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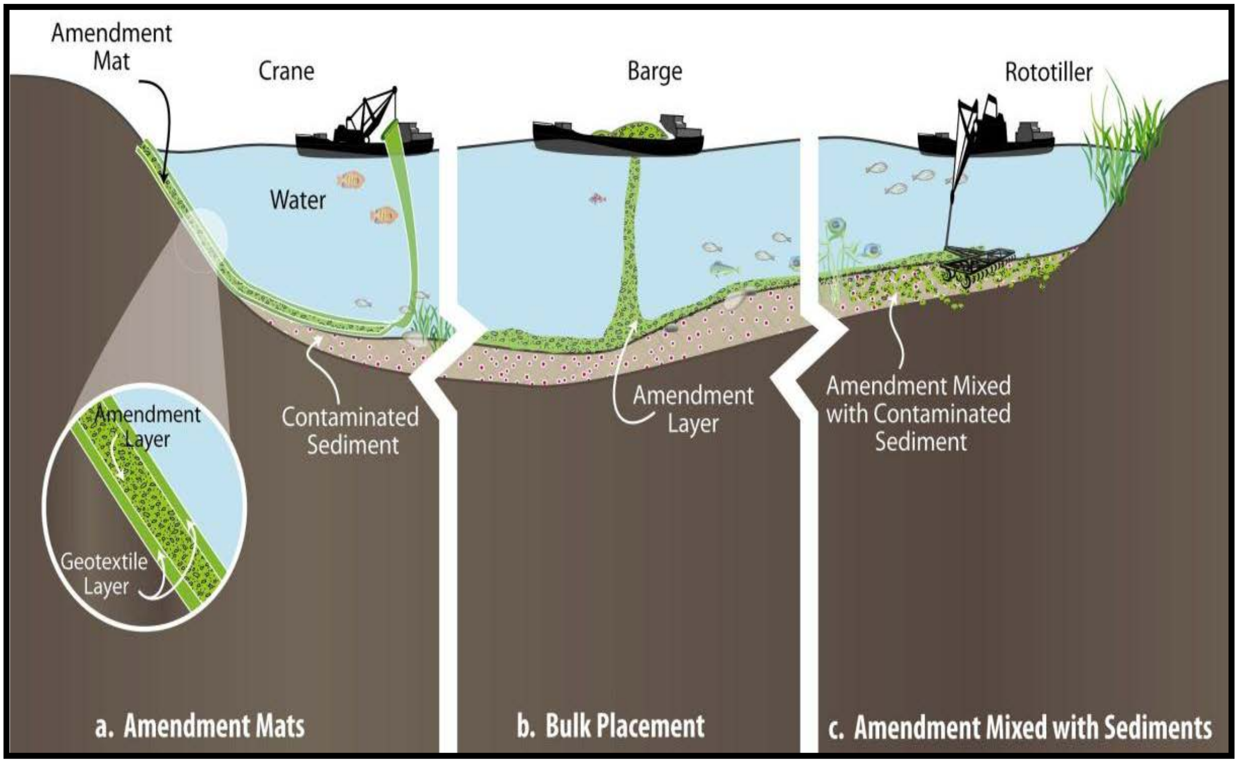
Office of Superfund Remediation and
Technology Innovation

Use of Amendments for In Situ Remediation at Superfund Sediment Sites



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Contents

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1. Introduction

The in situ sequestering or destruction of contaminants has the potential to reduce risks at Superfund sites. These technologies have successfully treated groundwater contamination, but only recently have technologies been developed to treat contaminated sediments. These technologies, referred to as amendments when applied to sediment remediation, are generally placed into or onto the sediment surface layer, into a sand cap, or within a geotextile mat. They can be used as a single remedial approach or in combination with other remedies. The most common amendments, such as activated carbon, Organoclay™, and apatite, are specialized materials that decrease contaminant bioavailability by sorption. Other amendments being considered promote the degradation of contaminants. The appropriate use of these amendments has much potential to limit exposure to contaminants and, thus, to reduce risks.

Contaminated sediments are a significant, widespread environmental issue. As of December 2012, EPA’s Superfund program has selected a remedy at 70 large sediment sites and is evaluating another 50 sites for cleanup. Remedies currently available for addressing contaminated sediments include Monitored Natural Recovery (MNR), enhanced MNR (EMNR), in situ capping, dredging or excavation, and a combination of these approaches. These remedial options all have advantages and limitations for controlling human health and ecological risks associated with contaminated sediment. More information about these remedial approaches can be found in EPA’s Contaminated Sediment Remediation Guidance for Hazardous Waste Sites (www.epa.gov/superfund/health/conmedia/sediment/guidance.htm).

Historically, most sediment remedies have included dredging or excavation as a significant component of the remedy. They also typically rely on MNR to achieve long-term risk reduction, even when not explicitly stated as part of the remedy. Recently, more sites are considering combination remedies where MNR, capping, and dredging are being concurrently selected, depending on conditions in different areas of the sites. Capping leaves contamination in place and is generally intended to isolate the contaminants of concern (COCs). Although traditional sand caps have effectively contained the COCs and prevented exposure of the benthic and pelagic communities, their large thickness can reduce the hydraulic capacity, flood storage, and depth of the water body. They may also be compromised by physical disturbances, gas ebullition (the transportation of contaminants via entrapment in migrating gas bubbles), non-aqueous phase liquid (NAPL) transport, or groundwater advection.

The use of amendments to reduce bioavailability of contaminants by sorption or promote the degradation of the contaminants is a relatively new option for in situ sediment remediation. This innovative technology is being developed and implemented to improve the risk reduction and cost-effectiveness of remedies at sediment sites. Amended caps have the potential to reduce the thickness of traditional caps and to improve their resistance to erosional events and advective transport of COCs by ebullition, NAPL, or groundwater flow. Amendments applied directly to the contaminated sediment may be particularly useful in areas where MNR, caps, or dredging are not likely to be effective in reducing risks.

The purpose of this document is to introduce the most promising amendments for in situ remediation of sediments and summarize some of the information on contaminated sediment sites that have already employed these amendments. This document is not a guidance or design document. The U.S. Army Corps of Engineers (USACE) Engineer Research Development Center is developing a technical guidelines document to provide a detailed guide to implementing in situ remedies, including amendments and a thorough discussion of their merits and limitations (Technical Guidelines for In Situ Sediment Remediation). The main audience for this document is Superfund Remedial Project Managers, but other stakeholders, such as federal, state, and local regulators, site owners and operators, and consultants, may also find it useful.

This document provides information on the state of the practice of the use of amendments for in situ remediation of contaminated sediments, as well as three case studies where these amendments have been used. This document also focuses on the use of amendments either by themselves or in conjunction with a conventional isolation cap or a thin layer cap and EMNR. The amendments discussed are designed to treat hydrophobic organic contaminants, metals, or both. Some of these amendments may also be effective in reducing risks from NAPL.

Amendments for hydrophilic organics (for example: PCE, BTEX, or munitions) are not discussed in this document. In situ technologies, such as in situ chemical oxidation and permeable reactive barriers, are well established for treating groundwater and well documented elsewhere. Additionally, there is less research on the effectiveness of using sediment amendments to remediate such hydrophilic organic contaminants. Information on types of amendments, placement methods, design considerations, modeling, monitoring, performance, and cost are included below. The appendix contains a list of sediment sites where amendments have been used as part of a remedy or as pilot studies, a brief description of the site remedies, and monitoring results.

2. Overview of Amendments for Sediments

Amendments can be introduced in sediments either as part of a cap, or directly into or onto the existing sediment. These two approaches are discussed separately below:

Amended caps. Where conditions preclude the use of a conventional cap, amendments show promise, especially for hydrophobic organic contaminants (HOCs): polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins/furans, and chlorinated pesticides. For example, the addition of amendments to a cap can increase the cap’s effectiveness by 1 to 2 orders of magnitude, as described in more detail later in this report. Amendments may also better achieve design objectives, such as maintaining navigation depths, because these approaches do not reduce water depths the way thicker, conventional caps do. Amended caps work primarily by retarding contaminant transport through the cap and acting as a barrier between the contaminated sediment and the new benthic layer, thus preventing exposure of the benthic and pelagic communities to the contaminants. Amendments can be introduced to a capping layer in a geotextile mat or added to capping materials before or during placement of caps.

Direct sediment amendments. The primary exposure pathway for hydrophobic and bioaccumulative pollutants often involves bioaccumulation in the benthic infauna and subsequent transfer into the aquatic food web. Direct amendment of surficial sediment with sorbents can reduce pollutant bioavailability to the food chain and flux of pollutants into the water column. Amendments can be spread on the surface of the contaminated sediment as a thin layer, intended to be mixed with the sediments through natural processes, or mixed into the surface using equipment similar to a rototiller. The intent in direct application is to change the native sediment geochemistry to reduce contaminant bioavailability without creating a new surface layer or cap. Figure 1 shows examples of various placement methods.

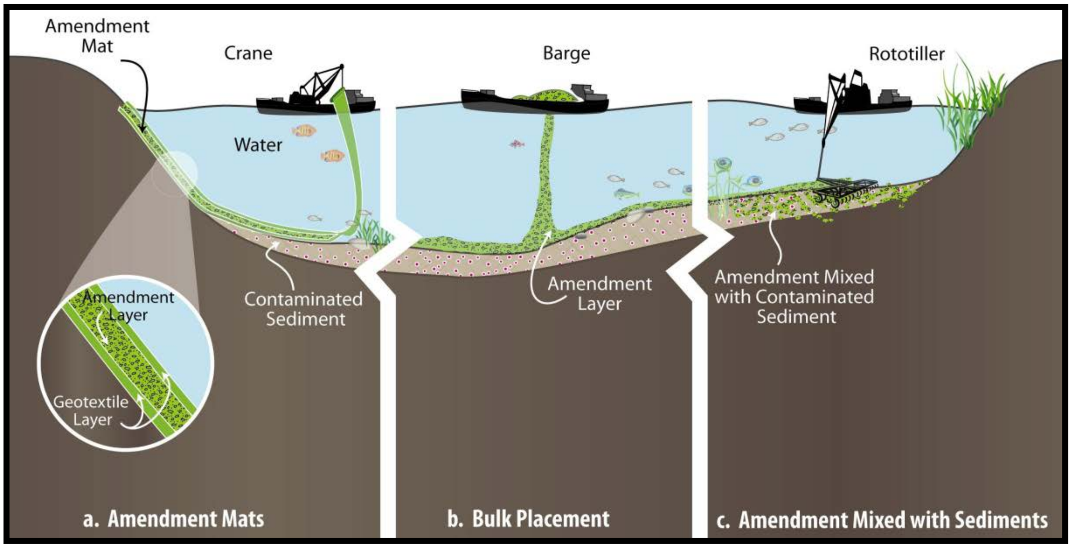

Figure 1: Placement Methods for Sediment Amendments

While amendments show promise, there are concerns and uncertainties that may limit their use in some site conditions. One current concern with using bulk amendments is the difficulty in placing some of these materials accurately in a dynamic, aqueous environment as a result of their potential for entrainment and movement within the water column. The unknown treatment capacity of some amendments, whether applied in bulk or in a mat, may also be a concern, particularly with respect to multiple contaminants and interactions with the natural system. As with other remedial alternatives (such as capping and dredging), the long-term permanence of amendments and their ability to retain contaminants over time are not well understood. Although laboratory tests and models can predict short- and long-term performance, there are few field applications currently in place to evaluate the effectiveness of amendments and to validate the models used. The success of in situ amendments also depends on the level of contamination in new sediment deposits that may form over time. Thus, ongoing source control is critical for the success of any in situ remedy. Additional field applications will increase the understanding of this technology and the key factors affecting its long-term effectiveness.

Currently, most of the amendment applications have been laboratory or pilot-scale (small scale, intended as a test or demonstration of effectiveness) research projects; there are a small number of sites where amendments have been used as demonstration projects or full scale in the field. Site-specific information is provided in the report where available. Mention of trade names or commercial products does not constitute EPA's endorsement or recommendation for use.

