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Appendix A

Updated Assessment of In Situ Treatment Technologies

Appendix A

Updated Assessment of *In Situ* Treatment Technologies

Section 3 of the *Corrective Measures Study Proposal Supplement* (CMS Proposal Supplement; ARCADIS BBL and QEA, 2007) submitted by the General Electric Company (GE) for the Rest of River in May 2007 presented a review and evaluation of *in situ* treatment technologies for sediment and soil. That section provided a justification for the screening of such technologies from further consideration in the Corrective Measures Study (CMS). A copy of that section is attached as Attachment A-1.

As part of the development of the Revised CMS Report, GE conducted a review of current innovative *in situ* treatment technologies for PCBs in sediment and soil to update the discussion included in the CMS Proposal Supplement. As with the prior review, potential *in situ* treatment options were evaluated using available information from several EPA websites (including EPA's Superfund Innovative Technology Evaluation [SITE] Program, Clu-in, and the Federal Remediation Technology Roundtable) and various other project and vendor websites. The information summarized below includes data and/or updates from projects that have become available since development of the CMS Proposal Supplement, and should be considered along with the information provided in the CMS Proposal Supplement (Attachment A-1).

Sediment

In situ treatment technologies (biological, physical, and chemical) for sediment sites continue to be under development, but none has been implemented full-scale at a PCB site. Research on *in situ* biological treatment of sediments is continuing, but at this time, it is unclear whether the limitations of this technology (as described in the CMS Proposal Supplement) can be overcome and, if so, when. The same is true for *in situ* chemical treatment technologies.

However, since submittal of the CMS Proposal Supplement, several efforts have been made to evaluate the effect of the application of activated carbon (AC) on bioavailability of contaminants in sediment. Laboratory studies by Sun and Ghosh (2008) have focused on the effects of AC amendment on bio-uptake reduction in PCB-containing sediment at four sites in the Great Lakes Area of Concern – Niagara River (NY), Grasse River (NY), and two locations on the Milwaukee River (WI). Results from these studies indicate that application of AC can reduce the aqueous dissolved PCB concentrations and bioavailable PCBs, resulting in reductions of PCB bioaccumulation by benthic organisms and, in turn, of PCB transfer up the food chain. Specifically, results from these studies showed that "[a]ctivated carbon addition at 0.5 times [the] native organic carbon to the sediments reduced PCB bioaccumulation by 42% for Niagara River sediment, 85% for Grasse River sediment, 74% for Milwaukee River sediment 1, and 70% for Milwaukee River sediment 2" (Sun and Ghosh, 2008). Sun and Ghosh (2008) concluded: "Although engineering challenges for amendment delivery remain to be addressed, these laboratory results indicate that AC application can be a potential *in situ* technology to reduce ecosystem exposure to PCBs."

Field pilot studies of AC have been performed at the Grasse River (NY) and Hunters Point (CA) (EPA, 2008; Sun and Ghosh, 2007; Cho et al., 2007, 2009; Luthy et al., 2009). These field studies included the placement and/or mixing of granular AC in the field over a relatively small treatment area. The data collected for the Grasse River (NY) field pilot study is currently under EPA review and have not been released to the public. A final report on the Hunters Point (CA) demonstration project was issued in 2009 (Luthy et al., 2009). In the initial field testing at Hunter's Point (CA), PCB bioaccumulation in clams exposed *in situ* to the treatment conditions for 28 days was evaluated 1 month and 7 months after adding AC to the sediment (Cho et al., 2007). By this analysis, PCB bioaccumulation was reduced by 24% and 53% in clams 1 and 7 months after treatment, respectively. After 18 months, PCB uptake by semi-permeable membrane devices, an analog for biological systems, was reduced by 50% to 65% in AC-amended plots compared to the unamended control plots (Cho et al., 2009). Sediment mixing and AC addition did not impact PCB bioaccumulation in amphipods among the treatments. It was postulated by these investigators that redeposition of contaminated sediments at the surface of the relatively small plots was the primary factor for inconsistencies between the laboratory and field bioassay results. Depth-discrete analysis of sediment cores illustrated significantly lower black carbon and higher aqueous equilibrium PCB concentrations in the surficial sediment after 24 months. In order to further assess the efficacy of this approach, *ex situ* tests were conducted at 24 months after AC application, using composite sediment samples collected from the site. Clams were added to these sediments and exposed for a period of 28 days. These tests showed a 30-50% reduction in PCB uptake by the clams in AC-treated sediment compared to the PCB uptake by clams in untreated control sediment (Luthy et al., 2009).

The Hunters Point (CA) demonstration project evaluated AC mixing technologies in a shallow, low-energy, depositional environment. These techniques may not be directly applicable to deeper or higher-energy sediment environments for technical feasibility reasons. Other recent developments in deployment technologies include a mechanical mixing apparatus (Chesner et al., 2008) and more passive methods that rely on bioturbation.[1] However, these techniques have not moved beyond pilot testing at this time.

Another new technique uses AC impregnated with reactive iron/palladium bimetallic nanoparticles (reactive activated carbon [RAC]) (Choi et al., 2008; 2009a; 2009b; Choi and Al-Abed, 2010). This treatment technology uses AC to physically sequester the PCBs and metals to dechlorinate the PCBs, since the use of metals in a zero-valent state has been documented to efficiently dechlorinate PCBs. This technology is currently being developed, and has not to date been demonstrated to degrade an Aroclor mixture of PCBs in a contaminated sediment environment.

In August 2008, the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) conducted a workshop focused on research and development needs related to the bioavailability of contaminants in soils and sediments. As a result of this workshop (SERDP and ESTCP, 2008), critical priorities were established for researching *in situ* remedies to reduce bioavailability of contaminants in sediments, with a high priority placed on better understanding the effect of black carbon on the bioavailability of contaminants in sediments. Long-term performance measures to evaluate the success of field-placed amendments in reducing bioavailability were also identified as a critical demonstration need.

