

Green PCB Remediation From Sediment Systems Project

Center Innovation Fund: KSC CIF Program

Space Technology Mission Directorate (STMD)

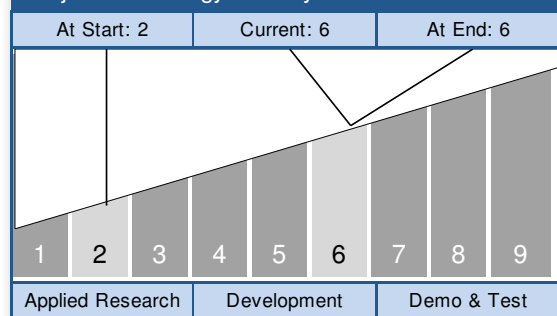
National Aeronautics and
Space Administration

Green PCB Remediation from Sediment Systems (GPRSS)

ABSTRACT

An ongoing problem facing the global environmental community including NASA centers is the removal and remediation of polychlorinated biphenyls (PCBs). PCBs were commonly used in a variety of materials including paints, caulking, and adhesives due to the advantageous physical and chemical properties that PCBs imparted to these various materials. Unfortunately, these properties have made the treatment of sites contaminated with these chemicals extremely difficult to deal with, due to their inherent chemical stability. The remediation of sediments contaminated with PCBs is especially difficult, primarily due to the risk of re-releasing the contaminant into the...***Read more on the last page.***

Project Technology Maturity



Technology Area: Environmental and Green Technologies TA13.2
(Primary)
Ground & Launch Systems Processing TA13
(Secondary)

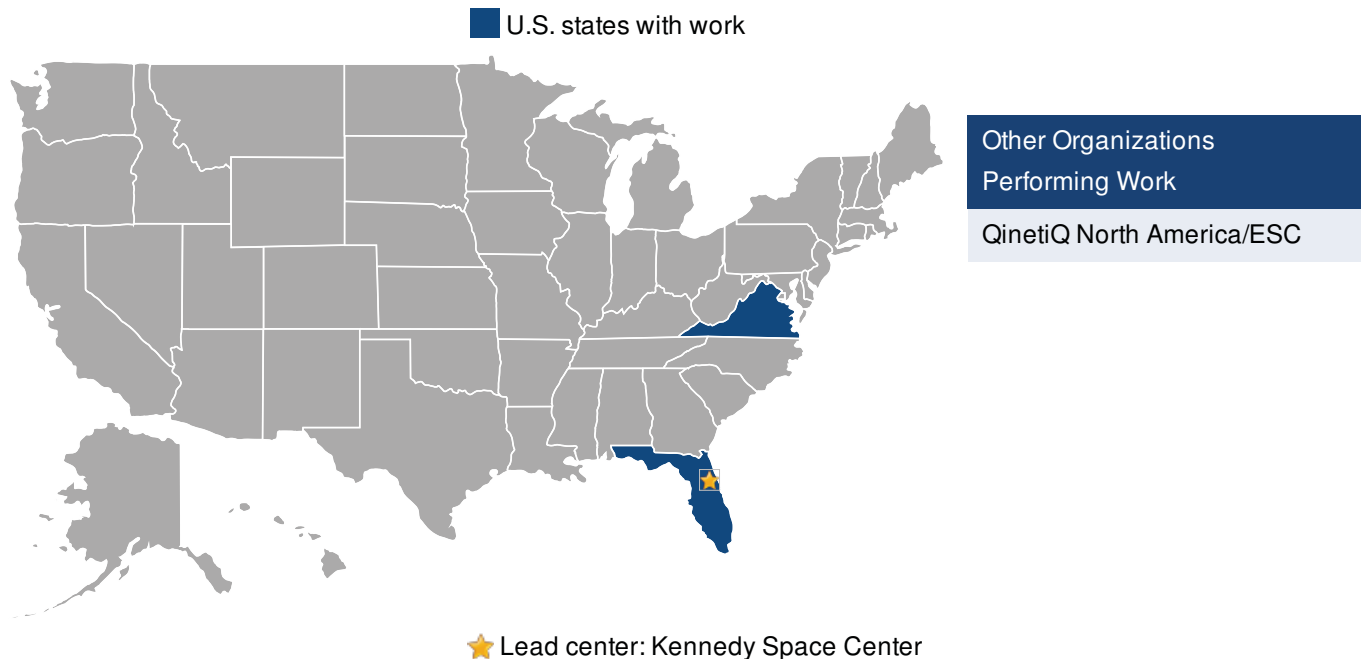
ANTICIPATED BENEFITS

To NASA funded missions:

The science associated with PCB destruction is continuing to evolve, and KSC has been working on a treatment system for PCB destruction on painted structures. The goal of this research is to create a polymer-based treatment system capable of removing PCBs from contaminated sediments.