3. Amendment Materials

The type of amendment used is dictated by the type of contamination, sediment characteristics, and site conditions. Activated carbon and other carbonaceous amendments are appropriate for sorbing organic contamination, while phosphate additives are useful for binding metals. Properly compounded Organoclays™™ are designed to capture NAPL while maintaining sufficient permeability to permit groundwater advection and gas migration. The effectiveness of some of the amendments, such as activated carbon and Organoclay™, has been demonstrated in a small number of field applications, while other amendments, such as zero valent iron, phosphate additives, and biopolymers, are still in the bench-scale or pilot-testing phase. Even though some of these materials have been used in other environmental applications, such as groundwater and off-gas treatments, there are a limited number of projects and available performance data on their effectiveness for treating contaminated sediments. Table 1 presents examples of amendments, the contaminant group targeted, and the developmental status of each as a sediment treatment technology[1]. Additional information about the full-scale and pilot projects is provided in the appendix.

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[1] For this document, the term "treatment technology" refers to any unit operation or series of unit operations that alters the composition or behavior of a hazardous substance, pollutant, or contaminant through chemical, biological, or physical means so as to reduce toxicity, mobility, or volume of the contaminated materials being treated.

Activated carbon and other carbonaceous amendments are attractive amendments because of their strong sorbent properties. PAHs, PCBs, dioxins/furans, and pesticides are strongly adsorbed by activated carbon (often in a granular form), making them less bioavailable. Adsorption of hydrophobic organic contaminants to activated carbon in sediments is often 10 to 100 times greater than absorption to organic carbon (OC). Organic carbon is generally thought to be the primary sorptive phase for hydrophobic organic contaminants in soils and sediment. Although different parent materials used to create the activated carbon result in variable degrees of sorption, activated carbon has a greater sorption capacity for hydrophobic organic contaminants than other types of carbonaceous amendments under most environmental conditions. Coke breeze, a carbonaceous material formed by heating coal in an oxygen-free environment, may be an inexpensive alternative to activated carbon, but it is less effective at adsorbing organic contaminants in sediments (Murphy and others 2006). Activated carbon, coal, and coke breeze have been used in pilot- and full-scale applications for in situ sediment remediation. In most capping applications, the placement difficulties have been overcome by containing the carbon in a mat or delivering the amendment as a clay agglomerate, such as AquaBlok™. Potential limitations associated with activated carbon include difficulty with placement through the water column (because of its low density and significant air entrapment), stability (it is easily resuspended after bulk placement), and cost. Information regarding the negative effects of activated carbon on benthic organisms is often contradictory, with some field and laboratory studies reporting detrimental effects and others showing no observable detrimental effects. Studies reporting detrimental effects typically note decreases in growth rates or in benthic diversity, but they also report 10 to 100 fold reductions in bioaccumulation and generally conclude that the amendment is a net benefit (for example: Millward and others 2005, Kupryianchyk and others 2011, and Cornelissen and others 2011). Pilot studies for direct sediment amendment applications have broadcast a slurry of activated carbon and water close to the sediment surface (with and without tilling), injected activated carbon into sediment through hollow tines, or delivered the amendment in a pelletized form that breaks up over time, such as SediMite™. Activated carbon in a reactive core mat was selected as a full scale remedy at the St. Louis River/Interlake/Duluth Tar Superfund site, where it was placed as part of a sediment cap.

Organoclays™ are created by replacing the surface cation of bentonite or hectorite with an organic molecule, such as tallow-based quaternary amines (Olsta and Darlington 2005). They are hydrophobic, permeable, and effective at absorbing dissolved hydrophobic organics and immobilizing metals (Knox 2008, Olsta and Darlington 2005). Organoclays™ have also been formulated to create an impermeable layer, but these applications are less useful in sediments because they are vulnerable to gas formation and may cause problems in areas of high groundwater flow. Organoclays™ can potentially control NAPL migration, as they are capable of absorbing two to four times their weight in free-phase product (Reible and Lampert 2008). However, the absorption capacity in the field typically varies between 0.5 and 1.5 times their weight (Reible and Lampert 2008). The absorption of the free-phase product or water, depending on the surface cation replacement, causes the Organoclays™ to swell and can reduce permeability. This loss of permeability must be accommodated in designing an amended cap with Organoclays™. An Organoclay™ with the appropriate surface cation can minimize swelling and maintain high permeability (Olsta and Darlington 2005). Information on the detrimental impacts of Organoclays™ on the benthos is limited. In some cases, Organoclays™ are used as a layer in a cap and are separated from the benthos. However, the use of these clays as the uppermost layer of a cap may greatly reduce the erosion potential of the cap. Organoclays™ may be particularly beneficial when NAPL is present and have been used in both pilot- and full-scale applications to address NAPL and HOCs and metals.

Phosphate additives reduce the bioavailability of metals through adsorption, ion exchange, isomorphic substitution, and precipitation (Olsta and Darlington 2005). The phosphate mineral apatite is most often used for sediment treatment. Apatite yields stable end products, can be placed on contaminated sediment by existing technology, can be mixed with other additives, is readily available, and is non-toxic. Similarly to carbonaceous amendments, there are multiple types of apatite that exhibit different sorption characteristics. Another phosphate additive being studied is phytic acid, a sugar additive (6-phosphate ester of inositol). This additive is applied in a soluble form and precipitates metals in the same manner as apatite (Knox 2008). Although effective at binding metals, phosphate additives do not treat organic contaminants. An important limitation of these amendments is the potential for releasing soluble phosphate and increasing eutrophication. The effectiveness of phosphate additives has been tested with pilot-scale studies but not with full-scale applications.

Bauxite is capable of sequestering many heavy metals, including mercury, arsenic, chromium, cadmium, lead, zinc, and nickel. Its unique surface properties allow bauxite to sequester both cationic and oxy-anionic forms of the metals through a combination of sorption, ion exchange, and precipitation (EPA 2007). A bench-scale study was conducted to evaluate possible effectiveness at the Dodge Pond Site in Connecticut to treat mercury (Gavaskar and others 2005). However, there have been no pilot- or full-scale applications.

Zero Valent Iron can reduce some organic contaminants to less toxic by-products and has been used successfully in permeable reactive barriers (PRBs) for the dechlorination of chlorinated hydrocarbons and the reductive precipitation of chromate in contaminated groundwater (Olsta and Darlington 2005). Laboratory studies conducted at the University of New Hampshire showed that micrometer-scale zero valent iron successfully promoted reductive dechlorination of PCBs in sediments. However, the study also noted that the dechlorinated products may include PCB congeners that are more toxic than the parent congeners and that dechlorination is slower for the larger PCB congeners (Gardner 2004). Additional limitations with zero valent iron may include alterations to sediment geochemistry, passivation of iron by the formation of a thin layer of iron oxide, and the high cost of microscale and nanoscale supported iron. The use of zero valent iron to treat sediments has been limited to bench-scale studies. There have been no pilot- or full-scale applications for in situ sediment remediation.

4. Placement Methods

Amendments can be contained in a mat, applied in bulk onto the sediment surface, mixed in the sediment, added as part of a sand cap, or as a layer within a sand cap (Figure 1). Mats consist of an amendment, or amendments, sandwiched between two geosynthetic layers. These mats allow for accurate placement of amendments with high total organic content and low density that could otherwise become suspended during placement. Synthetic geotextiles also provide a bioturbation barrier, prevent mixing of amendments with underlying sediments, allow a more uniform application of amendments, and reduce erosion. As they are composed of synthetic fibers, they do not easily biodegrade (Olsta and Darlington 2005). These mats are generally covered with conventional capping materials and, if needed, armoring layers to provide physical stability and further isolation. Such amendment mats are commercially available from a limited number of vendors. One such vendor, CETCO, produces mats with typical thicknesses of 6 millimeters (mm) and 11 mm. According to CETCO, typical material loadings are activated carbon – 0.4 pound per square foot (lb/ft^2), Organoclay™ – 0.8 lb/ft^2, and apatite – 0.8 lb/ft^2 (CETCO 2012).

Table 1: Examples of Amendments for In Situ Sediment Remediation

Amendment	Contaminant Group Targeted	Scale
Activated carbon (and other carbon sources)	PAHs, PCBs, dioxins/furans, pesticides[1, 2, 3, 4, 5, 6]	Full[2]
Organoclay™	NAPLs, PAHs, PCBs, metals[1, 3, 7, 8]	Full[9]
Phosphate additives (such as apatite)	Metals (lead) [1, 3, 7]	Pilot[10]
Bauxite	Metals (mercury, arsenic, chromium, cadmium, lead, zinc, and nickel) [11]	Bench[12]
Zero valent iron	Chlorinated hydrocarbons, chromate [3]	Bench[13]
Biopolymers	Metals, organics [7]	Bench[7]
Zeolite	Nitrates, metals (copper, lead, zinc)[3]	Bench[3]

References:

[1] CETCO 2012
[2] Olsta and Hornaday
[3] Olsta and Darlington 2005
[4] Murphy and others 2006
[5] Cho and others 2011
[6] Beckingham and Ghosh 2011
[7] Knox 2008
[8] Reible and Lampert 2008
[9] Ecology and Environment 2008
[10] Horne 2007
[11] EPA 2007
[12] Gavaskar and others 2005
[13] Gardner 2004

Before a mat is installed, it is important to remove rocks, debris, and dead trees from the sediment surface to minimize potential damage to the mat and provide a more even surface for placement (Barth and Reible 2008). Additional factors that affect placement of mats include the type of amendment used in the mat, shoreline accessibility, and the physical nature of the sediment where the mat is placed. Differential settling of the mat could lead to ruptured seams and contaminant migration through the seams. In addition, depending on the amendments and components of the mat, they may not sink readily. Although some amendments enclosed in the geotextiles are buoyant, it is possible to use geotextiles with a higher specific gravity or mix a fraction of sand with the amendment to create a mat that is easier to sink (Olsta and Darlington 2005).

Amendments can be spread on the sediment in bulk using conventional equipment or equipment that has been modified for aquatic use. At the Anacostia River demonstration, apatite was placed using a clamshell bucket on a barge-mounted crane (see the appendix for more information). Silt curtains were used to minimize the migration of cap material because of water movement. Equipment such as submerged diffusers, energy dissipaters, submerged discharge points, and tremies (specialized underwater pipes, typically used for pouring concrete) can be used to apply amendments evenly to a required thickness. Amendments can also be applied in bulk with fine-grained soil or sands to provide better dispersion, uniformity, placement controls, and contact time when the required quantity of the amendment is small. AquaBlok™ and SediMite™ serve as bulk delivery media for granular activated carbon by incorporating it in their formulation. Although historically AquaBlok™ particles were clays designed to expand and create an impermeable sediment cap, a permeable cap can also be designed using different AquaBlok™ amendments (AquaBlok™ 2008). SediMite™ is designed to disintegrate, slowly releasing the amendments, which can be mixed into the sediments by benthic organisms (Menzie and Davis 2009).

As with conventional caps, amendments placed in a slow and uniform manner will reduce the potential for resuspension of the material or sediment into the water column, promote even distribution, and allow the material to accumulate in layers that may minimize mixing with the underlying contaminated sediment and contaminant dispersion. Using amendments with an equal or lower density than the underlying sediments may also minimize contaminant dispersion and mixing during placement (USACE 1998). When used as a direct sediment amendment, rather than as an amended cap, mixing of amendments by benthic organisms is desired to incorporate the amendment into the sediment. In such cases, mixing may be promoted by injecting the amendment into the sediment with hollow tines or using equipment similar to a rototiller.

The current, energy, and depth of the waterway may also influence the type of placement method, especially for bulk materials that may become entrained in the water column and therefore be difficult to place accurately. Generally, a longer descent through the water column results in a thinner layer of amendments over a larger area. Delivery may need to be directed closer to the sediment surface in these situations. Slope of the waterway bottom may affect the placement of bulk material, as flat bottom and shallow slopes allow material to be placed more accurately. Currents can affect dispersion during amendment placement, while bottom currents can generate shear stresses on the materials. Depending on the hydrodynamics of the water body, the amendment may need to be protected from erosion. Protection may be accomplished by placing a sand or gravel armoring layer on top of the amendment. The type of material selected for this uppermost layer may also depend on habitat at the site (EPA 2005).