Soil

As with sediment sites, *in situ* treatment technologies for soil sites continue to be under development. GE's recent re-evaluation of such potential technologies indicated that, as previously stated in the CMS Proposal Supplement, various studies are underway to understand the applicability of these treatment technologies to PCBs and other constituents in soils. However, these studies remain in the research stage, and no new *in situ* soil treatment technologies were identified which have been implemented full-scale at PCB sites.[2]

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[1] One such passive method is the Sedimite™ method being developed by Sediment Solutions, Baltimore, MD. Two other ongoing research projects that are further developing the passive deployment methodology are: Superfund Basic Research Program grant number R01ES16182 - Pilot-scale Research of Novel Amendment Delivery for *in situ* Sediment Remediation; and Environmental Security Technology Certification Program project number ER-0835 - Evaluating the Efficacy of a Low-Impact Delivery System for In Situ Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals.

[2] This recent re-evaluation did indicate that a previously existing technology discussed in the CMS Proposal Supplement, cement-based *in situ* solidification/stabilization, has been demonstrated full-scale at an additional site, as discussed later in this appendix.

Chemical Treatment. An *in situ* chemical treatment technology identified since the submittal of the CMS Proposal Supplement reportedly uses persulfate and a surfactant to solubilize and subsequently destroy PCBs. This technology has been developed by VeruTEK® Technologies, Inc.; but to date, VeruTEK® has released only limited data from bench-scale tests for the treatment of PCBs in water (VeruTEK®, undated). The bench-scale data indicated that the surfactant-enhanced oxidant reduced the PCB concentration in the water from 1,700 milligrams per liter (mg/L) to approximately 250 mg/L (VeruTEK®, undated). However, no information was obtained regarding the testing of this technology on PCBs in soil; and no field-based (or peer-reviewed) studies, data, or literature have been made available to the scientific community on this technology.

A similar chemical treatment technology uses sodium persulfate ($Na_2S_2O_8$) and the related oxidant potassium peroxymonosulfate ($KHSO_5$), activated with heat and iron, which have been reported to degrade PCBs (EPA, 2006; Rastogi et al., 2009). Again, however, no field-scale reports of PCB-contaminated soil remediation using activated persulfate are publically available.

Any form of *in situ* chemical oxidation technology applied on floodplain soils would have similar limitations to those described in the CMS Proposal Supplement in 2007 (i.e., variable effectiveness depending on site stratigraphy, soil oxidant demand and pH; limitations due to land disposal restrictions and underground injection-related regulations; and the likelihood of leaving residuals [un-reacted oxidants] or byproducts in the floodplain soil).

Thermal Treatment. Since the evaluation of *in situ* thermal treatment in the CMS Proposal Supplement, the United States Army Corps of Engineers (USACE) published a design manual for *in situ* thermal remediation (USACE, 2009). That document provides guidance and background necessary for evaluating *in situ* thermal remediation. However, no new information regarding *in situ* thermal remediation appears to be presented; the document is consistent with previous guidance documents reviewed for the CMS Proposal Supplement and the case studies discussed by the USACE were conducted prior to 2001.

Solidification/Stabilization. EPA recently published a technology performance review of *in situ* solidification/stabilization (S/S) treatment (EPA, 2009), which involves the mixture of a stabilizing agent into the soil to physically or chemically bind the chemical of interest and reduce the potential for uptake or exposure by humans and biota. EPA's review states that "[t]here is potential to use S/S under a wide variety of site conditions." While not a new technology, information presented in Table 3-1 of that document shows that *in situ* S/S technology has been demonstrated as an effective treatment of PCBs in soil. The document describes the application of cement-based *in-situ* S/S at a Superfund site in Arkansas in 2000, where a cement-based stabilization agent was mixed in with approximately 40,000 cubic yards (cy) of soil containing PCBs at concentrations up to 14 mg/kg (other contaminants were also present) (EPA, 1994). Following implementation, the solidified mass extending over more than 4 acres was covered with 2 feet of soil and vegetated. Monitoring conducted 5 and 10 years following implementation showed that the relevant performance standards were achieved, including the standard of 0.0005 mg/kg PCBs in leachate from the S/S-treated soil (EPA, 1998, 2009, and 2010). EPA's technology performance review of S/S treatment (EPA, 2009) indicates that there are several future land use and environmental factors that could cause erosion of the solidified/stabilized soils, potentially leading to the release of PCBs.

While results from this application are similar to those at the Hialeah site (FL) and Caldwell Trucking site (NJ) discussed in the CMS Proposal Supplement, the drawbacks with applying this technology at the Rest of River site remain the same as noted in the CMS Proposal Supplement. Creation of a solidified mass of treated material like that performed at the Hialeah, Caldwell, and Arkansas sites would require placement of a soil cover over the treated material to support vegetative growth and provide habitat for floodplain organisms. The presence of the solidified mass would eliminate the flow of groundwater to the overlying soil cover and prevent the growth of deep rooted vegetation, greatly limiting vegetative restoration and future floodplain uses. Other drawbacks with in-situ S/S include potential flood storage or freeze/thaw issues due to volume expansion during implementation, and the higher costs and longer time frames for shallow-depth applications such as for the Rest of River floodplain soils.

Summary

Although several *in situ* treatment technologies have been, in part, demonstrated at a bench- or pilot-scale level, no new technologies have been successfully demonstrated full-scale with PCBs in sediment or soil since the development of the CMS Proposal Supplement;[3] and the limitations of the technologies that have been identified remain largely the same as described in that document. As noted by SERDP and ESTCP in November 2008 with regard to sediments: "Although several technologies for … in situ treatment have been developed, there remains a need for demonstration and validation of the effectiveness and permanence of these remedies" (SERDP and ESTCP, 2008). The same need for more successful bench/pilot-scale testing of technologies for PCB-contaminated soil is also necessary before full-scale implementation.

