	10.9010	7.5302
Error	42	60.801351	1.4477	**Prob > F**
C. Total	43	71.702391		0.0089*

Bivariate fit of the vertical speed of the blade during mixing and the average AC recovery for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of Recovery, % By Vert. vel., in/min



Linear Fit

Recovery, % = 60.372681 - 0.0430164*Vert. vel., in/min

Summary of Fit

RSquare	5.038e-6
RSquare Adj	-0.02173
Root Mean Square Error	33.82715
Mean of Response	60.06646
Observations (or Sum Wgts)	48

Lack Of Fit

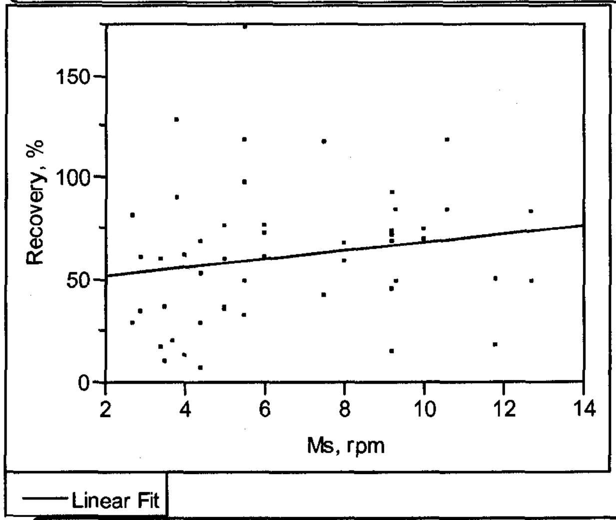
		Sum of		**F Ratio**
Source	**DF**	**Squares**	**Mean Square**	1.6732
Lack Of Fit	16	24821.454	1551.34	**Prob > F**
Pure Error	30	27815.244	927.17	0.1090
Total Error	46	52636.698		**Max RSq**
				0.4716

Analysis of Variance

		Sum of		
Source	**DF**	**Squares**	**Mean Square**	**F Ratio**
Model	1	0.265	0.27	0.0002
Error	46	52636.698	1144.28	**Prob > F**
C. Total	47	52636.963		0.9879

There was no significant relationship between the mixing speed and the average AC recovery at the 10% level according to the bivariate fit. The same factor was in fact significant at the 5% level when applying the fit model analysis with the interactions included (see Table 4.7):

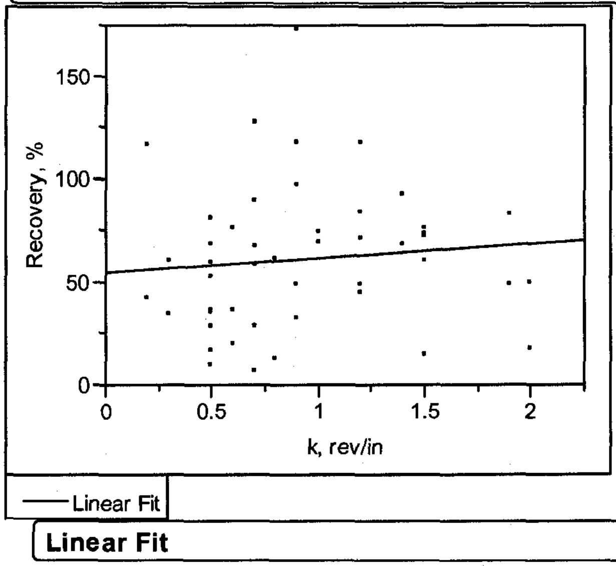
Bivariate Fit of Recovery, % By Ms, rpm



```
Linear Fit

Recovery, % = 47.149294 + 2.0576757*Ms, rpm

Summary of Fit

RSquare                        0.031963
RSquare Adj                    0.011796
Root Mean Square Error         33.61018
Mean of Response                60.7958
Observations (or Sum Wgts)           50

Lack Of Fit

                       Sum of                   F Ratio
Source        DF      Squares   Mean Square      1.4107
Lack Of Fit   17    23650.706       1391.22    Prob > F
Pure Error    31    30572.230        986.20      0.1974
Total Error   48    54222.936                   Max RSq
                                                 0.4542

Analysis of Variance

                     Sum of
Source      DF      Squares   Mean Square    F Ratio
Model        1     1790.354       1790.35     1.5849
Error       48    54222.936       1129.64   Prob > F
C. Total    49    56013.291                   0.2141
```