5. Design Considerations for Amendments

At Superfund sites, the most appropriate remedy is chosen after site-specific data and the nine remedy selection criteria in the National Contingency Plan (NCP) have been considered. All sediment remedies are designed to meet the remedial action objectives and cleanup levels defined in final decision documents for the site. These objectives may include contaminant concentrations in surficial sediment, pore water, surface water, and biota. As with all sediment remedies, short-term and long-term monitoring plans are needed to evaluate how well the remedy achieves these goals. It is also important to identify and adequately address the source of sediment contamination for all remedial alternatives. If the sources are not adequately controlled, they can limit the effectiveness of the remedy. Unlike other remedies, amendments applied to the surface sediments have some potential to adsorb contamination from continuing sources as well as from sediment sources. This ability to treat continuing sources is limited by the sorptive capacity of the amendment but may be useful for reducing risk while continuing sources are being addressed. Another unique benefit of amendments applied in bulk is that, once they are applied to and incorporated in the sediments, they will be transported with the sediments and continue to strongly sorb the contaminants. Erosion may expose contaminated sediments that have not been amended, but at sites where the contaminants are concentrated in the surface sediments, amendments may be useful for reducing risk.

There are numerous factors that affect both the design and performance of a remedy that uses in situ amendments. These factors include the fate and transport mechanisms of sediments, contaminants of concern, amendments, geotechnical issues, and site-specific conditions (including the potential for erosion and bioturbation). Many of these factors also apply to the design of conventional caps. The USACE is currently developing detailed technical guidelines on the use, design, and performance of in situ caps, including amendments and amended caps (Technical Guidelines for In Situ Sediment Remediation). Additional information regarding design considerations can be found in several EPA resources provided in Information Box 1. The most critical factors for selecting and applying amendments for in situ sediment remediation are presented below.

Information Box 1: Links to EPA Sediment Resources

Clu-In Sediments Web Site:
www.cluin.org/issues/default.focus/sec/Sediments/cat/Overview/

Superfund Sediment Resource Center:
www.epa.gov/superfund/health/conmedia/sediment/ssrc.htm

Guidance for In-Situ Subaqueous Capping of Contaminated Sediments:
www.epa.gov/grtlakes/sediment/iscmain/index.html

Contaminated Sediment Remediation Guidance for Hazardous Waste Sites:
www.epa.gov/superfund/health/conmedia/sediment/guidance.htm

Principles for Managing Contaminated Sediment Risks at Hazardous Waste Sites:
www.epa.gov/superfund/policy/remedy/pdfs/92-85608-s.pdf

5.1 Fate and Transport/Migration Pathways

Transport of contaminants at sediment sites is driven by physical movement of the contaminated sediments and by movement of dissolved contaminants into or out of the sediment. While caps may be effective at controlling the physical movement of sediments, amendments — either alone or in caps — may better control the movement of dissolved contaminants into the surface water (for example, by contaminant migration via advection, diffusion, or gas migration). Advection can be either (1) short-term, resulting from consolidation during or after cap placement and may occur through or around the cap, or (2) long-term, if there is an upward hydraulic gradient resulting from groundwater flow (upwelling), gas ebullition, or tidal fluctuation. Consolidation- or groundwater-induced advective forces may mobilize contaminants from the sediments into and possibly through the cap. Less consolidation, and thus less contaminant flux, may occur as a result of mat or bulk amendment placement because mats and amendment layers are generally thinner and lighter than conventional sand caps. When an amendment layer is used in a mat, it is necessary to consider preferential seepage or flux through seams between mats in the fate and transport analysis (Barth and Reible 2008). Another potential issue with using mats in locations with significant groundwater flow or gas ebullition is the potential for the mat to be lifted. The permeability of the mat and the method of anchoring the mat are important aspects of the remedy design.

The available sorption capacity of an amendment can greatly reduce both the rate the chemicals move through the cap and the bioavailability of chemicals in amended sediments (EPA 1998). Laboratory studies indicate that a centimeter (cm) thick layer of activated carbon or other carbon material beneath a sand cap can effectively mitigate contaminant flux of PCBs from sediment (under laboratory-simulated diffusion and advection dominated conditions) and isolate them from the bioactive region of the sand cap for decades to centuries (Murphy and others 2006). Another laboratory study evaluated the effectiveness of apatite, Organoclay™, and biopolymers in addressing metals, PAHs, and PCBs. The resulting models of amended caps predicted that apatite and Organoclay™ would delay contaminant breakthrough into the overlying surface water via diffusion by hundreds of years or more compared with sand caps (Knox 2008). In a laboratory study of amended sediments, activated carbon was added to sediment samples with a range of organic content and PCB concentrations. Results showed PCB concentrations in pore water decreased by 69 to 97 percent, and bioaccumulation of PCBs in an oligochaete (a worm) decreased by 42 to 85 percent after 28 days of exposure (Sun and Ghosh 2008).

Data obtained from field studies also show similar performance. At the Grasse River site, where activated carbon was used to amend the sediments and reduce the bioavailability of PCBs to benthic organisms, results indicated that PCB concentrations in benthic worms decreased by approximately 63 to 99 percent. Less hydrophobic congeners (Log K_{OW} [2] less than 6) decreased by more than 63 percent in the first year and remained low over 3 years. More hydrophobic congeners decreased gradually, but reached similarly reduced levels 3 years after they were put in place (Beckingham and Ghosh 2011). Similarly, results at the Hunters Point site, where activated carbon was used as a sediment amendment, showed (1) reductions in the availability of PCBs to water and biota, and (2) reductions in bioaccumulation without adversely affecting the natural benthic community or releasing PCBs into the overlying water (ESTCP 2009). Five years after activated carbon was applied to the sediment at Hunters Point, total PCB uptake in passive samplers was reduced by 73 percent, with greater reductions in the bioavailability of the less chlorinated congeners relative to the more chlorinated congeners (Cho and others 2011). Additionally, analysis of the coke breeze mat-amended cap at the Anacostia River shows a 3 to 4 order of magnitude decrease in PAHs between the contaminated sediment and the sand overlying the coke breeze mat, demonstrating that the coke efficiently isolated the PAHs from the surface of the cap. Analysis of the AquaBlok™-amended mat from the same study shows similar efficiencies in isolating PAHs and also shows reductions of several orders of magnitude for a variety of metals (Horne Engineering Services 2007).

Gas migration, another potential contaminant transport pathway, can be a factor at sites with sediments of high organic content and persistent anaerobic conditions. These gases can travel through the sediment or sand cap via advective and diffusive transport (EPA 2005). Ebullition enhances diffusive transport and provides preferential pathways for groundwater and NAPL transport of contaminants. Gas can also generate significant uplift forces and affect the physical stability of an amendment mat or layer (particularly one with low permeability) or carry contaminants through the amendments and potentially into the overlying water column.

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[2] Log Kow = The octanol/water partition coefficient, which is used as a measurement of a compound's bioaccumulation potential.

Amended cap designs may reduce the impact of gas migration by including vents with activated carbon filters to treat contaminants transported by the gas.

5.2 Amendment Characteristics

The key characteristics of amendments to consider for in situ sediment remediation are the sorption capacity, the sorption mechanism, and the contaminants targeted. It is also important to know the grain size distribution, specific gravity, buoyancy, and porosity of the amendment. Key properties of the contaminated sediments to be considered in designing the remedy, in addition to those mentioned for the amendment, are the organic content and the hydraulic conductivity. It is also critical to understand the potential for deposition onto and erosion of the sediment bed. The USACE is currently developing a technical guidance for assessing deposition and erosion in sediments (Technical Guidelines on Performing a Sediment Erosion and Deposition Assessment [SEDA] at Superfund Sites).

A study by Olsta and Darlington (2005), consisting of laboratory column testing and modeling, shows that for PCBs the sorption capacity of a thin layer of activated carbon is more than 100 times greater than the sorption capacity of sand or soil, assuming the fraction of natural organic carbon in the sand or soil equals 3.8 percent. Based on these results, a 1-cm-thick amendment layer of activated carbon and a 1-meter-thick cap of sand have similar potentials for chemically isolating contaminated sediments. However, project-specific conditions, such as bioturbation, will require a thicker cap to guarantee isolation. In a study by Murphy and others (2006), the physical properties of carbonaceous amendments were measured in the laboratory and then used in a numerical model to predict migration of 2,4,5-PCB in a 50-cm contaminated sediment layer capped by a 1.25-cm amendment layer and a 15-cm sand layer. The model predicted that sand caps amended with a 1.25 cm thick layer of activated carbon, coal, or organic-rich soils would isolate the PCBs for centuries when there was no groundwater advection. Estimated isolation times decreased to decades for coke and soil in areas with groundwater advection of 1 cm/day, while the activated carbon layer remained effective for centuries. Assuming a groundwater velocity of approximately 10 cm/day, which may be too fast to allow equilibrium partitioning, the numerical model predicted that activated carbon would isolate PCBs for about 200 years. The study also concluded that effective porosity, dispersivity, and bulk density had little effect on cap performance; the sorption strength of the amendment was the primary determinant of cap performance. Long isolation times afforded by sorbent-amended sediments could allow time for inherently slow natural degradation processes to further mitigate PCB flux (Murphy and others 2006). Although laboratory and modeling studies can predict performance, their results often vary from what actually occurs in a natural setting. Results from recent field studies, such as those discussed in Section 7, show promising reductions in the bioavailability and biotic uptake of sediment contaminants. Uncertainty in the long-term effectiveness of in situ amendments will only be reduced as these early studies are monitored into the future.

If groundwater upwelling is expected to be significant (more than about 1 cm/day), the hydraulic conductivity of the conventional or amendment materials to be placed on or in the sediment cap impacts remedial design (EPA 2005). Amendment materials, particularly clay amendments, may restrict groundwater and could result in uplift of the amendments or create preferential pathways through the amendment layer (Mutch and Kearney 2003,). Groundwater may also be diverted around the amendment layer and potentially lead to contaminant migration (Barth, Reible, Bullard 2008). Migration is of particular concern for contaminants that are less hydrophobic (log K_{OW} below 3). Sediment amendments are unlikely to be effective in treating highly water soluble contaminants. These factors will influence the effectiveness of the amendment and are important considerations in areas with significant groundwater flow, uncontrolled sources, or NAPL (EPA 2005).

The contact time between the amendments and groundwater or pore water may be short because mats or surface layers mixed with amendments are relatively thin. A short contact time is often adequate because of the high hydrophobicity of the most common hydrophobic organic contaminants in sediments, such as PCBs, PAHs, and dioxins. Depending on the solubility of the contaminants, the flow rate of the groundwater, and the kinetic rate of sorption to the amendment, the thickness of the amendment layer may need to be adjusted to ensure the contaminants are adequately sequestered. Amendments also have finite sorption capacity; understanding advective and diffusive fluxes is critical to ensure that treatment capacity is adequate to address the risks posed by the COCs. Although the amendment layer or mat is designed to provide sufficient capacity, on-going sources may compromise the remedy. The replenishment or replacement of the layer or mat may be necessary to ensure effectiveness of the remedy, which may disturb the benthic community.

5.3 Computer Modeling

Computer modeling at sediment sites may assist in site characterization, risk assessment, and evaluation of remedial alternatives. Models have various inputs and associated uncertainties. EPA recommends use of a modeling expert to determine if a model should be used and which models are most appropriate (EPA 2005). Additional information about the use of modeling at sediment sites is available in the Sediment Assessment and Monitoring Sheet (SAMS) #2: "Understanding the Use of Models in Predicting the Effectiveness of Proposed Remedial Actions at Superfund Sediment Sites" at www.epa.gov/superfund/health/conmedia/sediment/pdfs/Modeling_Primer.pdf.

Chemical isolation modeling can be used to predict expected changes associated with the application of amendments, such as changes in chemical flux to the overlying water or into the sediment surface layer. However, gas migration, factors relating to gas ebullition, and tidal effects are not typically included. Models to evaluate the effectiveness of amendments range in complexity but are typically vertically oriented, one-dimensional, and include transient and steady state conditions (Barth and Reible 2008). Some of the input parameters and variables include the thickness or mass of the amendment, sediment density, sediment organic content, groundwater flow, and contaminant partitioning coefficients. Physical modeling is typically used to predict the degree of (1) consolidation in capping materials and underlying sediments, and (2) erosion potential in the capped or amended area (including erosion from flows, waves, and vessel traffic). Three of the more commonly used models for documenting the effects of caps and amendments are the USACE Recovery Model, the USACE CAP Model, and Dr. Reible's Analytical Cap Active Layer Model (www.caee.utexas.edu/reiblegroup/downloads.html). The USACE models are available at http://el.erdc.usace.army.mil/products.cfm?Topic=model&Type=drgmat.