[3] As noted above, while not a new technology, cement-based *in situ* S/S was identified as having been demonstrated full-scale at an additional site.

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Attachment A-1

CMS Proposal Supplement
Section 3

3. Further Justification for Screening of In Situ Treatment Technologies

3.1 Introduction

This section provides additional justification for the screening of *in situ* treatment technologies and addresses the following EPA comment:

- **General Condition 2.** *GE shall provide further justification and discussion (in the Supplement) of the screening of* in situ *treatment technologies for sediment and soil.*

3.2 Overview of Screening Process

In the CMS Proposal, *in situ* sediment and soil treatment technologies for the Rest of River were identified and screened in a two-step process. This Supplement elaborates on this process and provides additional detail regarding the evaluation of potential *in situ* treatment technologies. Potential *in situ* treatment options were identified using available information from several EPA websites, including the EPA's Superfund Innovative Technology Evaluation (SITE) Program, Clu-in, and the Federal Remediation Technology Roundtable.

The two-step screening process used in the CMS Proposal consisted of an initial and secondary screening step. The initial screening generally consisted of an evaluation based on technical implementabilty to eliminate those technologies that are not appropriate based on site conditions or chemical/physical characteristics of the site media, or that have not been successfully applied on a full-scale basis at other PCB-impacted sites.

Those technologies that were retained as a result of the initial screening were then subject to a secondary screening based on effectiveness and implementability. The effectiveness of each treatment technology was evaluated based on: (a) its general ability to reduce the potential for human and/or ecological exposure to PCBs; and (b) the extent to which long-term maintenance and/or monitoring is required to ensure effectiveness. Implementability included consideration of both the technical and administrative feasibility of implementing a technology process option, as well as the availability of equipment, materials, and personnel.

An expanded and more detailed discussion of the identification and screening of potential *in situ* treatment technologies is provided below.

3.3 Overview of Identified *In Situ* Treatment Process Options

In situ treatment typically involves using physical, chemical, biological, or thermal processes to destroy or degrade contaminants or immobilize the contaminants in place within the soil or sediment. Each of these process options is summarized below, as it would apply to the Rest of River area.

- ***In situ* physical treatment** can be applied to sediment or soil and involves injecting and/or mixing an immobilization agent to reduce the mobility of PCBs. The agent can be coal, coke breeze, activated carbon, Portland cement, fly ash, limestone, or other additive. It is injected/mixed into the sediment or soil to encapsulate the contaminants in a solid matrix and/or chemically alter the contaminants by converting them into a less bioavailable, less mobile, or less toxic form.

- ***In situ* chemical treatment** can be applied to sediment or soil and involves injecting chemical surfactants/solvents or oxidants into the treatment area to remove or destroy PCB constituents. Chemical treatment processes may include common or proprietary solvents and other liquids.

- ***In situ* biological treatment** can be applied to sediment or soil and involves introducing microorganisms and/or nutrients into the treatment zone to increase ongoing biodegradation rates of PCBs. Biodegradation of PCBs may occur either in the absence of oxygen (anaerobic conditions) or with oxygen present (aerobic conditions).

- ***In situ* thermal treatment** is applicable only to soil media and involves heating the PCB-containing soil to high enough temperatures to remove and/or destroy PCBs in the floodplain soils. It could include the use of steam or direct heat (via heat elements) and thermal conductivity to heat soils and vaporize contaminants for collection and treatment/disposal. In addition, resistance heating could be employed, which uses electromagnetic waves to heat targeted soils in an effort to enhance contaminant removal. *In situ* vitrification, a higher energy form of thermal treatment, uses temperatures high enough to vitrify the soil (i.e., turn it into a stable glass-like material), destroying or immobilizing contaminants that are present. The success of any of these forms of *in situ* thermal treatment is highly dependent on soil homogeneity, subsurface conditions, and the effectiveness of the delivery system.

These treatment options are evaluated individually below for sediment and soil applications. However, as a general matter, all *in situ* treatment technologies, regardless of type, are subject to a number of general challenges that could make their application to the Rest of River problematic. Physical access to the area to be treated must be obtained. Additionally, for the floodplain soils, removal of all vegetation (including clearing and grubbing of root systems) would likely be required to achieve effective treatment. The effectiveness of *in situ* treatment technologies is also dependent upon subsurface characteristics, such as moisture content and material type, which can be highly variable, especially in the floodplain, and would make technologies such as *in situ* thermal treatment prohibitive for the sediments. Moreover, these technologies require an effective *in situ* delivery system and adequate process controls/containment, which have been shown to be difficult to design, effectively operate, and maintain. In addition, unreacted treatment reagents and/or byproducts generated by the reagents may remain in the subsurface, with potentially unknown environmental effects. Following remediation, treated areas would likely not be suitable for restoration without nutrient amendment or covering with clean materials, which could affect the flow of surface water or groundwater, flood storage capacity, and future use by both humans and wildlife. Finally, given the lack of full-scale use of most *in situ* technologies, little is known about their long-term effectiveness and permanence.

3.4 Evaluation of Identified *In Situ* Treatment Technologies for Sediment

Methods for *in situ* treatment of sediments are currently under development, but few options are commercially available. EPA has noted that "significant technical limitations currently exist for many of the treatment technologies," especially in terms of their effectiveness (EPA, 2005a). The efficiency of *in situ* treatment is summarized by Renholds (1998) as "almost always less than ex situ treatment." The EPA has also cited *in-situ* mixing as "most difficult alternative in terms of control of safety and environmental considerations" (EPA, 1986). In the CMS Proposal, each of the *in situ* treatment process options for sediments was screened out in the initial screening step. Additional information and justification for such screening are provided in the following subsections.