1 Patent
1 Publication



DETAILED DESCRIPTION

The GPRSS technology is an in situ remediation technique for PCB-contaminated sediments. The technique provides an effective and safe method for sediment cleanup operations, eliminating some of the inherent risks associated with more traditional cleanup methods such as sediment dredging followed by incineration. The GPRSS technique offers both removal and degradation of the contaminant, in contrast to the capping in place method, which retains significant long-term environmental reliability. The envisioned re-useable, polymer-based PCB treating blanket has the potential to be a global, cost saving, game-changing technology.

This technology utilizes a two-step process for the removal and degradation of the PCBs. In the first step, a "blanket" of inert material (such as a simple polymer, i.e. polyethylene) is gently lowered into the water system and pushed into the top layer of the sediments, penetrating into the zone where benthic population is at the greatest risk for bioaccumulation. This "blanket" acts as a PCB "sponge", absorbing the PCBs that are bound to the sediments. The second step consists of removing the "blanket", extracting the contaminants trapped within the blanket structure, and exposing the extracted PCBs to activated zero-valent magnesium in an acidified ethanol solvent to commence degradation.

The "blanket" has a solid upper surface, providing a temporary cap to the contaminated sediments during the...

MANAGEMENT

Program Director:
John Falker

Program Executive:
John Falker

Program Manager:
Karen Thompson

Project Manager:
Nancy Zeitlin

Principal Investigator:
Jacqueline Quinn

DETAILED DESCRIPTION (CONT'D)

treatment period. Additionally, the "blanket" is manufactured with extruding points, or "fingers", that depress into the upper ten centimeters of the sediment layer, allowing for increased surface area contact with the deeper contaminated zone. Both the "fingers" and the backing of the "blanket" are hollow to allow for the incorporation of ethanol into the interior. This ethanol interior provides a major advantage to the GRPSSs.

Since PCBs are lipophilic and hydrophobic, they prefer to dissolve into the ethanol (or similar non-aqueous solvent) if given the opportunity. This system affords that opportunity by generating a concentration gradient which enhances the rate of PCB transport from the sediment across the polymer blanket membrane and into the ethanol interior. Once the PCBs are in the "blanket," the entire system is removed from the sediment and the contaminants are extracted out of the blanket and degraded using stepwise reductive dechlorination in the presence of the magnesium reactant described above as step two. The polymer "blanket" is capable of being re-used multiple times. An entire riverbed for example would not be treated at a single event, but rather portions would be treated at a time. The reusability of the blankets allows them to be reapplied to different regions of the contaminated zone as remediation activities progress. Should additional applications prove necessary to remediate high starting PCB concentrations to acceptable levels at a single site, such as a holding or sludge pond, the reusability of the blanket adds to its cost competitive nature, or to simply treat another contaminated sediment zone.

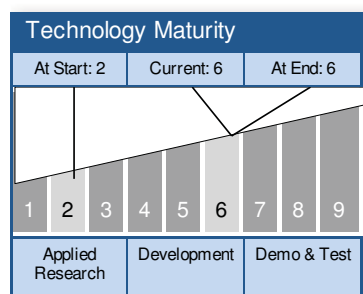
ADDITIONAL AND DETAILED TECHNOLOGY AREAS

- TA12: Materials, Structures, Mechanical Systems & Manufacturing

TECHNOLOGY DETAILS

Green PCB Remediation from Sediment Systems (GPRSS)

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- This technology is categorized as a material for other applications
- Technology Area
 - TA13.2 Environmental and Green Technologies (Primary)
 - TA13 Ground & Launch Systems Processing (Secondary)
 - TA12 Materials, Structures, Mechanical Systems & Manufacturing (Additional)



CAPABILITIES PROVIDED

The GPRSS environmental remediation technology allows for in-situ removal and subsequent degradation of polychlorinated biphenyls (PCBs) from contaminated sediments, offers a safer method for cleanup operations than traditional treatment methodologies, and potentially provides a global, cost competitive, game-changing technology for major waterways and harbors.