Bivariate fit of the "k" value and the average AC recovery for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of Recovery, % By k, rev/in



Linear Fit

Recovery, % = 54.28696 + 6.9538884*k, rev/in

Summary of Fit

RSquare	0.009751
RSquare Adj	-0.01088
Root Mean Square Error	33.99359
Mean of Response	60.7958
Observations (or Sum Wgts)	50

Lack Of Fit

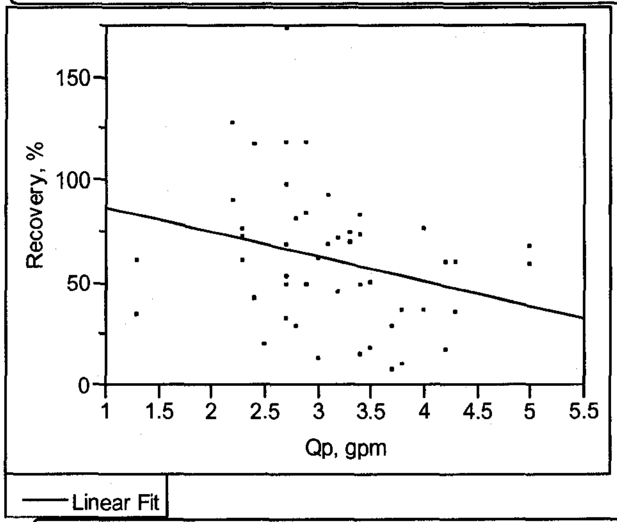
Source	DF	Sum of Squares	Mean Square	F Ratio
				1.2701
Lack Of Fit	11	15203.022	1382.09	**Prob > F**
Pure Error	37	40264.072	1088.22	0.2793
Total Error	48	55467.094		**Max RSq**
				0.2812

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	546.197	546.20	0.4727
Error	48	55467.094	1155.56	**Prob > F**
C. Total	49	56013.291		0.4951

Bivariate fit showing a significant relationship between the pump flow rate and the average AC recovery for each core at the 10% level (the fit model analysis indicated significance at the 5% level for the same variable):

Bivariate Fit of Recovery, % By Qp, gpm



Linear Fit

Recovery, % = 98.09216 - 11.938656*Qp, gpm

Summary of Fit

RSquare	0.074891
RSquare Adj	0.055618
Root Mean Square Error	32.85651
Mean of Response	60.7958
Observations (or Sum Wgts)	50

Lack Of Fit

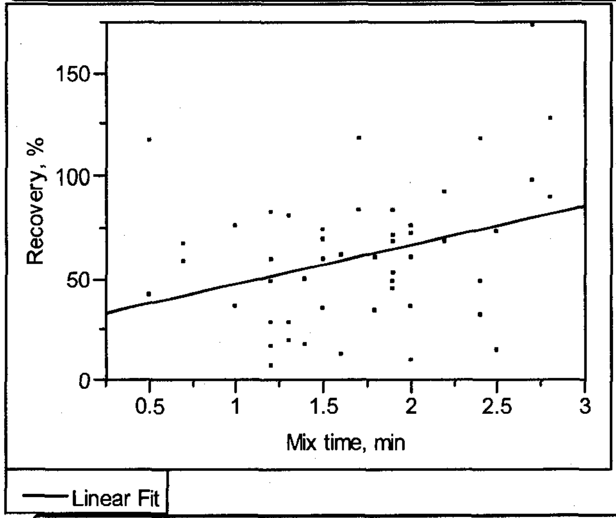
		Sum of		F Ratio
Source	**DF**	**Squares**	**Mean Square**	1.2318
Lack Of Fit	18	22021.698	1223.43	**Prob > F**
Pure Error	30	29796.719	993.22	0.2986
Total Error	48	51818.418		**Max RSq**
				0.4680