3.4.1 *In Situ* Physical Treatment

In situ physical treatment processes have not yet been sufficiently developed for sediment nor been successfully implemented full-scale for PCBs. The problems noted by others with implementation of *in situ* physical treatment processes for sediments include:

- Lack of an effective delivery system (EPA, 2005a), including difficulties in maneuvering about rocks and cobbles that may be on the river bottom;
- Lack of good process controls, particularly for mixing conditions and curing temperatures (Kita and Kubo, 1983);
- Lack of good quality control during the mixing process (EPA, 1986);
- Difficulty in controlling safety and environmental considerations during *in-situ* mixing since the entire process is open to the atmosphere, leading to environmental problems such as generation of odors, vapors, and fugitive dust (EPA, 1986);
- Potential need for frequent and potentially sizeable onshore staging areas to support application;
- Ability to control the mixing process to mitigate impacts to the water column and surrounding environment;
- High degree of sediment handling (EPA, 1994); and
- Potential to increase in place sediment volume due to the addition of a stabilizing agent.

Based on a review of two sediment projects (Fox River [WI], which included the field implementation of a stabilization treatment technology, and the Manitowoc River [WI], which consisted of a pilot-scale evaluation of a solidification treatment technology), Renholds (1998) noted that although there was a relatively high treatment efficiency observed in most laboratory studies for *in situ* physical treatments, there was difficulty in the implementation of the treatment and engineering controls in the field. The feasibility of *in situ* physical treatment must consider the technology's environmental impact on the water column and aquatic environment. For instance, *in situ* physical treatment technologies, which often include mixing processes, need to operate without dispersing the sediments or creating conditions more harmful to aquatic life than already exist (EPA, 1994). Significant issues with mixing were encountered during the Manitowoc River (WI) demonstration project. The river sediments contained polycyclic aromatic hydrocarbons (PAHs) and several heavy metals from a former coal gasification plant. During the demonstration project, good controls could not be established for the mixing of cement/fly ash slurry with the sediment (Renholds, 1998), resulting in the dispersal of sediments and little treatment (according to the Wisconsin Department of Natural Resources). On the Fox River, *in situ* stabilization was implemented on sediments containing lead in a small scale application (500 tons of sediment treated) using a shoreline-based crane and clamshell. While the mixing process was reportedly successful at stabilizing the lead to a sufficient degree that the material would not be classified as a hazardous waste under RCRA, several stages of mixing were required, and the stabilized material was subsequently removed and transported to an off-site landfill, precluding any opportunity to record/monitor this project as a true *in situ* process. Issues with resuspension were reported during mixing, and the need for containment was noted if a similar mixing process were to be considered on a larger scale (Renholds, 1998).

According to the National Research Council in *A Risk Management Strategy for PCB-Contaminated Sediments,* (NRC, 2001), the lack of adequate process controls has relegated the use of *in situ* physical treatment to instances when the contaminated sediment can be isolated from the water body. Even if some sort of containment system such as cofferdams were used, the effects on groundwater/surface water interaction beneath the river bottom would need to be considered and its use may be limited by water depth and river bottom conditions. In addition, other substantial issues associated with using a containment system include: the presence of variable river bottom and debris which would interfere with the mixing process; the potential need for removal following stabilization to address any concerns regarding loss in flow capacity resulting from the addition of a stabilization agent; and the potential need to add cover material to provide a viable habitat for biota. It is likely that *in situ* physical treatment has not been attempted full-scale on river sediments because of the many factors that preclude effective implementation.

In light of the fact that *in situ* physical treatment processes have not yet been sufficiently developed to treat sediment *in situ* nor been successfully implemented full-scale for PCBs, coupled with the potential concerns regarding implementation noted above, there is insufficient precedent or technical information available to retain this technology as a potentially viable remedial option for the Housatonic River sediments at this time.

3.4.2 *In Situ* Chemical Treatment

In situ chemical treatment processes have not been successfully demonstrated full-scale for PCBs in sediment. The problems associated with implementation of *in situ* chemical treatment processes include:

- Lack of an effective delivery and homogenization system;
- Addressing toxicity associated with the chemical additives and/or byproducts of the treatment process;
- Difficulties in maneuvering about rocks and cobbles that may be on the river bottom for reagent delivery;
- Potential need for frequent and potentially sizeable on-shore staging areas to support application;
- Elevated biological oxygen demand that requires more oxidant than expected (Murphy et al., 1995);
- Difficulty in controlling the mixing reagent from spreading outside the targeted treatment area; and
- Lack of ability to control the mixing process such that mixing reagents and sediments are not released to the environment (EPA, 1994).

Current studies are underway at the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET), founded by the National Oceanic and Atmospheric Administration (NOAA) and the University of New Hampshire, on an *in situ* sediment ozonator that may eventually have the potential to remediate PCBs *in situ*. However, at this time, the project remains in the research stages and has not been applied full-scale (Hong and Hayes, 2006). In addition, investigators at the University of New Hampshire are currently carrying out studies on *in situ* dechlorination of PCBs through application of zero-valent iron (ZVI) or magnesium. While these investigators' laboratory testing on sediments from the Housatonic River has shown promising results (e.g., 84% PCB removal in one day), mass balance analyses have not yet been able to account for all PCBs removed from the sediment (Mikszewski, 2004). As this technology is still in the experimental stage, no information is yet available on the performance of a demonstration-scale or full-scale application.