POTENTIAL APPLICATIONS

Beyond NASA centers which themselves have PCB-contaminated sediments, there are major waterways and harbors extending from Tokyo Harbor, to Pearl Harbor, to the Housatonic River in New England where PCB contamination is pervasive in the sediments. Because of the inherent stability of PCBs, remediation technologies have seen limited success in the past, and are perceived as having the potential to cause additional harm to the surrounding the environment simply by deploying them into the sensitive sediment ecosystem. The GPRRSs technology allows for a safer, passive remediation technology for contaminated sediments in comparison to more traditional cleanup techniques, such as dredging and incineration. This technology has strong preliminary evidence suggesting that a passive, reusable polymer system combined with a proton donating solvent and magnesium could work towards returning an ecosystem to a healthy status.

IMAGE GALLERY



Field Work Green PCB Treatment



*Green PCB Remediation from
Sediment Systems (GPRSS)*



Green PCB Treatment Blanket

TECHPORT PROJECT LIBRARY REFERENCES

FINAL REPORTS

Green Removal of PCBs from Sediment Systems:

EXECUTIVE SUMMARY

An ongoing problem facing the global environmental community including NASA centers is the removal and remediation of polychlorinated biphenyls (PCBs). PCBs were commonly used in a variety of materials including paints, caulking, and adhesives due to the advantageous physical and chemical properties that PCBs imparted to these various materials. Unfortunately, these properties have made the treatment of sites contaminated with these chemicals extremely difficult to deal with, due to their inherent chemical stability. The remediation of sediments contaminated with PCBs is especially difficult, primarily due to the risk of re-releasing the contaminant into the environment during the treatment process. Traditional treatment options involve the use of dredging and incineration of the contaminated soils/sediments, in which the chance of releasing of the contaminants is greatly increased. The purpose of this project is to develop a cleanup technology capable of remediating contaminated sediments in-situ, with minimal intrusion. This allows for the minimization of any potential contaminant release during the treatment process, providing a safer method for cleanup operations (as opposed to dredging/incineration) and still treating the basic problem of PCB contamination (as opposed to capping).

INTRODUCTION

The scientific advances of the past century, while technologically impressive have not occurred without both harmful and long-lasting consequences. Specifically, an area which has seen dramatic negative impacts has been in the environment, where unintended effects have had dramatic and extremely long-lived consequences. Many of the chemicals produced in the last 100 years have exhibited this kind of legacy behavior. One prime example is polychlorinated biphenyls, which are a class of man-made molecules first produced back in the 1920's. These compounds are both chemically and thermally stable, and have high dielectric constants and high thermal conductivity. These favorable characteristics led PCBs to be used in a wide variety of applications, including coolants and lubricants in transformers and capacitors. PCBs also were used as reactive flame retardants, plasticizers in paints, structural additives, and even as water-proofing agents due to the hydrophobic nature of the molecule. The use/production of PCBs was eventually banned in 1979 by the US Environmental Protection Agency (EPA), due to concerns involving the chemical's possible toxic effects on humans. Unfortunately, even though production was stopped, it did not alleviate the environmental problems caused by PCBs already in use. The very...

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FINAL REPORTS (CONT'D)

characteristics which made PCBs so useful (high thermal and chemical stability) are now the cause for the environmental concern they are generating. Once PCBs have been released into the environment (through regular use and manufacture, transportation of wastes, leaking of hazardous waste sites, leaking of PCB-containing transformers/capacitors, etc...) they are extremely difficult to remediate. In addition, PCBs are capable of being transported great distances through the atmosphere, making them a ubiquitous pollutant found worldwide. PCBs are extremely resistant to chemical, thermal, and biological means of degradation, making treatment of contaminated areas difficult. PCBs are by design hydrophobic and lipophilic, which promotes the buildup of PCBs in animal tissues, including humans.