Analysis of Variance

		Sum of		
Source	**DF**	**Squares**	**Mean Square**	**F Ratio**
Model	1	4194.873	4194.87	3.8858
Error	48	51818.418	1079.55	**Prob > F**
C. Total	49	56013.291		0.0545

Bivariate fit showing a significant relationship between the mixing time and the average AC recovery for each core at the 5% level (this was due to the significance of the 2-way interaction between pump flow rate and mixing time as seen in the fit model analysis where mixing time by itself was not significant):

Bivariate Fit of Recovery, % By Mix time, min



Linear Fit

Recovery, % = 28.280736 + 18.970282*Mix time, min

Summary of Fit

RSquare	0.108066
RSquare Adj	0.089484
Root Mean Square Error	32.26201
Mean of Response	60.7958
Observations (or Sum Wgts)	50

Lack Of Fit

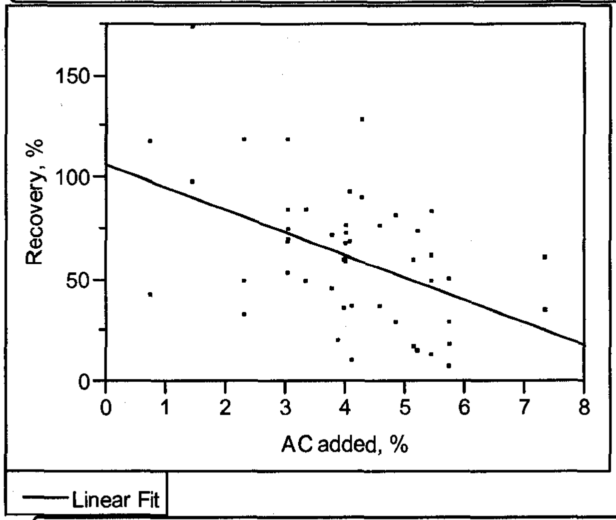
Source	DF	Sum of Squares	Mean Square	F Ratio 1.8287
Lack Of Fit	15	22677.741	1511.85	Prob > F
Pure Error	33	27282.438	826.74	0.0730
Total Error	48	49960.178		Max RSq
				0.5129

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	6053.112	6053.11	5.8156
Error	48	49960.178	1040.84	Prob > F
C. Total	49	56013.291		0.0198*

Bivariate fit showing a significant relationship between the AC added (expressed as % by dry sediment weight) and the average AC recovery for each core at the 1% level:

Bivariate Fit of Recovery, % By AC added, %



Linear Fit

Recovery, % = 106.1469 - 11.07475*AC added, %

Summary of Fit

RSquare	0.217476
RSquare Adj	0.201174
Root Mean Square Error	30.21855
Mean of Response	60.7958
Observations (or Sum Wgts)	50

Lack Of Fit

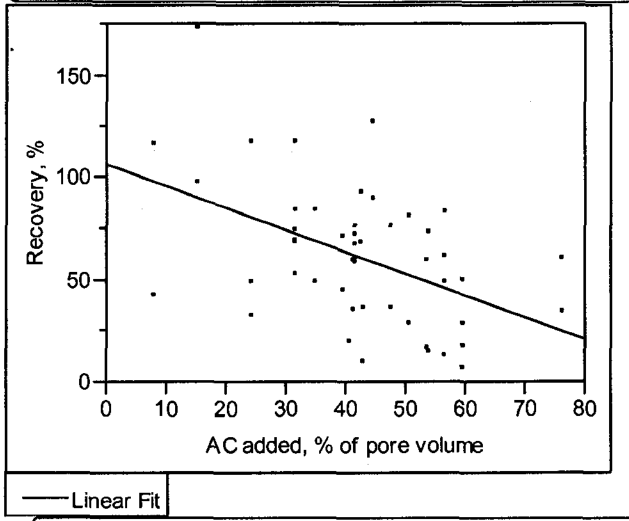
Source	DF	Sum of Squares	Mean Square	F Ratio
				1.5428
Lack Of Fit	17	20088.483	1181.68	**Prob > F**
Pure Error	31	23743.245	765.91	0.1436
Total Error	48	43831.728		**Max RSq**
				0.5761

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	12181.563	12181.6	13.3400
Error	48	43831.728	913.2	**Prob > F**
C. Total	49	56013.291		0.0006*