Oil-Free Technologies, Inc. (Oil-Free) has developed a proprietary enzyme mixture (Enzymmix) that is reported to be able to break down PCBs. Although this technology has not been demonstrated in a full-scale application for sediments, laboratory tests on soils have been performed. These tests have reportedly shown that Enzymmix, with multiple applications in a laboratory setting using soils, reduced PCB concentrations approximately 43% from an initial average concentration of 117 parts per million (ppm) (University at Albany, 2006); however, it is unknown what fraction of PCBs were lost to volatilization since the experiment was not conducted under air-tight conditions (EPA, 2005b). The vendor has indicated that diversion of river water with installation of a series of pipes installed in a 10-foot grid would be necessary as a potential procedure for applications to sediment. In fact, the Housatonic River Initiative (HRI) submitted a request to EPA to evaluate Enzymmix for possible application at the Housatonic River as part of EPA's SITE Demonstration Program.[8] Based on the information provided by HRI and the vendor, EPA concluded that the Oil-Free process would not be evaluated under the SITE Program due to incomplete data from previous studies and an absence of demonstrated performance (EPA, 2005c).

Further, the pilot-scale *in situ* chemical/biological study (via chemical injection of oxidants and/or nutrients) conducted on sediments from Hamilton Harbor (Canada) and the 1991 field research study conducted on Hudson River sediments to study the potential for *in situ* biological/chemical treatment of sediment both resulted in approximately 50% treatment efficiencies, which are low compared to treatment efficiencies of *ex situ* processes (Renholds, 1998).

In light of the fact that *in situ* chemical treatment processes have not yet been sufficiently developed for sediment *in situ* nor been successfully implemented full-scale for PCBs, coupled with the potential concerns regarding implementation noted above, there is insufficient precedent or technical information available to retain this technology as a potentially viable remedial option for the Housatonic River sediments at this time.

3.4.3 *In Situ* Biological Treatment

In situ biological treatment processes have not been successfully demonstrated full-scale for PCBs in sediment. The problems associated with implementation of *in situ* biological treatment processes include:

- Lack of an effective delivery system, including difficulties in maneuvering about rocks and cobbles that may be on the river bottom;
- Difficulty in identifying the microbes responsible for PCB biodegradation/dechlorination;

[8] EPA's SITE Demonstration Program was established by EPA's Office of Solid Waste and Emergency Response and Office of Research and Development (ORD), and is administered by ORD National Risk Management Research Laboratory in the Land Remediation and Pollution Control Division (LRPCD). The SITE Demonstration Program encourages the development and implementation of innovative treatment technologies for remediating hazardous waste sites, as well as measurement and monitoring technologies. In the demonstration program, a technology is field-tested and engineering and cost data are collected. EPA then documents the testing, including performance and cost data, provides an evaluation of all available information on the technology, and analyzes its overall applicability to other site characteristics/wastes (EPA, 2007a).

- Bioavailability of key contaminants such that the microorganisms feed on the target compounds rather than other substrates (Renholds, 1998);
- Lack of ability to achieve low ppm residual PCB concentrations in sediments;
- Lack of ability to establish/enhance variable sediment conditions (e.g., aerobic versus anaerobic, pH, etc.) sufficient to effectively support microbial degradation and/or dechlorination;
- Lack of ability to control the mixing process to mitigate impacts to the water column and surrounding environment;
- Potential need for frequent and potentially sizeable onshore staging areas to support application; and
- Overall resistance of PCBs to microbial degradation.

A field study was performed by GE in the Housatonic River to assess chemical activation of microbial dechlorination on Woods Pond sediments for approximately one year (Bedard et al., 1995, 1998). In this study, two caissons were driven 18 to 24 inches into the sediment, and the sediments in each caisson were mixed for homogenization twice prior to treatment. One cell was treated with 2,6-dibromobiphenyl (2,6-BB) as a microbial primer and the other was left untreated as a control. The preliminary results indicated that some dechlorination of highly chlorinated PCB congeners could be performed by native microbial populations with the addition of 2,6-BB, but significant changes in PCB concentration were not noted (Bedard et al., 1995). Further research exhibited positive results for accelerated *in situ* microbial dehalogenation of PCBs through use of brominated biphenyls, but progress was slowed by lack of naturally occurring and effective priming compounds, and again significant changes in PCB concentration were not noted (Bedard et al., 1998). Reasons that PCBs are resistant to microbial degradation include the following (Renholds, 1998):

- Preferential feeding of microorganisms on other substrates;
- Microorganisms' inability to use a compound as a source of carbon and energy;
- Unfavorable environmental conditions in sediments for propagation of appropriate microorganisms; and
- Poor contaminant bioavailability to microorganisms.

Recent research has identified specific anaerobic microorganisms (*Dehalococcoides*) that are capable of partially dechlorinating PCBs and obtain energy from this process (Bedard et al., 2007). However, this research is still in the early stages and the authors have indicated that more research is necessary before it can be determined if this technology can be implemented for full-scale *in situ* applications. In addition, the subject experiment looked at only an aqueous medium and did not consider any factors that would affect *in situ* sediment applications (e.g., desorption of PCBs). Further, the experiment used a fresh source of PCBs, but the PCBs found in the environment have been "aged," which may affect the microorganisms' ability to dechlorinate the biphenyl ring.

Overall, this recent research has shown that the microorganisms only partially dechlorinate PCBs, which may mean that the form of the PCBs might be altered without reduction in total PCB concentrations in the sediment. The research indicates that another mixed culture of organisms previously studied could continue the PCB dechlorination process; however, these two groups of microorganisms were not obtained from the same source/location (i.e., they have not been found together in the environment). Therefore, it is likely that the sediments of the Rest of River would need to be amended with non-native microorganisms for the dechlorination process to occur. In addition, the microorganism population had to grow to a minimum level before measurable dechlorination occurred in this study. The investigators indicated that this microorganism population level is not likely to occur naturally in a sediment environment (such as the Rest of River) and that further research would be required to determine the necessary changes to environmental conditions that could increase the microorganism population (Bedard et al., 2007).

In light of the fact that *in situ* biological treatment processes have not yet been sufficiently developed for sediments nor been successfully implemented full-scale for PCBs, coupled with the potential concerns regarding implementation noted above, there is insufficient precedent or technical information available to retain this technology as a potentially viable remedial option for the Housatonic River sediments at this time.