6. Remedial Action Monitoring

EPA guidance recommends monitoring of short- and long-term remedy performance and risk reduction for all Superfund sites where a remedy has been implemented. Monitoring of remedies that involve amendments typically includes monitoring to evaluate (1) whether reductions in chemical toxicity, bioavailability, or fluxes have been achieved and maintained, and (2) evidence of contamination on the surface layer. Monitoring amended caps also should evaluate the long-term integrity and stability of the mat or amended cap. The use of amendments may require an intensive monitoring effort during and shortly after placement operations and immediately after unusual events (for example, severe storms), with a declining level of effort in future years if the remedy is performing as designed (EPA 2005). Examples of monitoring methods are listed in Information Boxes 2 and 3. A database of sediment monitoring tools developed by the Space and Naval Warfare Systems Center under the Navy's Environmental Sustainability Development to Integration program is available at www.israp.org/.

Since amended sediments and amended caps are intended to have long design lives, periodic maintenance, in addition to monitoring, may be necessary. Although studies of pilot- and full-scale amendment based remedies indicate strong performance over 1 to 5 years, the performance of amendments over decades has not been evaluated. The lifetime of amendments may be limited either by the sorption capacity of the amendments or by their deterioration. The amendments should be designed to allow adequate time for natural recovery processes to occur, limit maintenance needs, and minimize benthic disruption.

Information Box 2:
Construction Monitoring

Goal: Determine if cap or amendments are placed properly and assess impacts to water quality and downstream areas.

Methods:
- Bathymetric surveys
- Sediment coring
- Sediment profiling camera
- Contaminant resuspension monitoring
- Total suspended solids monitoring
- Visual aids (viewing tube or diver observations)

Monitoring during placement of amendments ensures design specifications and proper installation are achieved and placement operations do not cause unacceptable adverse

Information Box 3: Performance Monitoring

Goal: Determine if the remedy is performing as intended, and determine if the contaminant exposures and corresponding risks are reduced to acceptable levels. This is critical to determining if RAOs have been, or are expected to be, achieved.

Methods:
For Amended Caps or Amended Sediments:
- Passive sampling of porewater
- Seepage meters
- Sediment coring
- Surface water quality monitoring
- Sediment traps
- Sediment profile imaging
- Tests of toxicity to invertebrates
- Tests of bioaccumulation in benthos
- Fish tissue concentrations

Specific to Caps:
- Gas flux chambers
- Inclinometers
- Bathymetric and side-scan sonar surveys
- Sedflume analysis

effects to the water body. Methods for monitoring include bathymetric surveys, sediment cores, sediment profiling camera, and contaminant resuspension monitoring. For some sites, visual observation in shallow waters using a viewing tube or diver observations can also be useful. Bathymetric surveys and coring were conducted at the Anacostia River demonstration to measure cap and mat thickness. Water column monitoring of suspended sediments and COCs during placement of amendments is helpful in assessing sediment and contaminant movement. Concentrations of suspended solids can be measured using grab samples from the water column or using acoustic Doppler current profilers. Total suspended solids measurements may include capping material stripped during placement in addition to contaminated sediments and do not necessarily indicate resuspension of contaminated sediment (Lyons and others 2006). Total suspended solids can be measured and used in conjunction with water samples analyzed for contaminants to distinguish between the types of particles present.

As with conventional capping remedies, monitoring is typically conducted before and after placement to evaluate whether sediment cleanup levels have been reached and whether remedial action objectives are or are expected to be achieved. The type and extent of monitoring depend on the objectives of the cap. More details on the monitoring of in situ amendments will be provided in the USACE technical guidelines document for in situ remedies currently in development.

7. Recent Applications of Amendments for Sediments: Case Studies

The amendments discussed above are at various stages of development and implementation. The appendix to this report summarizes the pilot- and full-scale applications that are under way or completed. The most common types of amendments used are activated carbon and Organoclay™. Most of these applications address PCBs and PAHs, which are common contaminants in sediment. Three sites where amendments have been applied either as a remedy or for a pilot study are discussed below. The Grasse River, Spokane Upriver Dam PCB, and McCormick & Baxter Sites were included here because of the availability of monitoring data and the representative nature of the chosen amendments. Data on the effectiveness of amendments are limited because of the small number of field applications, the length of time necessary to assess long-term effectiveness, and, in some cases, the lack of monitoring data. Available information is presented; also some of the data presented here were obtained from project managers, and were not in the public record during development of this document.

7.1 Grasse River Site, Massena, New York

The Grasse River Superfund Site, located in New York State near the St. Lawrence River, was contaminated with PCBs by the activities of a local aluminum smelter. In the early 1900s, the lower Grasse River was dredged to accommodate the needs of a nearby hydro-power plant. Today, the river is generally flat-bottomed and 10 to 25 feet deep. This section of the river is depositional, on average, and currently has a deposition rate of approximately 1 cm/year. Consumption of fish that have accumulated PCBs from these contaminated sediments is the primary driver of risk for humans (Alcoa 2011).

A pilot study at this site used activated carbon to reduce the bioavailability of PCBs to benthic organisms. In the fall of 2006, activated carbon, derived from both bituminous coal and coconut shells, was applied to the sediment surface over a 0.5-acre pilot area (Oen and others 2012). The activated carbon was either mixed mechanically into the sediments or left undisturbed, allowing the benthic organisms to incorporate it into the sediment. The amendment was mixed using a rototiller for one test area and a tine-sled at another. Water quality monitoring conducted during

Grasse River Site Characteristics:

- COC: PCBs
- Amendment: granular activated carbon
- Placement Method: (1) Rototiller with rotors, (2) Tine Sled, and (3) Rototiller without rotors
- Design: Addition of activated carbon dose of 2.5 percent of sediment. Placement methods 1 and 2, the sediments and activated carbon were mixed; method 3 was unmixed.
- Construction Complete: Fall 2006
- Cost: Not Available
- Results: 1 year after construction, approximately 72 to 94 percent reduction in PCB concentrations in benthic worms and 63 to 99 percent reduction after 3 years of treatment.

placement indicated no measurable changes in water column PCB concentrations, which remained below detection limits (0.065 microgram per liter [µg/L] or part per billion [ppb]) at locations upstream, local, and downstream. A slight turbidity increase was noted but concentrations remained below the action level (25 nephlometric turbidity units above background). Data collected in 2006 (after placement) and 2007 showed that activated carbon was applied at or above its target dose of 2.5 percent, with the exception of small-scale variability. The applied activated carbon remained in place over 3 years of monitoring. Biological monitoring conducted before and 1 year after activated carbon placement included ex situ laboratory bioaccumulation studies and in situ cage deployment. Those results showed PCB concentrations in benthic worms decreased between 72 and 94 percent (Alcoa 2007, Beckingham and Ghosh 2011). Three years after the activated carbon placement, aqueous equilibrium concentrations were 95 to 100 percent lower than the reference contaminated site and more than 93 percent lower than the pre-treatment concentrations. Bioaccumulation in benthic worms was reduced by 63 to 99 percent in laboratory exposures and 62 to 93 percent in caged exposures. Measurements of individual PCB congeners over 3 years indicate that activated carbon amendments decrease the bioavailable fraction of less hydrophobic congeners (Log K_{OW} below 6.0) by 90 percent within a year. Concentrations of the more hydrophobic congeners decreased gradually and reached 90 percent reductions in benthic worms after 3 years (Beckingham and Ghosh, 2011).

7.2 Spokane River, Upriver Dam PCBs Sediment Site, Spokane, Washington

The Spokane River, Upriver Dam PCBs Sediment Site, located in eastern Washington State, covers 3.5 acres directly behind the Upriver Dam in the City of Spokane and is a state-lead site. Consumption of PCB-contaminated fish is the primary driver of risk. Measured sediment concentrations of PCBs were as high as 1,430 ppb (micrograms per kilogram [µg/kg] dry weight). The Washington State Department of Ecology issued a fish consumption advisory recommending that no fish from this location be consumed (State of Washington 2011). An amended cap, using coal as the carbonaceous amendment, was constructed in fall 2006 to sequester PCB contamination. A minimum of 1,300 tons of coal was necessary to cover this area with a 4-inch thick coal layer. An additional 780 tons was applied to compensate for uneven distribution or losses from currents or placement techniques. Before coal was put in place at the site, a pilot study was conducted on various placement methods. Results showed a more even distribution was achieved when the coal was released just above the water surface rather than just above the sediment surface. The coal layer was covered with a 6-inch sand layer followed by a 3-inch gravel layer. Water quality was monitored during amendment placement, and no results that exceeded water quality standards were observed during construction. Piston core sampling and bathymetric surveys were conducted after placement. Coring verified that the minimum thickness of 4 inches was achieved for the coal layer; the average was 6.3 inches (Anchor 2007). The first post-construction monitoring event was conducted in fall 2008 and included bathymetric surveys, collection of sediment cores

Spokane River, Upriver Dam PCBs Sediment Site Characteristics:

- COC: PCBs
- Amendment: Coal
- Placement Method: A long reach excavator released the cap amendments above the water surface and allowed them to settle through the water column.
- Design: 4 inches of coal covering the contaminated sediments, 6 inches of sand over the coal, and 3 inches of gravel over the sand.
- Construction Complete: Fall 2006
- Cost: $1,578,000 (estimated in the draft Clean-up Action Plan for the entire remedy)
- Results: By the fall of 2008, consolidation and sediment deposition had occurred. Total PCBs were below detection limits in the sand and coal layers of the cap, indicating that the contaminated sediments were effectively isolated by the cap.

and surficial sediment samples, and visual observations. Total PCBs were below detection limits in the sand and coal layers, indicating that the cap is efficiently isolating the PCB contaminated sediment (Anchor 2009). Additional information about this site and project is available at https://fortress.wa.gov/ecy/gsp/Sitepage.aspx?csid=4213 and in the appendix.

7.3 McCormick & Baxter Former Creosoting Company Superfund Site, Portland, Oregon

The McCormick & Baxter Superfund Site is located on the Willamette River, in Portland, Oregon. Wood treatment operations between 1944 and 1991 have contaminated the sediments with PAHs, creosote, diesel, pentachlorophenol, and a variety of heavy metals. PAH contamination is extensive; the depth of contamination for PAHs is up to 80 feet below the sediment surface. Direct contact with and ingestion of contaminated media (sediments, groundwater, and soils) are the main drivers of risk at this site.

The sediment remedy at this site consists of (1) 23 acres of a 2- to 5-foot-thick sand cap with armoring, including 600 tons of bulk granular Organoclay™ placed over the active creosote seep areas, and (2) 25,000 square feet (0.6 acre) of Organoclay™ reactive core mat placed over nearshore areas with ebullition-induced creosote sheens. The bulk Organoclay™ was placed in 2004, covering 20,000 ft^2 (0.5 acre), and the Organoclay™ mats were deployed in 2005 to cover 3 areas of the sediment cap where ebullition-induced sheen was observed (GSI 2007). Since fall 2005, post-construction monitoring has been conducted semi-annually (in spring and fall). Monitoring included periodic multi-beam bathymetry and side-scan sonar surveys, visual and diver inspection of the cap, crayfish tissue sampling, and monitoring of surface water, inter-armoring water and sub-armoring water from 22 locations within the 23-acre footprint of the sediment cap (ODEQ and EPA 2007). Additional activities to monitor the bulk Organoclay™ and Organoclay™ mat were conducted between 2006 and 2008, including collection of sediment cap and Organoclay™ cores, Organoclay™ mat samples, sheen, surface water, and pore water samples. The samples of Organoclay™ and Organoclay™ mats (after they had been in place for 2 and 4 years) were tested for available sorption capacity, water content, permeability, and percent hexane extractable material to determine to what extent the Organoclay™ had absorbed NAPL and the potential for further NAPL retention. In addition, flux chambers were placed over ebullition pathways where gas and water were monitored to assess the significance of ebullition as a contaminant pathway through the sediment cap. Strength of the bulk Organoclay™ was also measured to assess structural integrity. Activities conducted since the mat was put in place in 2005 also included installation of additional mats as needed.