NASA KSC (in collaboration with Scientific Specialists) has successfully created a technology capable of remediating PCBs in a variety of materials including paints, caulking, adhesives, and concrete. This patented and licensed technology is entitled Activated Metal Treatment System (AMTS), and has been targeted for both in-situ and ex-situ removal/remediation of PCBs from the aforementioned materials. AMTS utilizes zero-valent magnesium which has been activated with a weak acid to reductively dechlorinate PCBs in a protonated solvent. While AMTS has been specifically targeted for application to paints and concrete, reactive chemistry associated with the degradation of PCBs can be applied to the remediation of PCB-contaminated sediments. The major hurdle in such an application is the need to bring the PCBs into contact with the activated magnesium surface. Unfortunately, the remediation of contaminated sediments is a much more difficult task than the remediation of materials such as painted structures. The most commonly used technique for remediation of sediments is to first dredge the contaminated area, and then remove the contaminated sediment and allow it to be disposed of in a landfill. Dredging is not a highly attractive option for PCB-contaminated sediments due to the increased likelihood of re-suspending the contaminants into the surrounding water column during the excavation effort. Once PCBs are re-suspended during an excavation activity, they once again become available to the local benthic community and other aquatic species.

Due to these factors, a more novel approach must be used in order to create a truly successful remediation system. The idea behind this technology is to utilize a two-step process for the removal and degradation of the PCBs. In the first step, a "blanket" of inert material (such as a simple polymer, i.e. polyethylene) would be gently lowered into the water system and pushed into the top layer of the sediments. This "blanket" would act as a PCB "sponge", capable of absorbing the PCBs that are bound in the sediments. The second step would consist of removing the "blanket", extracting the contaminants, and exposing the extracted PCBs to activated zero-valent magnesium in an acidified ethanol solvent to commence degradation. The second step has already been successfully demonstrated in the use of AMTS, which means that the major obstacle to overcome in this research is...

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FINAL REPORTS (CONT'D)

to produce a "blanket" capable of the removal efficiencies necessary to make the technique viable.

The idea to allow for creation of such a system has been captured in a New Technology Report (KSC-13579) for a system entitled Green Removal of PCBs from Sediment Systems (GRPSSs). The "blanket" would have a solid backing to provide a temporary cap to the contaminated sediments, which will prevent/minimize the possibility of contaminant release during the insertion and removal process. Additionally, it would utilize many extruding points, or "fingers", which would depress into the upper ten centimeters of the sediment layer, allowing for increased surface area contact with the contaminated zone. Also, both the "fingers" and the backing of the "blanket" would be hollow to allow for the incorporation of ethanol into the interior. This ethanol interior will provide a major advantage to the GRPSSs. Since PCBs are lipophilic and hydrophobic, they should prefer to dissolve into the ethanol (or similar non-aqueous solvent) if given the opportunity and this system will produce a concentration gradient which enhances the rate of the transport of PCBs across the membrane. Once the PCBs are in the interior of the polymer system, the "blanket" can be removed and the contaminants extracted and treated in the second step described previously. Additionally, the polymer "blanket" would be capable of being re-used multiple times should additional applications prove necessary to remediate the PCBs to acceptable levels at a single site, or to simply treat another contaminated sediment zone.

RESEARCH/DATA

A variety of polymers were initially analyzed for PCB-absorption capacity, which allowed for the best performing materials to be down-selected for additional testing. Testing started in aqueous systems but moved into more complex (but realistic) sediment systems where it was quickly realized that the addition of an ethanol interior would be of primary importance to increase the absorption/transfer of contaminants into the polymers, due to its ability to impart both a solvent reservoir and to produce an inherent concentration gradient within the system. Polymers were initially chosen for contaminant absorption ability; however consideration of materials properties were also an important factor as well. The chosen polymer had to be capable of withstanding insertion into the sediment system, as well as be compatible with the ethanol solvent interior. Testing eventually led to the selection of high-density polyethylene (HDPE) as the polymer of choice. In addition, mechanical properties were evaluated through the use of a 3-D printer which allowed for the rapid production of possible spike and blanket geometries. This capability allowed for rapid and cost-effective evaluation of considerations without the need for multiple expensive molds to be created, as the designs could be produced and manufactured in-house (such as spike geometry). Recent work has focused on the development and design of the polymer blanket system for use in the field, moving beyond simple laboratory-scale testing into more real-world scenarios. A full-scale demonstration unit was designed for testing purposes, and a commercial...