3.4.4 Summary of Evaluation of *In Situ* Treatment Technologies for Sediment

Based on the above evaluation, none of the *in situ* treatment technologies that were evaluated is considered a potentially viable remedial option for the Rest of River sediments at the present time. Although several of the technologies have been, in part, demonstrated at a bench- or pilot-scale level, none of the technologies has been successfully demonstrated full-scale with PCBs in sediment. The lack of success of these technologies in reducing PCB concentrations is governed in part by the fact that, by their nature, PCBs are persistent compounds.

Although each technology presents its own individual challenges, in general adding media (e.g., stabilization agent, chemical reagent, microorganisms, etc.) to sediment through the water column is difficult at best. According to the EPA, "developing an effective in-situ delivery system to add and mix the needed levels of reagents to contaminated sediment is more problematic" (EPA, 2005a). Delivery systems are affected by the depth of water and river bottom substrate; a layer of cobble and/or gravel at the sediment surface will likely be difficult to penetrate in these application situations. Many of these technologies may require multiple on-shore staging areas to promote application. Further, once the added media are introduced into a dynamic river system, it is difficult to control the endpoint of the application. Several of these technologies require significant mixing of sediment in order to promote success, and resuspension created by the mixing process may be difficult to control or manage in areas of variable river conditions (e.g., increased river velocities, uneven river bottom, deep water, etc.) There is a need for more successful bench/pilot-scale testing showing some promise at overcoming the challenges noted above before full-scale implementation is considered. However, GE will re-evaluate these technologies during the CMS if future information or test results become available indicating that any of them may prove to be a potentially effective and implementable option for application to the Rest of River sediments.

3.5 Evaluation of Identified *In Situ* Treatment Technologies for Soil

In the CMS Proposal, *in situ* physical treatment of floodplain soil was carried forward for secondary screening because it has been used at a limited number of sites with PCB-impacted soils. However, that process option was not retained for further evaluation in the CMS due a number of issues relating to its effectiveness and implementability. *In situ* chemical and thermal treatment processes for soil were screened out in the initial screening step because such process have not been successfully demonstrated full-scale to address PCBs in soil. Similarly, although aerobic and anaerobic biodegradation of PCBs are known to occur both naturally and through enrichment, *in situ* biological treatment for soil was also screened out in the initial screening step because no *in situ* biological processes or sites were identified in the literature where significant reductions in PCB concentrations have been documented. Additional information and justification for the screening of each of these *in situ* treatment process options for floodplain soil are provided in the following subsections.

3.5.1 *In Situ* Physical Treatment

In situ physical treatment (via immobilization) has been applied at a number of sites employing a variety of deep and shallow mixing techniques using Portland cement or some other stabilization agent to reduce the potential mobility of contaminants in soils through physical and/or chemical fixation of the contaminants (Lehr, 2004). Most of the documented *in situ* applications have been at sites containing a variety of PAHs and metals, and were done to address deep soils that would be difficult to excavate and/or performed in part to improve the geotechnical characteristics of the soil for subsequent redevelopment (Carleo et. al, 2006; Wilk, 2005; Wilk and DeLisio, 2002). The use of *in situ* physical treatment to address soils containing PCBs appears to be very limited, with only one site demonstration and one full-scale project identified through a literature search and discussions with vendors. A summary of those projects is provided below..

Physical immobilization was evaluated in 1988 through EPA's SITE Demonstration Program at a GE service shop in Hialeah, FL. Contaminants of concern included PCBs at concentrations ranging up to 950 mg/kg, as well as a variety of volatile organic compounds (VOCs) and metals. The demonstration process involved deep soil mixing using Geo-Con equipment and International Waste Technologies (IWT) HWT-20 cementitious additive. The mixing process was based on a combination of an auger and caisson, which operated in the waste. The stabilization/solidification agent was fed into the auger and then into the waste through a hollow stem. Inside the caisson, the auger mixed the agent with the waste by a lifting and turning action (EPA, 1989). The test was performed on two 10x20 ft areas to depths up to 18 feet. Among the objectives, the study was designed to evaluate the extent to which the Geo-Con process could immobilize (i.e., reduce the leachability of) the PCBs in the soil, evaluate the performance and effectiveness of the mixing process, and assess the potential long term durability of the solidified mass. The conclusions drawn (EPA, 1990) were that:

(a) immobilization of PCBs appeared likely, although this could not be confirmed due to low PCB concentrations in the mixed soil (due to dilution through mixing with lower concentration soils and some dilution from the additive) and in the leachate from the treated and untreated soils;

(b) a modest volume increase of 8.5% occurred, which could provide land contouring difficulties in many locations;

(c) the solidified material showed satisfactory physical properties (e.g., unconfined compressive strengths, permeability, and integrity) indicating a potential for long-term durability, but unsatisfactory integrity for the freeze/thaw samples, with cumulative relative weight losses ranging from 0.5% to 30 % and averaging 6.3%; and

(d) a dense, low-porosity, monolithic block of treated waste was produced, which groundwater would flow around, not through.

In situ stabilization was also implemented as a final remedial component to address in-place soils at the Caldwell Trucking Site (NJ) (EPA, 2006a). The primary constituents of concern at the Caldwell site were lead, cadmium, and VOCs. PCBs were also detected in soil stabilized at the site at concentrations below 50 mg/kg. In total, approximately 40,000 cubic yards of soil were stabilized in place using an excavator, to depths up to 35 feet, using Portland cement. The stabilization process was suspended for 17 months due to high levels of odors and emissions coming from the soils, which were addressed through construction of a soil vapor extraction system. The treatment process created a large monolithic block of concrete/soil, which was bulked by approximately 20% (protruding above grade) due to the addition of concrete slurry. Once complete, a 2-foot soil cover was placed over the treatment area and seeded (Hebert, 2007). Although no specific data were found, review of a 5-year review report by EPA indicated that the stabilization of contaminated soil was “intact and in good repair,” and that it “has greatly reduced the potential for exposure and mobility of site related contaminants” (EPA, 2002b).