The mean pore water concentration of total carcinogenic PAHs in 2005, measured at the interface of the contaminated sediment and the sand cap, was 0.2 µg/L; in the surface water, the mean concentration carcinogenic PAH was 0.04 µg/L. Pore water concentrations at the bottom of the cap decreased steadily through 2010 when the mean pore water concentration of carcinogenic PAHs was 0.02 µg/L. In 2010, all PAH concentrations in the cap were below the National Recommended Water Quality Criteria (NRWQC), with the exception of chrysene. At one sampling location, the chrysene concentration was 0.035 µg/L compared with an NRWQC of 0.018 µg/L, but was below the NRWQC at all other sampling stations (Hart Crowser and GSI 2011). Sheen, surface water, and pore water samples, as well as sediment cap cores, collected in 2007 and 2008, were used to determine whether the sheen observed in the summer/fall periods were potentially caused by NAPL penetrating the sediment cap

McCormick & Baxter Former Creosoting Company Site Characteristics:

- COC: PAHs, creosote, and NAPL
- Amendment: Organoclay Reactive Core Mat along the beach head and bulk Organoclay over the NAPL hotspots.
- Placement Method: The reactive core mat was deployed using a barge and crane, while the bulk Organoclay was placed from shore using a backhoe.
- Design: 1 foot of sand above the contaminated sediments, 1 foot of Organoclay over the sand, 4 inches of gravel over the Organoclay, and 10 inches of rock armor over the gravel.
- Construction Complete: Bulk placement - 2004, reactive core mat placement – 2005.
- Cost: The total cost is not available. The reactive core mat cost was $2 per square foot.
- Results: Monitoring in 2006 indicated that the Organoclay had similar sorptive capacity as fresh Organoclay. No significant signs of NAPL migration and no decrease in permeability were observed. Bubble migration was observed but no NAPL was associated with the gas bubbles.

(Ecology and Environment 2008, GSI and Hart Crowser 2008). The sheen samples did not differ significantly from nearby surface water samples (approximately 5 feet away from collocated sheen samples). Pore water and sediment cap cores showed no evidence of NAPL entering or penetrating the sediment cap and total petroleum hydrocarbons were only detected in one of six samples in a location where PAHs were not detected. The Organoclay™ at this site continues to have similar sorption capacity to water-saturated fresh Organoclay™ and retains sufficient permeability to allow for groundwater transport through the sediment cap. Using flux chambers, the calculated rate of ebullition over the top of the Organoclay™ was 2.9 liters per square meter per day (liters/m^2/day), while the rate outside of the Organoclay™ footprint where residual creosote is known to be present in the native sediment was calculated to be between 0.02 to 0.09 liters/m^2/day (Hart Crowser and GSI 2009). While the high rate of ebullition over the bulk Organoclay™ was not expected, it does not appear to be a significant contaminant pathway affecting the sediment cap performance.

8. Cost

Available cost data for amendments are limited and often do not include installation costs. Table 2 shows total material cost estimates for several amendments based on the Anacostia River demonstration. According to the reactive core mat vendor, CETCO, costs are approximately $2.50 per square foot for mats with activated carbon and $2.00 per square foot for Organoclay™. In addition, based on the Anacostia River demonstration, construction costs for the large-scale application (1,000 acres) were estimated to be $2.80 per square foot plus the cost of materials. The principal costs within this estimate include monitoring costs ($1.10 per square foot) and construction costs for cap placement ($1.10 per square foot). The costs of bulk activated carbon is about $1.00 per square foot, assuming a typical application of 5 percent activated carbon dry weight to the top 10 cm of sediment. For activated carbon applied using SediMite™, the price is about $2.00 per square foot (Menzie-Cura and Associates).

Table 2: Estimated Material Costs for In Situ Sediment Amendments

Cap Type (thickness)	Material cost ($ per square foot in 2005)
Apatite (6”)	$3.10*
Sand (6”)	$0.45*
AquaBlok™ (4-6”)	$3.00*
Reactive Core Mat with coke breeze (0.5”)	$1.11
Reactive Core Mat with activated carbon (0.5”)	$2.00
Reactive Core Mat with bulk iron (0.5”)	$1.25
Reactive Core Mat with 10% nano-iron (0.5”)	$3.62
Bulk Activated Carbon+	$1.00
SediMite™ Activated Carbon+	$2.00

References: Reible, Constant and Zhu 2005; Menzie and Cura Associates
RCM: Reactive Core Mat
*Excludes shipping costs
+Assumes a typical dose of 5 percent AC dry weight to the top 10 cm of sediment, which is about 1 pound per square foot.

9. Ongoing Research and Development

The EPA, Navy, USACE, Department of Defense’s Environmental Security Technology Certification Program (ESTCP)/Strategic Environmental Research and Development Program (SERDP), and many others are actively involved in developing and testing amendments and placement processes. Several universities are conducting research with amendments or application techniques through the Superfund Research Program under the National Institute of Environmental Health Sciences - National Institutes of Health.

In addition to the amendments discussed above, there are a variety of amendments used for treating other contaminated media (soil and groundwater) that may also be applicable for contaminated sediments. These materials include manganese and iron oxides, alumina, magnetite and substrates containing reactive thiol groups for the removal of mercury from liquid media, and silica for removal of heavy metals from liquid media (Dong and others 2000, Melamed and

Benvindo da Luz 2006, Pacific Northwest Laboratory 2009, Spark and others 2005). In addition, activated carbon can be impregnated with various compounds to enhance its treatment capabilities. For example, activated carbon mixed with zero valent iron and palladium has the potential to degrade PCBs through dechlorination, thereby reducing their bioavailability, but this mixture has been tested on PCBs in sediments only in the laboratory (Choi 2009). There have been no studies on using impregnated activated carbon materials for sediment remediation.

Some additional amendments being developed or adapted to sediments include biopolymers and zeolites. Biopolymers are naturally occurring materials that can bind metals and organics. When the polymers are cross-linked, they resist biodegradation. They have a plugging effect (increasing the shear strength of porous media to resist erosion), can be injected into sediments, and are economical and non-toxic. One biopolymer evaluated in bench-scale studies is chitosan (Knox 2008). Zeolites are porous crystalline aluminosilicates that can be natural or synthetic. They are used commercially for their adsorption, ion exchange, molecular sieve, and catalytic properties. They have been used in water treatment for the removal of nitrates and metals (Olsta and Darlington 2005). However, their applicability for use as in situ sediment capping material is speculative. There have been no pilot- or full-scale applications to test the longevity and efficiency of biopolymers or zeolites as amendments.

A new method for placing amendments into contaminated sediments is being investigated by researchers at the Missouri University of Science and Technology. This method adapts existing water jet technology to inject the amendment into the sediment. Under laboratory controlled conditions, powdered activated carbon was injected into columns of PAH-contaminated sediment. By varying the pressure and nozzle diameter of the water jet and the duration of the injection, this study was able to place the powdered activated carbon at a specified depth in the sediment column up to 30 cm, with minimal resuspension of the contaminated sediment. Injections of 9.5-seconds duration placed 3 percent powdered activated carbon at a maximum depth of 30.5 cm, with an average powdered activated carbon concentration of 14 percent between 0 and 27 cm. Solid-phase microextraction (SPME) measurements of phenanthrene indicated more than 95 percent reduction in the pore water concentrations after the injection. This method may be useful at locations where the contaminated sediment is buried by cleaner sediment or where resuspension caused by rototillers or tine sleds would be unacceptable. However, this method has been tested only in the laboratory, and challenges remain to adapting the commercially-available equipment to this method (Redell and others 2011).

Available data suggest that the use of in situ amendments is a feasible remedial option at some sites. However, limited data are available on the long-term effectiveness and stability of amendments because of the low number of installed projects and the lengthy timeframe required for monitoring. As more data become available, it will be easier to assess the long-term effectiveness of amendments at future sites under a range of site conditions. In addition, limited field information is available about potential threats to mat integrity, such as gas ebullition, ice, and benthic organisms. There are also limited pilot-scale applications or field studies in high-energy waterways, marine sediments, and colder environments that experience freeze/thaw cycles (Barth and Reible 2008). These issues are potential topics for future research and development.

10. Summary

Contaminated sediments are a continuing concern for regulatory agencies and the public. An emerging alternative in sediment remediation is the use of in situ amendments. These specialized materials can be applied in different ways to the sediment surface, within a cap, or within a mat to minimize contaminant flux via sequestration and degradation. A variety of amendments, such as activated carbon, Organoclay™, and apatite, are being used or studied that can serve this purpose. Some of the better developed amendments have shown large reductions in the bioavailability of contaminants over months to several years with minimal impacts to benthic communities. Although uncertainty remains regarding the long-term effectiveness of these amendments, ongoing studies will continuously improve our understanding.

There are several factors to consider in selecting, designing, and implementing a sediment remedy using amendments. Sediment characteristics, contaminant fate and transport mechanisms, amendment characteristics, and placement methods are four of the most critical design considerations. Modeling is often used to predict the performance associated with these applications, while monitoring (both short-term and long-term) is conducted to ensure proper placement and performance are achieved. Institutional controls may be required to ensure long-term effectiveness. In addition, periodic maintenance or replacement of the layer or mat may be necessary.

This document highlights three field projects across the country using amendments for in situ sediment remediation and provides a compendium of pilot and full-scale in situ remediation projects in the appendix. The field projects, including some addressing large areas of contamination, show excess amendment capacity remaining several years after remedy construction and significant reductions in pore water concentrations. Studies and monitoring are ongoing to evaluate the long-term effectiveness of these amendments. As more of these applications are implemented and their performance is evaluated, there will be a greater understanding and information to gauge the effectiveness and applicability of these technologies under different site conditions. Further information about in situ amendments, as well as other sediment remedies, is available at www.cluin.org/sediments.

11. Glossary of Terms

Absorption	Process by which chemicals penetrate into a three-dimensional matrix.
Activated Carbon (AC)	A highly reduced and recalcitrant form of organic carbon, typically formed by the incomplete combustion of carbon, such as wood, coal, or oil. Particles or granules of Activated Carbon are highly adsorptive for organic molecules and have a high capacity to selectively remove certain trace and soluble materials from water.
Adsorption	Process by which chemicals adhere to the surface of particles.
Advective Transport	The transport of particles or dissolved material resulting from the motion or velocity of a fluid.
Amendment	A remediation method that reduces the toxicity of the contaminants using biological, chemical, or physical processes to treat the contaminated sediments in place.
Apatite	Phosphate mineral that sorbs metals through a surface precipitation reaction.
Bathymetric analysis	Bathymetric analysis involves the measurement of the water depths in a water body and modeling of the depth to the sediment surface.
Bauxite	A clay like mineral and a primary ore of aluminum consisting of aluminum oxides and aluminum hydroxides.
Benthic Layer	Surface layer of sediment where benthic organisms are active.

Benthic Organism	The biota living on the bottom of the water body or very near the bottom of the water body, including the surface layer of sediment.
Bioavailable	Available for uptake by living organisms.
Biopolymer	Naturally occurring material that can bind metals and organics.
Bulk density	Mass of sediment and pore water per unit volume of soil or bed material.
Capping	Covering of contaminated sediment with clean sediment with the intention of isolating the contaminants.
Thin Layer Cap	The placement of a thin layer of clean sediment (on the order of a few inches thick) over contaminated sediment with the intention of enhancing natural recovery processes, such as deposition and burial.
Carbonaceous amendment	An amendment rich in organic carbon.
Dredging	An excavation activity or operation usually carried out underwater for the purpose of removing bottom sediments and disposing of them at a different location.
Diffusive Transport	Movement across a concentration gradient from Brownian or random thermal motion.
Dispersivity	Tendency or ability to scatter or spread widely.

Excavation	The removal of contaminated sediment using conventional dry land equipment. This requires the isolation of contaminated sediment from the overlying body of water by pumping or diverting water from the area and managing any continuing inflow prior to beginning the excavation.
Enhanced MNR	(See Monitored Natural Recovery for a definition of MNR.) MNR combined with thin-layer placement of clean sediment at sites where the natural rate of sedimentation is insufficient to bury contaminants in a reasonable time frame, but where thin-layer placement can accelerate reductions in surface sediment concentrations
Gas Ebullition	The transportation of contaminants via entrapment in migrating gas bubbles.
Hydraulic conductivity	A coefficient describing the rate at which water can move through a permeable medium. Hydraulic conductivity is a function of both the intrinsic permeability of the porous medium and the kinematic viscosity of the water which flows through it.
Hydrophilic	The property of attracting or associating with water molecules; characteristic of polar or charged molecules.
Hydrophobic	With regard to a molecule or sub-group of a molecule, tending to dissolve readily in organic solvents, but not in water, resisting wetting, not containing polar groups or sub-groups.
In Situ Amendment	(See Amendment.)
In Situ Capping	(See Capping.)