Bivariate fit showing a significant relationship between the AC added (expressed as % of the sediment pore volume) and the average AC recovery for each core at the 1% level:

Bivariate Fit of Recovery, % By AC added, % of pore volume



Linear Fit

Recovery, % = 106.114 - 1.0669633*AC added, % of pore volume

Summary of Fit

RSquare	0.217052
RSquare Adj	0.20074
Root Mean Square Error	30.22675
Mean of Response	60.7958
Observations (or Sum Wgts)	50

Lack Of Fit

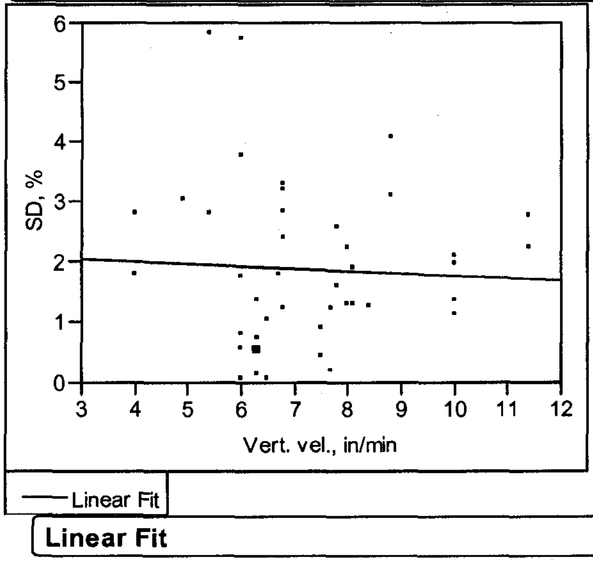
Source	DF	Sum of Squares	Mean Square	F Ratio
				1.5447
Lack Of Fit	17	20112.257	1183.07	**Prob > F**
Pure Error	31	23743.245	765.91	0.1429
Total Error	48	43855.502		**Max RSq**
				0.5761

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	12157.789	12157.8	13.3067
Error	48	43855.502	913.7	**Prob > F**
C. Total	49	56013.291		0.0007*

Bivariate fit of the vertical speed of the blade during mixing and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By Vert. vel., in/min



Linear Fit

SD, % = 2.1275236 - 0.0366256*Vert. vel., in/min

Summary of Fit

RSquare	0.002129
RSquare Adj	-0.02221
Root Mean Square Error	1.38099
Mean of Response	1.86186
Observations (or Sum Wgts)	43

Lack Of Fit

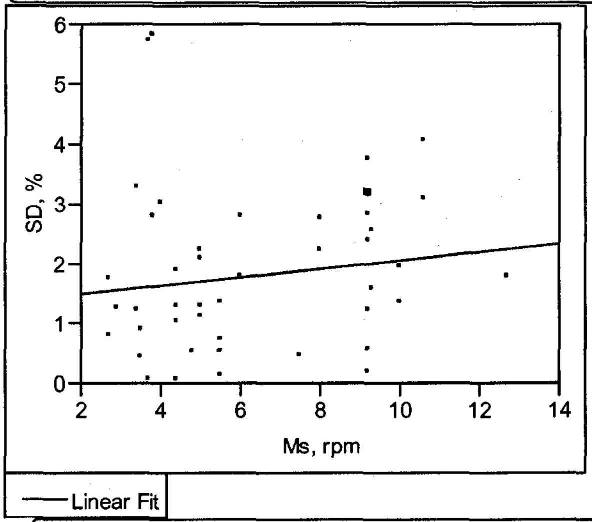
Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
				1.9571
Lack Of Fit	15	41.466933	2.76446	**Prob > F**
Pure Error	26	36.725515	1.41252	0.0645
Total Error	41	78.192448		**Max RSq**
				0.5313

Analysis of Variance

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	1	0.166803	0.16680	0.0875
Error	41	78.192448	1.90713	**Prob > F**
C. Total	42	78.359251		0.7689

Bivariate fit of the mixing speed and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By Ms, rpm