Given its prior use at these sites (despite the considerations discussed above), *in situ* physical treatment of soils (via immobilization) was retained for secondary screening under the effectiveness and implementability criteria, as discussed below.

If applied to the Housatonic River floodplain soils, physical immobilization would involve mixing the floodplain soils *in situ* with Portland cement or some other stabilization agent to reduce the bioavailability of PCBs in the soils. For areas with extensive vegetation, clearing, grubbing, and site grading would be required prior to implementation. This option could be implemented alone or may need to be combined with other technologies/process options. For example, to maintain flood storage capacity in the area, soil removal might be required prior to soil stabilization so as to accommodate the increased volume that would be caused by the addition of the stabilization agent and/or to accommodate a soil cover, which may need to be placed over the stabilized soils to support vegetative growth. The impact of using certain stabilization agents on surface water/groundwater movement and interaction would also need to be considered.

Effectiveness – Physical immobilization could reduce the bioavailability of PCBs in floodplain soils, thereby reducing the potential for human or ecological exposure. For those sites noted above where *in situ* physical treatment has been implemented, the bioavailability was essentially reduced by converting the soils into a cement-like monolithic block. While a cement-like product may be acceptable at an industrial site where the potential for leaching to groundwater is the primary driver, use of such a product in the Housatonic floodplain would greatly inhibit the functional value of the soils, requiring a new soil cover to be placed over the top of the solidified material to sustain vegetation and provide habitat for floodplain organisms. Since the concentration of PCBs in the soil matrix is not significantly reduced through the physical immobilization process, the effectiveness of this technology using non-cement additives (if one were identified) at reducing the bioavailability to organisms which ingest soil is questionable, and would likely also require placement of a clean soil cover. Additional problems and challenges noted at the Hialeah site, which would also need to be considered for the Housatonic River floodplain soils, include volume increase and freeze/thaw integrity issues.

Implementability – It is currently assumed that the equipment, materials, and operating personnel needed to implement *in situ* physical treatment in the Housatonic River floodplain would be readily available. However, there could be some technical and administrative issues, such as incompatibility with future uses of floodplain soils and restoration options (i.e., may not be able to support vegetative growth), flood storage issues due to volume expansion during implementation of this option, and potential difficulty obtaining permission from property owners to carry out the immobilization on their properties. None of these were issues at the Hialeah, FL. and Caldwell, NJ sites, because both are industrial sites, and physical treatment was performed to support future site use without consideration for use and inhabitance by wildlife or potential wetlands restoration. Also, this option is best suited for deeper applications within a relatively small footprint, rather than a potentially large, shallow-depth application such as the floodplain soils of the Housatonic River. Unlike the Housatonic River floodplain soils, the use of *in situ* physical treatment at the Hialeah, FL. and Caldwell, NJ sites was driven by the presence of deep soils requiring remediation (up to 35 feet deep) and the fact that excavation to such depths was deemed impracticable. Finally, this option would be costly to implement given the relatively shallow vertical distribution of PCBs in the floodplain soil (which would make this an expensive remedy per unit area applied) and the likely need to remove material prior to or following implementation to accommodate flood storage capacity.

Due to potential effectiveness and implementation issues noted above and the relatively high implementation costs compared to other more proven and effective floodplain soil remedial options, physical immobilization has not been retained for further evaluation as a floodplain soil remedial option at this time.

3.5.2 *In Situ* Chemical Treatment

In situ chemical treatment processes have not been successfully demonstrated full-scale for PCBs in soil. EPA has noted that while injecting chemical surfactants/solvents to treat soils is common in oil field applications, “it has found limited application in the environmental arena” (EPA, 2006b).

Several chemicals that are known to break down PCBs have been identified in the laboratory. Fenton’s reagent, a form of chemical oxidation, has been found to be an effective method of remediating PCB-impacted soils through oxidation by hydroxyl radicals. The toxicity of the parent PCB, potential Fenton’s remediation byproducts, and the byproduct mixture may require further evaluation (Satoh et al., 2003). As another example, nanoscale zero-valent iron has been shown to dechlorinate PCB; however, a study reporting this noted that pilot and full-scale field tests are ultimately needed to further assess the appropriateness of these technologies (Mikszewski, 2004).

In addition, Oil-Free Technologies, Inc. has developed a proprietary enzyme mixture (Enzymmix) which is reported to be able to break down PCBs and which has been demonstrated in laboratory tests on soils. That technology was discussed in Section 3.4.2. As explained in that section, the effectiveness of this technology is uncertain since the tests were not conducted under air-tight conditions and hence the faction of PCBs lost to volatilization is unknown (EPA, 2005b). In addition, there is no documentation regarding the toxicological effects of the enzyme mixture, and it is unclear how its migration would be controlled or how it would be recovered from the subsurface. As noted above, in response to a request from HRI to evaluate Enzymmix for possible application at the Housatonic River site, EPA concluded that this process would not be evaluated under the SITE Demonstration Program due to incomplete data from previous studies and an absence of demonstrated performance (EPA, 2005c).

General problems associated with the implementation of *in situ* chemical treatment processes in soils include the following:

- Effectiveness can be greatly affected by site stratigraphy, soil oxidant demand, and pH;
- Multiple applications are needed when using chemical oxidants; some unreacted oxidants may remain in the subsurface (EPA, 2006b);

- Land disposal restrictions and underground injection-related regulations may limit the viability of using chemical treatment (EPA, 2006b); and
- Byproducts from oxidation may present additional toxicity issues that would need to be further evaluated as part of a bench scale and/or pilot study.

Given these problems, *in situ* chemical treatment is not considered a potentially viable remedial option for the Housatonic River floodplain soils at this time.