Institutional Control	Non-engineered instruments, such as administrative and legal controls, that help minimize the potential for human exposure to contamination or protect the integrity of the remedy.
Log K_{OW}	The octanol/water partition coefficient, which is used as a measurement of a compound's bioaccumulation potential.
Monitored Natural Recovery	A remedy for contaminated sediment that typically uses ongoing, naturally occurring processes to contain, destroy, or reduce the bioavailability or toxicity of contaminants in sediment.
Organoclay™	A hydrophobic and permeable clay in which the surface molecules are modified to include an organic carbon molecule.
Pelagic	The area of a water body that is neither near the bottom of the water body nor near the shore, such as the open water column where there is less interaction with the sediments.
Phytic acid	A sugar additive (6-phosphate ester of inositol); it may be used as an amendment to bind metals in sediments.
Porosity	Ratio of the volume of void space (i.e., pores) to the total volume of an undisturbed sediment or soil sample.
Sediment	Particles derived from rocks, biological material, or both that is transported, suspended, and deposited by flowing water.
Sorption	Process in which chemicals become associated with solid phases; this process includes both absorption and adsorption.

Specific gravity	The dimensionless ratio of the density of a substance with respect to the density of water. The specific gravity of water is equal to 1.0 by definition.
Turbidity	Measure of the extent to which light passing through water is reduced due to suspended matter in the water column.
Zero-valent iron	(ZVI) Elemental metallic iron typically used in granular form to reduce metals or reductively dechlorinate organic solvents such as PCE or TCE.
Zeolite	Porous crystalline aluminosilicates (natural or synthetic) that are used commercially for their adsorption, ion exchange, molecular sieve, and catalytic properties.

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Appendix: Summary of Sediment Sites Using Amendments for In Situ Remediation

EPA Region and Site Name / Page Number

EPA Region 1

Cocheco River, Dover, New Hampshire [Howe 2008, University of New Hampshire 2008]

Design of Amendment Layer	8 mats (2 m x 2 m) with a mixture of 0.231 lb/ft^2 activated carbon, 0.284 lb/ft^2 Organoclay™, and 0.284 lb/ft^2 apatite. Mats were constructed of a non-woven geotextile as the bottom layer and a woven 40-mesh geotextile as the top layer.
COCs/ Extent of Contamination	PAHs (low levels)
Site Conditions/ Physical Setting	Tidal river
Goal of Amendment	Determine how technology performs in the field compared with laboratory results.
Scale/ Status	Pilot (32 m^2)/ Installed (spring 2008)
Placement Method	Mats were unrolled and placed manually with the non-woven geotextile face down in contact with the sediment. Each mat was secured with eight anodized steel stakes.
Performance Monitoring	Amendment mats will be monitored over a period of 2 years. Monitoring techniques will include peepers, SPME, sediment sampling, push point sampling, and biological monitoring.
Cost	N/A
Comments	Cocheco River was selected for demonstration because of its characteristics and proximity to University of New Hampshire, not because it was highly contaminated. The mats with amendments are being compared with mats containing sand.
Contact Information	Lead Investigator: Kevin Gardner, University of New Hampshire, 603-862-4334, kevin.gardner@unh.edu Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

Former industrial site, Silver Lake, Massachusetts [CETCO 2008 and 2009]

Design of Amendment Layer	Reactive core mat with 8 percent Organoclay™ and 92 percent sand (7-mm thick over 13,500 ft^2)
COCs/ Extent of Contamination	PCBs
Site Conditions/ Physical Setting	Lake sediment
Goal of Amendment	Control PCB transport
Scale/ Status	Pilot (13,500 ft^2)/ Installed (2006)
Placement Method	Deployed off the back of a barge. Three rolls on racks were sewn side-to-side, and rebar was attached every 30 feet to stabilize the 45-foot-wide panel.

Former industrial site, Silver Lake, Massachusetts [CETCO 2008 and 2009] *(Continued)*	
Performance Monitoring	N/A
Cost	Approximately \$2/ft^2 for reactive core mat materials
Comments	None
Contact Information	Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

Former manufactured gas plant, Everett, Massachusetts [CETCO 2008]	
Design of Amendment Layer	Reactive core mat with Organoclay™ (7-mm thick over 33,000 ft^2)
COCs/ Extent of Contamination	NAPL
Site Conditions/ Physical Setting	Bay sediment
Goal of Amendment	Control NAPL seepage
Scale/ Status	Full (33,000 ft^2) /Installed (2008)
Placement Method	Mat attached to bottom of Tensar Marine Mattress, deployed by crane.
Performance Monitoring	Visual inspection for sheen
Cost	Approximately \$2/ft^2 for RCM materials
Comments	None
Contact Information	Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

Pine Street Barge Canal Superfund Site, Burlington, Vermont [Arcadis 2010 and 2011; USEPA 2011b]	
Design of Amendment Layer	Reactive core mat with Organoclay™ (3 layers overall, with up to 6 layers near west bank); underlain by geotextile mat; overlain by turf reinforcement mat
COCs/ Extent of Contamination	NAPL
Site Conditions/ Physical Setting	Canal sediment

Pine Street Barge Canal Superfund Site, Burlington, Vermont [Arcadis 2010 and 2011; USEPA 2011b] *(Continued)*	
Goal of Amendment	Control NAPL seepage
Scale/ Status	Full (27,000 ft^2)/ Installed (2011)
Placement Method	Deployed from a barge and the banks of the canal. Secured on the west bank by an anchor trench and on the east bank by epoxy-coated rebar anchors. Secured in canal by concrete pavers.
Performance Monitoring	Visual inspection and settlement plate monitoring
Cost	N/A
Comments	Partially replaced a 1.5- to 2-foot-thick sand cap installed in 2003. Supplemented by 10 passive NAPL recovery wells (five on each bank).
Contact Information	EPA RPM: Karen Lumino, 617- 918-1348, lumino.karen@epa.gov
Salem Manufactured Gas Plant, Salem, Massachusetts [CETCO 2008 and 2009]	
Design of Amendment Layer	Tensar marine mattresses (for armoring) reactive core mat with Organoclay™ (7-mm thick over 36,000 ft^2) over gravel-filled geoweb
COCs/ Extent of Contamination	NAPL / Two distinct NAPL types in beach and intertidal sediments
Site Conditions/ Physical Setting	Beach and intertidal sediment
Goal of Amendment	Control NAPL seepage
Scale/ Status	Full (36,000 ft^2) / Installed (2007)
Placement Method	Backhoe from the shore used for deployment.
Performance Monitoring	Monitoring will be conducted, and reactive core mat to be replaced as needed.
Cost	Approximately \$2/ft^2 for reactive core mat materials
Comments	None
Contact Information	Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

EPA Region 2

Berry's Creek, Bergen County, New Jersey

Design of Amendment Layer	Activated carbon was placed on the surface of a phragmites marsh using three approaches: 1) granular carbon only, 2) granular carbon with a 2 inch coarse sand cap, and 3) fine granular carbon in the form of SediMite™. Activated carbon dose was 5 percent by dry weight of sediment in the top 10 cm. SediMite™ application rate was 5 kg/m^2
COCs/ Extent of Contamination	PCBs, Hg and other metals
Site Conditions/ Physical Setting	Tidal marsh covered with phragmites
Goal of Amendment	Determine how technology performs in the field compared with laboratory treatability results.
Scale/ Status	Pilot scale with 30 feet by 30 feet plots for each treatment and control. Installed in Fall 2012.
Placement Method	Granular activated carbon was placed in a slurry form using a hydroseeder. Coarse sand was delivered to plot using a telebelt and manually layered over the treatment area. SediMite™ was applied using a Vortex TR Aquatic spreader.
Performance Monitoring	Treatment performance will be monitored over 2 years. Monitoring plan includes 1) assessment of activated carbon levels in sediment core sections to assess persistence and mixing, 2) measurement of porewater PCBs using passive samplers and porewater Hg/MeHg using seepers, 3) PCB/Hg/MeHg bioaccumulation in native and field caged invertebrates, and 4) PCB/Hg/MeHg bioaccumulation in intact cores transported to the laboratory.
Cost	N/A
Comments	N/A
Contact Information	Lead Investigator: Dr. Charles A. Menzie, Exponent. camenzie@exponent.com

Central Hudson Gas & Electric Corp, North Water Street Manufactured Gas Plant Site, Poughkeepsie, New York [Bessingpas and others 2008, Clock 2009, EPRI 2011]

Design of Amendment Layer	Three Tensar Triton mattress configurations: (1) 6 inches of stone with an Organoclay™-filled RCM layer below; (2) 3 inches of stone and 3 inches of sand wrapped in a geotextile; and (3) 3 inches of stone, 3 inches of sand/Organoclay™ (at a ratio of 5:1) wrapped in a geotextile with an Organoclay™-filled reactive core mat layer below. Each configuration comprises 25 mattresses measuring 6.5 feet by 20 feet and covers approximately one-third of the 10,000-ft^2 test area.
COCs/ Extent of Contamination	NAPL, PAHs / Near-surface coal tar NAPL-impacted sediments. Sheens have been observed on the water surface.
Site Conditions/ Physical Setting	Hudson River
Goal of Amendment	Control NAPL migration, primarily as PAH. This project is a performance and implementability study.
Scale/ Status	Pilot (10,000 ft^2) / Installed (May 2009)

Central Hudson Gas & Electric Corp, North Water Street Manufactured Gas Plant Site, Poughkeepsie, New York [Bessingpas and others 2008, Clock 2009, EPRI 2011] *(Continued)*	
Placement Method	Placed by a crane on barge with assistance from divers. Sonar system also used to minimize gaps between adjacent mat sections. Oil booms were posted around the work area to control NAPL/sheen migration.
Performance Monitoring	Turbidity monitoring and sheen observations were conducted during placement. First round of post-construction monitoring was performed in June and July 2009 and included diver and video inspections, assessment of PAHs and NAPL within the cap, and monitoring of sediment deposition above cap. Diver inspections reported no NAPL breakthrough, significant (approximately 5 inches) sediment deposition, and some debris accumulation. Video monitoring was not useful because of turbidity in the river. NAPL was found in two locations but was determined to be likely from adjacent sediments rather than through the cap. Staining/spotting from organic material was observed in surface sediments.
Cost	N/A
Comments	The mattresses were removed in November 2010 after 18 months in place and analyzed for NAPL and PAH distribution. The Type 1 (6 inches of stone with an Organoclay™-filled reactive core mat layer below) caps had the highest levels of success.
Contact Information	Project Manager: Jeff Clock, EPRI, 845-608-0642, jclock@epri.com Vendor: Tensar International Corp., 888-828-5126, www.tensarcorp.com and James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com
Grasse River, Massena, New York [Alcoa 2006, 2007 and 2011; Beckingham and Ghosh 2011; Oen and others 2012]	
Design of Amendment Layer	Activated carbon (75 x 300 microns) derived from either bituminous coal or coconut shells over 0.5-acre test area
COCs/ Extent of Contamination	PCBs
Site Conditions/ Physical Setting	Shallow and wide part of the river, contiguous fine sediment
Goal of Amendment	Reduce bioavailability of PCBs
Scale/ Status	Pilot (0.5 acre) / Installed (2006)
Placement Method	Different placement methods were used to mix the carbon into the upper layer of sediment. The three application techniques tested included: (1) rototiller with rotors, (2) rototiller without rotors, and (3) tine sled alone.
Performance Monitoring	A 2-year post-treatment physiochemical and biological assessment was conducted. A third year may be added based on results. Data collected in 2006 and 2007 showed that activated carbon was applied at or above its target dose of 2.5 percent with the exception of small-scale variability. Where activated carbon doses equaled native TOC levels, reductions in aqueous equilibrium PCB concentrations approached 100 percent. Water quality monitoring conducted during placement activities indicated no measurable changes in water column PCB concentrations, which remained below detection limits (0.065 µg/L) at all locations (upstream, local, and downstream). A slight turbidity increase was noted but concentrations remained below the action level (25 NTUs above background). In addition, biological monitoring conducted before and one year after activated carbon placement included ex situ laboratory bioaccumulation studies and in situ cage deployment. Those results showed PCB concentrations in benthic worms decreased by approximately 72 percent to 94 percent.