Linear Fit

SD, % = 1.3646043 + 0.0690642*Ms, rpm

Summary of Fit

RSquare	0.018444
RSquare Adj	-0.00438
Root Mean Square Error	1.369125
Mean of Response	1.799556
Observations (or Sum Wgts)	45

Lack Of Fit

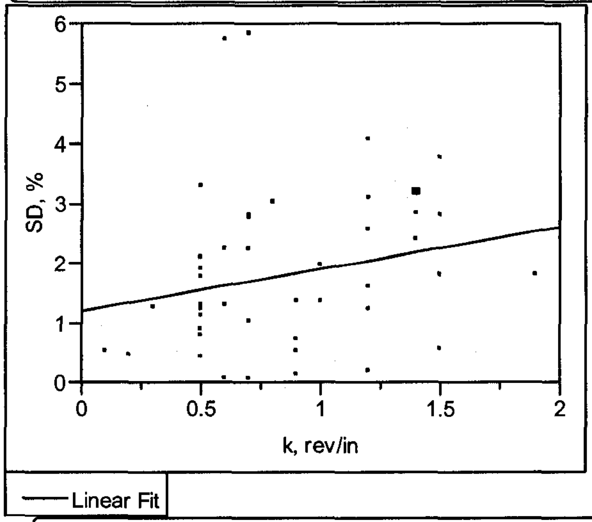
Source	DF	Sum of Squares	Mean Square	F Ratio 1.5305
Lack Of Fit	17	40.316124	2.37154	Prob > F
Pure Error	26	40.287491	1.54952	0.1598
Total Error	43	80.603615		Max RSq
				0.5094

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1.514576	1.51458	0.8080
Error	43	80.603615	1.87450	Prob > F
C. Total	44	82.118191		0.3737

Bivariate fit of the "k" value and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By k, rev/in



Linear Fit

SD, % = 1.1994789 + 0.6959652*k, rev/in

Summary of Fit

RSquare	0.043564
RSquare Adj	0.021322
Root Mean Square Error	1.351492
Mean of Response	1.799556
Observations (or Sum Wgts)	45

Lack Of Fit

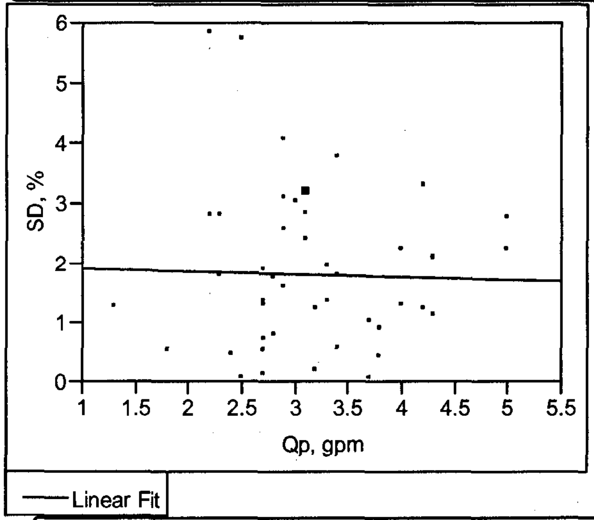
Source	DF	Sum of Squares	Mean Square	F Ratio 0.8748
Lack Of Fit	11	18.157433	1.65068	Prob > F
Pure Error	32	60.383327	1.88698	0.5726
Total Error	43	78.540760		Max RSq
				0.2647

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	3.577431	3.57743	1.9586
Error	43	78.540760	1.82653	Prob > F
C. Total	44	82.118191		0.1688

Bivariate fit of the pump flow rate and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By Qp, gpm



Linear Fit

SD, % = 1.9336524 - 0.0427665*Qp, gpm

Summary of Fit

```
RSquare                          0.000594
RSquare Adj                      -0.02265
Root Mean Square Error           1.381518
Mean of Response                 1.799556
Observations (or Sum Wgts)             45
```