3.5.3 *In Situ* Biological Treatment

In situ biological treatment processes have not been successfully demonstrated full-scale for PCBs in soil. While aerobic and anaerobic biodegradation of PCBs are known to occur both naturally and through enrichment (e.g., through addition of nutrients and/or microbes which are know to degrade PCBs), no processes or sites were identified in the literature where significant reductions in PCB concentrations have been documented.

One study (Mikszewski, 2004) assessed the potential for anaerobic and aerobic biodegradation of PCBs. The study concluded that, despite years of research and many promising leads, an effective biodegradation *in situ* remediation technique for PCB-contaminated soils and sediments does not exist. It was also recognized by the author that the controversial use of genetically modified organisms (such as used in this research) must be carefully monitored.

In 1998, Green Mountain Laboratories, Inc. (GML) and the EPA conducted a SITE project to evaluate the effectiveness of a bioremediation process for the treatment of PCB contaminated soils at the Beede Waste Oil/Cash Energy Superfund site in Plaistow, NH. The treatment process involved inoculation/augmenting of the PCB contaminated soils with bulk microbial inoculum and nutrients, allowing the microbes to aerobically degrade the PCBs. The bulk inoculum was produced on-site by the developer using animal feed-grade oatmeal as the substrate, shredded pine needles that provided certain specific co-metabolite compounds, nutrients and a proprietary consortium of microorganisms believed capable of degrading the PCBs to their eventual endpoints (carbon dioxide and mineral halides). The results of the field evaluation of the technology, which are based on the data collected from the treatability study conducted in the third quarter of 1998, indicated no removal/degradation of the PCBs (EPA, 2005a).

In general, the problems associated with implementation of *in situ* biological treatment processes in soils include:

- Lack of an effective nutrient/chemical delivery and containment system for materials injected or mixed into the soils to promote degradation (Renholds, 1998);
- Difficulty in identifying the microbes responsible for PCB biodegradation/dechlorination;
- Inability to achieve low ppm residual PCB concentrations;
- Inability to establish/enhance variable sediment conditions (e.g., aerobic versus anaerobic, pH, etc.) to a sufficient degree to effectively support microbial degradation and/or dechlorination; and
- Overall resistance of PCBs to microbial degradation.

Given these problems, *in situ* biological treatment of soils has not been retained as a potentially viable remedial option for the Housatonic River floodplain soils at this time.

3.5.4 *In Situ* Thermal Treatment

In situ thermal treatment has been pilot tested at several sites containing PCBs. The technology was applied in a field application in Glens Falls (NY), where near-surface PCBs were detected at concentrations up to 5,000 ppm. Following treatment, PCB concentrations were reportedly reduced to less than 2 ppm (TerraTherm Environmental Services, 1997). In another case study, *in situ* thermal treatment was tested at a 30-acre Naval facility in Ferndale, CA, which contained PCBs in soils at concentrations up to 860 ppm. From September 1998 to February 1999, approximately 1,000 cubic yards (cy) of PCB-impacted soils were treated using *in situ* thermal treatment. Treatment goals were met in the bulk of the treatment area with the exception of one portion (178 cy) where elevated PCB concentrations remained (EPA, 2007b).

Despite these pilot tests, *in situ* thermal treatment processes have not been implemented full-scale to address PCBs in floodplain soils similar to those in the Rest of River. The problems with such application of *in situ* thermal treatment processes include the following:

- The process boils off water in the soil before it boils off the contaminants (the maximum achievable temperature is 212 degrees Fahrenheit (°F) until all of the water is boiled off). In locations where the control of soil moisture would be difficult (e.g., such as in soils that are saturated by surface waters), this technology cannot be used effectively unless the soils are excavated and treated above ground. Therefore, the high temperatures would likely need to be applied over a period of days depending on the water content of the soils being treated (Iben et al., 1996).

- *In situ* thermal treatment would require the installation of numerous electrodes and/or injection/extraction wells to allow for sufficient coverage. If thermal treatment were applied to the floodplain soils at temperatures sufficient to volatilize or destroy the PCBs (700 to 900 degrees Celsius [°C]), the soils would need to be amended with nutrients or removed/covered with new soil (if vitrified) following treatment to support vegetative growth.

- The effectiveness of *in situ* thermal treatment can be limited by the presence of large inclusions in the area to be treated. Inclusions are highly concentrated contaminant layers, void volumes, containers, metal scrap, general refuse, demolition debris, rock, or other heterogeneous materials within the treatment volume.

- Thermal treatment could vitrify the soils, which would form a glass-like monolithic product. The treated material may not readily support vegetative growth following treatment. If needed, the addition of soil on top of the treated material to support vegetative growth would reduce the available floodplain storage capacity.

Given these problems and potential drawbacks with applying *in situ* thermal treatment to floodplain soils, coupled with the lack of use of this technology full-scale at a similar site, *in situ* thermal treatment of soil has not been retained at this time as a potentially viable remedial option for the Rest of River floodplain soils.

3.5.5 Summary of Evaluation of *In Situ* Treatment Technologies for Soil

Since *in situ* physical treatment (immobilization) has been applied at a limited number of PCB sites, it was subject to secondary screening. However, it was eliminated during the secondary screening because it may be incompatabile with future floodplain uses and vegetative restoration options, may cause flood storage or freeze/thaw issues due to volume expansion during implementation, and is best suited for deeper applications within a relatively small footprint, rather than a potentially large, shallow-depth application such as the Rest of River floodplain soils. *In situ* biological, chemical, and thermal treatment processes were eliminated during initial screening because none of these technologies has been applied full-scale for soils containing PCBs at a site similar to the Housatonic River floodplain and because each has additional implementation issues as described above. Nevertheless, GE will re-evaluate these technologies during the CMS if future information or analyses become available indicating that any of them may prove to be a potentially effective and implementable option for application to the Rest of River floodplain soils.