Grasse River, Massena, New York [Alcoa 2007, Beckingham and Ghosh 2011, Oen and others 2012] ***(Continued)***	
Cost	N/A
Comments	Fish consumption advisory is in place in the lower Grasse River because of elevated PCB levels.
Contact Information	EPA RPM: Young Chang, (212) 637-4253, chang.young@epa.gov Lead Investigator: Larry McShea, ALCOA, (724) 337-5458, Larry.McShea@alcoa.com Vendor: Calgon Carbon Corporation, 800-4CARBON, www.calgoncarbon.com

EPA Region 3

Anacostia River Demonstration Project, Washington DC [Arcadis and Hart Crowser 2008, Horne 2007, McDonough 2007, Reible and others 2005]	
Design of Amendment Layer	Apatite applied in bulk (6 inches) over 8,000 ft^2. Coke breeze (less than 1 inch) contained within reactive core mat over 11,840 ft^2. RCM was constructed of polyester fabric and covered with 6 inches of sand.
COCs/ Extent of Contamination	PAHs, PCBs, coal tar NAPL, metals Sediment hydrocarbon concentrations ranged from 5,000 to 60,000 mg/kg. PAHs detected at levels up to 82,360 µg/kg to depths of 7 feet.
Site Conditions/ Physical Setting	Tidal river with silty clay to silty, fine sand
Goal of Amendment	Apatite to promote sorption and reaction of metals Coke breeze to promote sequestration of contaminants
Scale/ Status	Pilot (19,840 ft^2) / Installed (spring 2004)
Placement Method	Apatite was placed using a clamshell bucket of a crane on a barge. Reactive core mat with coke breeze was submerged, and a diver and barge-mounted crane unrolled the reactive core mat underwater. Each mat was anchored with a bucketful of sand.
Performance Monitoring	The following monitoring was conducted at Months 1, 6, 18, and 30 after placement: bathymetric, sub-bottom profiling, and sediment profile imaging surveys; surface water quality monitoring and groundwater movement studies; chemical analyses of cap and sediment samples; and biological monitoring. In 2006, analysis of the cap samples indicated that contaminants of interest (PAHs, PCBs, and metals) had not migrated upward into the cap. However, some contamination was noted at the sediment surface because of re-deposition of sediments. Cores of the cap material also showed that placement methods minimized mixing of sediments and cap materials.
Cost	Total material costs: Apatite - \$3.1/ft^2 ; Coke - \$1.1/ft^2 ; Sand - \$0.45/ft^2
Comments	None
Contact Information	Lead Investigator: Danny Reible, reible@mail.utexas.edu Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

Bailey Creek, Fort Eustis, Virginia	
Design of Amendment Layer	Activated carbon was placed on sediment surface in the form of SediMite™. Dose of activated carbon was 5 percent by dry weight of sediment in the top 10 cm plus a 25 percent safety factor. SediMite™ application rate was 3.4 kg/m^2. Total treatment area was 225 m^2. The treatment area included part of a marsh and adjacent creek. A similar upstream area was used as a control plot for monitoring.
COCs/ Extent of Contamination	PCBs
Site Conditions/ Physical Setting	Tidal estuary/shallow wetland. Application performed over water from a boat at high tide.
Goal of Amendment	Determine how technology performs in the field compared with laboratory treatability results.
Scale/ Status	Pilot scale (225 m^2). Installed in Summer 2009.
Placement Method	SediMite™ was applied using a Vortex TR Aquatic spreader mounted on a shallow-draft boat.
Performance Monitoring	Post application monitoring conducted 2 months and 15 months after application. Monitoring included: 1) assessment of activated carbon levels in sediment core sections to assess persistence and mixing, 2) measurement of porewater PCBs using passive samplers, 3) laboratory biouptake studies to assess changes in PCB bioavailability in sediments, and 4) benthic community changes in treated and control plots.
Cost	N/A
Comments	Project was funded by the NIEHS Superfund Research Program. Samples were collected and examined before treatment, two months, and 15 months after treatment. Activated carbon measurement in sediment cores demonstrated that the applied activated carbon remained in sediment after application and was found in the top 5 cm of sediment. A greater lateral dispersion of the carbon was observed in the creek compared to the marsh possibly due to tidal action. Bioaccumulation studies using the benthic organism *Leptocheirus plumulosus* as well as aqueous concentration measurement using a passive sampler showed reductions in PCB bioavailability at the treatment sites after deployment. The percent reduction in total PCB bioaccumulation after 2 months of treatment in the field was 90 percent which reduced to 50 percent after 15 months. The lower bioaccumulation reduction seen in 15 months compared to 2 month is likely due to the ongoing influence of contaminated sediment movement and deposition within the large contaminated area of which the treatment plot was a very small fraction. Benthic community sampling after application demonstrated no significant impact of the application on native biota.
Contact Information	Lead Investigator: Upal Ghosh, University of Maryland Baltimore County, ughosh@umbc.edu. SediMite™ technology being commercialized by startup company Sediment Solutions: www.sedimite.com

Canal Creek, Aberdeen Proving Ground, Maryland	
Design of Amendment Layer	Activated carbon placed in a marsh and a creek in the contaminated site. SediMite™ application rate was 4.5 kg/m^2 in the Lower Canal Creek area and 4.3 kg/m^2 in the Upper Canal Creek area. (A parallel study performed by AECOM evaluated alternative placement methods of activated carbon)
COCs/ Extent of Contamination	PCBs and mercury
Site Conditions/ Physical Setting	Tidal estuary/shallow wetland.

Canal Creek, Aberdeen Proving Ground, Maryland *(Continued)*	
Goal of Amendment	Determine how technology performs in the field compared with laboratory treatability results.
Scale/ Status	Pilot scale, 0.25 acres total area, installed in Winter 2010.
Placement Method	Activated carbon was placed in two areas: 1) in the creek using a spreader mounted on a barge, and 2) in the marsh using a Vortex TR Aquatic spreader during low tide.
Performance Monitoring	Treatment performance monitored over 2 years. Monitoring plan included 1) assessment of activated carbon levels in sediment core sections to assess persistence and mixing, 2) measurement of porewater PCBs using passive samplers and porewater Hg/MeHg using seepers, 3) PCB/Hg/MeHg bioaccumulation in intact cores transported to the laboratory.
Cost	N/A
Comments	Project was funded by the DoD ESTCP program. Pilot study work plan was jointly evaluated and approved by EPA Region 3, Army Corps, and Maryland Department of the Environment. Results of the study will be available in 2013.
Contact Information	Lead Investigator: Charles A. Menzie, Exponent. camenzie@exponent.com SediMite™ technology being commercialized by startup company Sediment Solutions: www.sedimite.com

EPA Region 4

Chattanooga Creek, Tennessee Products Superfund Site, OU 1, Chattanooga, Tennessee [USEPA 2011a]	
Design of Amendment Layer	To address NAPL: 1) Placement of a minimum of 12 inches of sub-grade soil over the excavated creek bed and banks to a level that is a minimum of 3 feet above the highest point of observed NAPL and then hydrated. 2) A 6-inch layer of AquaBlok™ 3070 FW (blended 50:50 on a volume basis with AASHTO #8 aggregate or equivalent) was placed on top of the soil layer and hydrated as well. 3) A minimum of 6 inches of clay rich soil was placed over the AquaBlok™ layer. To address coal tar–contaminated sediments: 1) 6 inches of AquaBlok™ was placed over the excavated creek bed and then hydrated. 2) 6 inches of native clay material were placed on the AquaBlok™.
COCs/ Extent of Contamination	NAPL, coal tar, PAHs, PCBs, dioxins and furans, metals, pesticides, VOCs The capping remedy covers 5,750 linear feet of the creek for a total of 7.1 acres addressed by the sediment cap.
Site Conditions/ Physical Setting	2.5-mile section of the Chattanooga Creek. It is a small, forested creek and is adjacent to industrial, residential, and undeveloped areas.
Goal of Amendment	To provide a protective barrier to prevent recontamination from sub-surface NAPL.
Scale/ Status	Full (308,878 ft^2 cap) / Installed (September 2007)

Chattanooga Creek, Tennessee Products Superfund Site, OU 1, Chattanooga, Tennessee [USEPA 2011a] *(Continued)*

Placement Method	Water flow in the creek was diverted around the contaminated area, contaminated sediments were excavated from the dried creek bed, and the cap was placed using an excavator and construction personnel raking the cap to achieve a uniform distribution.
Performance Monitoring	SPME monitoring of the cap was conducted in 2009 and 2010, and was scheduled again for 2011. SPME results in 2009 and 2010 showed very low (parts per trillion-range) concentrations in cap pore water. Moreover, the concentration of PAHs in the cap materials changed very little between 2009 and 2010. Therefore, EPA has concluded that the cap is effectively isolating residual NAPL. EPA suggested that additional inspections and monitoring of the cap be included in the RCRA Post-Closure Permit issued by the state. However, the permit had not been finalized at the time of the 5-year review (September 2011).
Cost	N/A
Comments	None
Contact Information	EPA RPM: Craig Zeller, 404-562-8827, zeller.craig@epa.gov

EPA Region 5

Former creosoting wood treating site, Escanaba, Michigan [CETCO 2008]

Design of Amendment Layer	Reactive core mat with Organoclay™ (7-mm thick over 6,000 ft^2) on beach head and in PRB upgradient of RCM Covered with 6 inches of 0.75 in stone and 2 feet of rip rap
COCs/ Extent of Contamination	NAPL / Further delineation ongoing
Site Conditions/ Physical Setting	Groundwater contaminated with NAPL threatening nearby fresh water bay, which had a re-occurring sheen.
Goal of Amendment	Control NAPL seepage
Scale/ Status	Full (6,000 ft^2) / Installed (2005)
Placement Method	Backhoe from the shore used for deployment.
Performance Monitoring	Visual inspection for sheen
Cost	Approximately \$2/ft^2 for reactive core mat materials
Comments	None
Contact Information	Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

St. Louis River/Interlake/Duluth Tar Superfund Site (Stryker Bay), Duluth, Minnesota [Arcadis and Hart Crowser 2008, CETCO 2008, Olsta and Hornaday 2007]

Design of Amendment Layer	Reactive core mat with 60 percent activated carbon and 40 percent sand was constructed of polypropylene geotextiles at a loading of 0.4 lb/ft^2. Mat thickness was typically 11 mm. 11 acres: 6 in of sand, 11-mm thick reactive core mat (60 percent activated carbon and 40 percent sand), 36 in of sand, and 6.5 to 8 ft temporary surcharge.
COCs/ Extent of Contamination	PAHs (including naphthalene) and metals 11-acre area contaminated with naphthalene (greater than 1,000 mg/kg). 135,000 cubic yards contaminated with NAPL.
Site Conditions/ Physical Setting	35-acre shallow water embayment (3 to 5 feet depth)
Goal of Amendment	Reactive core mat was added to help adsorb contamination from the consolidation water. Dredging was not an option for areas with naphthalene greater than 1,000 mg/kg because it would result in failure to achieve ambient air quality standards at the site.
Scale/ Status	Full (11 acres) /Installed (2006)
Placement Method	Mats were unrolled and floated to allow panels to be attached and then sunk as they absorbed water (see Olsta and Hornaday 2007 for additional details). Reactive core mat placed with temporary surcharge of sand, which was placed by either backhoe bucket (near shore) or from a barge (off shore).
Performance Monitoring	Coring and settlement monitoring. Compliance monitoring every 5 years.
Cost	Approximately \$2/ft^2 for reactive core mat materials
Comments	Pre-remediation migration pathway: NAPL migration via gas ebullition, groundwater advection, and pore water migration caused by consolidation. Sheet pile was installed along the area to be capped.
Contact Information	EPA RPM: James Hahnenberg, 312- 353-4213 hahnenberg.james@epa.gov Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

EPA Region 6

Cottonwood Bay, Grand Prairie, Texas [SAIC 2008a, 2008b, 2009]