Lack Of Fit

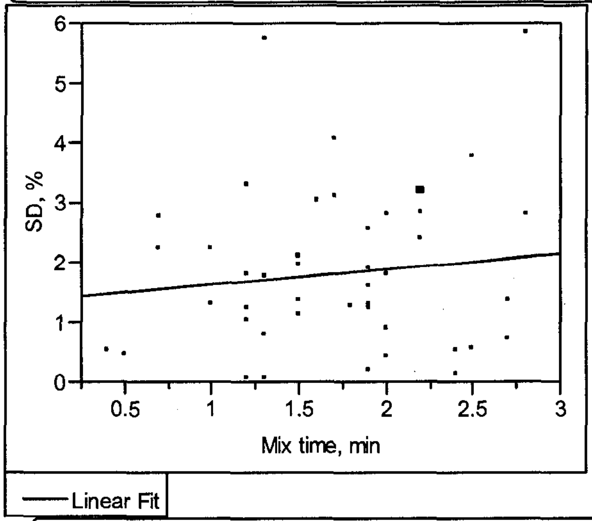
```
                        Sum of                   F Ratio
Source         DF      Squares   Mean Square      1.6408
Lack Of Fit    18    44.446090       2.46923    Prob > F
Pure Error     25    37.623335       1.50493      0.1245
Total Error    43    82.069425                   Max RSq
                                                  0.5418
```

Analysis of Variance

```
                      Sum of
Source       DF      Squares   Mean Square    F Ratio
Model         1     0.048766       0.04877     0.0256
Error        43    82.069425       1.90859   Prob > F
C. Total     44    82.118191                   0.8738
```

Bivariate fit of the mixing time and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By Mix time, min



Linear Fit

SD, % = 1.3542332 + 0.2585743*Mix time, min

Summary of Fit

RSquare	0.013579
RSquare Adj	-0.00936
Root Mean Square Error	1.372513
Mean of Response	1.799556
Observations (or Sum Wgts)	45

Lack Of Fit

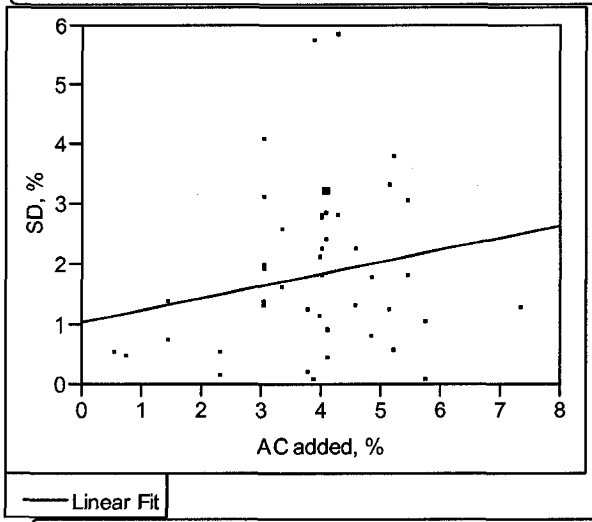
Source	DF	Sum of Squares	Mean Square	F Ratio 1.6196
Lack Of Fit	15	37.630766	2.50872	Prob > F
Pure Error	28	43.372338	1.54901	0.1314
Total Error	43	81.003104		Max RSq
				0.4718

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	1.115087	1.11509	0.5919
Error	43	81.003104	1.88379	Prob > F
C. Total	44	82.118191		0.4459

Bivariate fit of the AC added (expressed as % by dry sediment weight) and the standard deviation of the measured AC concentrations for each core showing lack of a significant relationship at the 10% level:

Bivariate Fit of SD, % By AC added, %



Linear Fit

SD, % = 1.0240993 + 0.1998141*AC added, %

Summary of Fit

```
RSquare                        0.038377
RSquare Adj                    0.016013
Root Mean Square Error         1.355152
Mean of Response               1.799556
Observations (or Sum Wgts)           45
```

Lack Of Fit

```
                         Sum of                  F Ratio
Source          DF      Squares   Mean Square     1.4211
Lack Of Fit     18    39.936472       2.21869   Prob > F
Pure Error      25    39.030308       1.56121     0.2050
Total Error     43    78.966780                  Max RSq
                                                  0.5247
```

Analysis of Variance

```
                       Sum of
Source       DF       Squares   Mean Square    F Ratio
Model         1      3.151411       3.15141     1.7160
Error        43     78.966780       1.83644   Prob > F
C. Total     44     82.118191                   0.1972
```

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