Design of Amendment Layer	Mats consisted of AOS 80 (8 oz/yd^3) polypropylene non-woven geotextile, a woven backing geotextile and a mixed amendment core made up of 0.23 lb/ft^2 crushed apatite, 0.28 lb/ft^2 coconut shell activated carbon and 0.28 lb/ft^2 Organoclay™. Each individual “mat” consisted of two 25-foot x 15-foot panels to be placed with a 5-foot overlap for an overall footprint of 25 feet x 25 feet.
COCs/ Extent of Contamination	PCBs, PAHs, some metals
Site Conditions/ Physical Setting	N/A

Cottonwood Bay, Grand Prairie, Texas [SAIC 2008a, 2008b, 2009] *(Continued)*

Goal of Amendment	Study compares four designs with an undisturbed, uncapped area: (1) single layer geotextile (2) double layer geotextile (3) single layer geotextile with sand cover (4) sand cover only
Scale/ Status	Pilot / Installed (spring 2008)
Placement Method	Mats were transported using jet skis and placed by commercial divers. The mats were unrolled at the surface and pinned to the sediment using 36-inch screw anchors. Within minutes, air escaped from the mats, and they rested flat on the sediment surface.
Performance Monitoring	Monitoring is being conducted to assess contaminant adsorption and flux properties by passive sampling and groundwater seepage surveys. Passive samplers (SPMD, SPME fibers, and peepers) were placed at each of the test areas in October 2008 and retrieved in December 2008. Peeper data (concentrations of nickel and zinc) suggest effective sequestration of metals, and results indicate the single-layer mat with sand and the double-layer mat are most successful. SPMD data show sequestration of PAHs was 5 to 6 times greater in the single-layer mat with sand and the double-layer mat than the single mat with no sand. SPME data were inconclusive, as all concentrations were below detection levels. Bathymetric, sub-bottom, side-scan sonar, and sediment profiling imaging surveys were also conducted.
Cost	N/A
Comments	This demonstration is a continuation of a smaller-scale study at the site conducted in 2007 where mats were smaller (6 feet x 6 feet) than the 25 feet x 25 feet mats in this field demonstration. Modeling was conducted to determine whether sediment deformation caused by the weight of the mat and capping materials compromises groundwater flow and reactivity of the amendments.
Contact Information	Lead Investigator: Amy Hawkins, Navy, 805-982-4890, amy.Hawkins@navy.mil Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

EPA Region 9

Hunters Point Shipyard Superfund Site, Parcel F, San Francisco, California [Cho 2011, ESTCP 2009, Oen and others 2011 and 2012, Stanford University 2005, Tomaszewski and Luthy 2008]

Design of Amendment Layer	3.4 percent by weight activated carbon (virgin) mixed to a depth of 1 foot at two test plots (370 ft^2 each). 1,250 pounds of activated carbon applied per plot. Four plots (370 ft^2 each) are included in the demonstration: (1) activated carbon mixed with a rotovator (2) mixed with the rotovator (no activated carbon) (3) activated carbon mixed with injection slurry (4) control plot (no activated carbon and no mixing)
COCs/ Extent of Contamination	PCB concentrations ranged from approximately 1 to 2 mg/kg in the test area.
Site Conditions/ Physical Setting	The tests plots are located in a tidal mudflat. The top 4 inches of sediment consist of small gravel, shells, and clay particles with a homogeneous clay layer underneath. The top foot of sediment has a bulk density of 1.3 to 1.4 g/cm^3.

Hunters Point Shipyard Superfund Site, Parcel F, San Francisco, California [Cho 2011, ESTCP 2009, Oen and others 2011 and 2012, Stanford University 2005, Tomaszewski and Luthy 2008] *(Continued)*	
Goal of Amendment	Stabilize PCBs and reduce bioavailability
Scale/ Status	Pilot (1,480 ft^2) / Installed (2006)
Placement Method	Activated carbon was mixed into the sediment using two available large-scale equipment technologies (slurry injector and rotovator).
Performance Monitoring	Baseline samples were collected before activated carbon was applied. Sediment core and overlying water samples were collected at 6 and 18 months post-treatment, and biological monitoring was conducted at 6, 18, and 24 months post-treatment. Results showed (1) 60 percent reductions in the freely dissolved pore water concentrations of PCBs relative to the reference site after 18 months, (2) 80 percent reductions in the freely dissolved pore water concentrations after 30 months, and (3) reductions in bioaccumulation without impairing the natural benthic community or releasing PCBs into the overlying water. After 5 years, total PCB uptake in passive samplers was reduced by 73 percent, with greater reductions in the bioavailability of the less chlorinated congeners relative to the more chlorinated congeners.
Cost	Total cost for the demonstration is approximately \$1 million. Breakdown of costs is available in Table 5-1 of Stanford University 2005.
Comments	None
Contact Information	Lead Investigator: Ryan Ahlersmeyer, Southwest Division Naval Facilities Engineering Command, 619-532-0960, ryan.ahlersmeyer@navy.mil

EPA Region 10

Gasco, Portland, Oregon [Anchor 2006, 2009a, and 2012; CETCO 2008]	
Design of Amendment Layer	Reactive core mat with Organoclay™ (7-mm thick over 3,000 ft^2) installed over 6 inches of sand to protect from underlying rip-rap; covered with 6 inches of sand plus 2 feet of quarry spalls
COCs/ Extent of Contamination	NAPL
Site Conditions/ Physical Setting	River shore intertidal sediment
Goal of Amendment	Control NAPL seepage
Scale/ Status	Pilot (3,000 ft^2) / Installed (2005)
Placement Method	Barge and crane
Performance Monitoring	Visual inspections have been conducted monthly (approximately) since late 2005. Results show that the mat has remained in place and controlled the release of potential sheen from the underlying sediment, although some portions have become exposed.
Cost	Approximately \$2/ft^2 for RCM materials

Gasco, Portland, Oregon [Anchor 2006, 2009a, and 2012; CETCO 2008] *(Continued)*

Comments	None
Contact Information	EPA RPM: Eric Blischke, 503-326-4006, Blischke.Eric@epa.gov Vendor: James Olsta, CETCO, 847-818-7912

McCormick & Baxter Creosoting Co. (Portland Plant) Superfund Site, Portland, Oregon [Arcadis and Hart Crowser 2008, CETCO 2008, Ecology & Environment 2008, GSI and Hart Crowser 2008, Hart Crowser and GSI 2009 and 2011]

Design of Amendment Layer	Organoclay™ reactive core mat installed along beach head and bulk Organoclay™ media deployed over NAPL hot spots. 600 tons of bulk Organoclay™ (20,000 ft^2 total) added to three areas of sand cap: sand (1 foot), Organoclay™ (1 foot), gravel (4 inches), rock armor (10 inches). Three 7-mm thick Organoclay™ mats over 25,000 ft^2.
COCs/ Extent of Contamination	PAHs, creosote, NAPL / PAHs detected up to 35 feet below sediment surface, NAPL in upper 7 feet of sediment.
Site Conditions/ Physical Setting	Willamette River with poorly graded fine to medium grained, clean to slightly silty sand
Goal of Amendment	Organoclay™ applied in bulk to control NAPL seeps and in mats to control gas migration. Specific cleanup goals are listed in the 2007 operations and maintenance report (Ecology & Environment 2008).
Scale/ Status	Full (bulk: 20,000 ft^2; mats: 25,000 ft^2) / Installed (bulk in 2004 and mats in 2005)
Placement Method	Bulk Organoclay™ deployed by backhoe on shore and reactive core mat deployed by barge and crane.
Performance Monitoring	Diver inspection, along with collection of Organoclay™ cores, samples from the mat, and water quality samples were conducted in October 2006. Results indicated that Organoclay™ had an available sorption capacity similar to freshly placed Organoclay™, no significant changes were measured in permeability, and minimal evidence of NAPL (less than 1 cm thick) was noted at the sediment-Organoclay™ interface. Observations noted the migration of gas bubbles, but the bubbles contained no NAPL. Evidence suggested that Organoclay™ is absorbing NAPL prior to gas bubbles breaking the surface of the cap. Cap pore water concentrations were also measured. In 2005, total carcinogenic PAH concentrations was 0.2 µg/L. In 2010, PAH concentrations in the pore water were all below the NRWQC, with the exception of chrysene at one location. Sheen, surface water, and pore water samples, as well as sediment cores, were collected in 2007 and 2008. Sheen samples did not differ significantly from nearby surface water samples, and pore water and sediment core concentrations showed no evidence of NAPL entering or penetrating the sediment cap. Results confirm that Organoclay™ continues to have sufficient sorption capacity and permeability. Additional information about the monitoring of this cap is available at www.mandbsuperfund.com.
Cost	Approximately \$2/ft^2 for reactive core mat materials
Comments	Pre-remediation migration pathway: Methane-mediated NAPL migration observed. Before capping, a sheet pile wall was installed to minimize the flow of NAPL to the river.
Contact Information	State RPM: Scott Manzano, ODEQ, 503-229-6748, manzano.scott@deq.state.or.us EPA RPM: Nancy Harney, 206-553-6635, harney.nancy@epamail.epa.gov Vendor: James Olsta, CETCO, 847-818-7912, Jim.Olsta@cetco.com

Spokane River Upriver Dam PCB Site (Deposit 1), Spokane, Washington [Anchor 2007 and 2009b, Washington State Department of Ecology 2005]	
Design of Amendment Layer	3.5 acres of <u>coal</u> (4 inches minimum), sand (6 inches), gravel (3 inches) applied in bulk. Modeling predicted that a 1-inch-thick cover would ensure PCB pore water concentrations remain below cleanup goals at 10 cm below mudline for 500 years (below 1 picogram per liter). Washington Department of Ecology required a minimum 4-inch-thick cap, based on a safety factor of 4.
COCs/ Extent of Contamination	PCBs up to 1,430 µg/kg dry weight.
Site Conditions/ Physical Setting	Fine-grained (silty sand) sediments, low energy area behind a dam
Goal of Amendment	Control and minimize benthic exposure to contaminated sediments, reduce potential remobilization of sediments by hydraulic or other processes, and reduce the potential transport of PCBs into overlying water column and groundwater.
Scale/ Status	Full (3.5 acres) / Installed (fall 2006)
Placement Method	Based on results from a placement demonstration, a long reach excavator released amendments above the water surface and allowed them to settle through the water column.
Performance Monitoring	Water quality monitoring was conducted during placement, and no turbidity or dissolved oxygen impacts were observed. Piston core sampling and bathymetric surveys verified that the minimum thickness of the coal layer was achieved (average was 6.3 inches). First round of post-construction monitoring was conducted in fall 2008 and included bathymetric surveys, collection of sediment cores and surficial sediment samples, and visual observations. Results showed consolidation and sediment deposition had occurred in some areas, and the cap and its layers were intact in all locations. Total PCBs were not detected in the sand isolation layer or coal layer, indicating the cap is functioning as designed. Unscheduled monitoring will be conducted after the occurrence of a 50-year or higher flood event in the Spokane River.
Cost	$1,578,000 (estimate in draft Cleanup Action Plan [Washington State Department of Ecology 2005] for entire remedy at Deposit 1)
Comments	Sediment cleanup level is 62 µg/kg (dry weight) for PCBs.
Contact Information	State RPM: Brendan Dowling, WA Dept. of Ecology, 509-329-3611, bdow461@ecy.wa.gov Vendor: Palmer Coking Coal Company, 425-432-4700, www.palmercc.com

Notes:

Underlined text indicates amendment types to allow for easier identification.

AASHTO – American Association of State Highway and Transportation Officials
AOS - apparent opening size
COCs – contaminants of concern
cm – centimeter
ft – foot
ft^2 – square foot
g/cm^3 – gram per cubic centimeter
in – inch
lb/ft^2 – pound per square foot
m – meter
mg/kg – milligram per kilogram
mm – millimeter
MeHg -Methylmercury
N/A – Not available
NAPL – non-aqueuse phase liquid
NTU - Nephelometric Turbidity Units
oz/yd^3 – ounce per square yard
PAH – polycyclic aromatic hydrocarbon
PCB – polychlorinated biphenyl
PRB – permeable reactive barrier
RCM™ – Reactive Core Mat™
SPMD - Semi-permeable membrane device
SPME – Solid phase microextraction
TOC – Total organic carbon
µg/kg – microgram per kilogram
µg/L – microgram per liter

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