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FINAL REPORTS (CONT'D)

vendor was contracted to produce injection-molded spikes. A total of 18 full-scale units were prepared for initial testing purposes and fully assembled. Initial insertion testing was performed at KSC at a local river to determine the real-life feasibility of the GPRSS technique (as can be seen in Fig. 3). As a result of this initial testing, a method for the automated insertion of the polymer “blankets” was developed which led to the generation of a New Technology Report (NTR).

Based upon the data gathered in the lab, NASA KSC has entered into a Space Act Agreement with a commercial vendor who is willing to test this innovative cleanup system at a contaminated sediments site in the State of Virginia using their internal funding. They have committed up to \$20,000 in assessment costs and testing support in order to propel the technology forward. Initial deployment of the GPRSS technology was successfully accomplished in September 2013 where two separate contaminated zones were treated. Initial analysis of the pre-treatment concentrations is currently underway, and the PCB “blankets” are scheduled to be removed in late November. Analysis of the blankets and post-treatment sediment samples will be performed at that time to determine the remediation efficacy of the GPRSS technology and to evaluate the need (if any) for supplemental treatments.

FUTURE WORK

Remediation of the GPRSS Virginia field site will continue for an additional month, at which point post-treatment analysis will be performed to determine the effectiveness of the GPRSS technology. An abstract has been submitted on the field deployment for the Battelle 9th International Conference on Remediation of Chlorinated and Recalcitrant Compounds which will be held in May 2014. Additional funding for further development and maturation of the GPRSS remediation technology will be pursued from the ESTCP Environmental Technologies Solicitation in January 2014.

Jacqueline Quinn, Ph.D.
Kennedy Space Center
Jacqueline.W.Quinn@nasa.gov

CONFERENCE PAPERS

In-Situ Remediation of PCB-Contaminated Sediments using Polymeric Absorption System:
7th International Conference on Remediation of Contaminated Sediments; Feb 2013, Dallas,...

TECHPORT PROJECT LIBRARY REFERENCES

CONFERENCE PAPERS (CONT'D)

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ABSTRACT (CONTINUED FROM PAGE 1)

environment during the treatment process. Traditional treatment options involve the use of dredging and incineration of the contaminated soils/sediments, in which the chance of releasing of the contaminants is greatly increased. The purpose of this project is to develop a cleanup technology capable of remediating contaminated sediments *in-situ*, with minimal intrusion. This allows for the minimization of any potential contaminant release during the treatment process, providing a safer method for cleanup operations (as opposed to dredging/incineration) and still treating the basic problem of PCB contamination (as opposed to capping).



ANTICIPATED BENEFITS

To NASA unfunded & planned missions: (CONT'D)

and has sponsored previous successful environmental technology development. Customers are world-wide and include owners of any PCB-impacted sediment.

To other government agencies:

PCBs were widely used in coolants, paints, transformer lubricants and in capacitors on government facilities nation-wide due to their favorable thermal and chemical stability. Over the years, these PCBs have leached out into the surrounding environment, to include sediment systems such as river beds, harbors, and lakes. Because of this, there exists a strong need for a technology capable of safely remediating PCB-impacted sediments. The envisioned re-useable, polymer-based PCB-treating GPRSS "blanket system" is capable of performing this function in a cost-effective, environmentally-friendly manner.

To the commercial space industry:

Because PCBs were widely used in coolants, paints, transformer lubricants and in capacitors prior to 1977, they have permeated many industrial settings to include the commercial space industry. The potential application to this industry of the GPRSS technology carries with it many of the same advantages as could be experienced by the government or any private sector application.

To the nation:

PCB contamination is widespread across the U.S. Nearly one-third of all sites on the EPA National Priorities List, which is a list of U.S. sites in most serious need of cleanup (mostly non-federal), have PCB contamination in soils and/or sediments. In addition, the EPA estimates 10% of all sediments in U.S. surface waters (~1.2 billion cubic yards) are so contaminated with chemicals, such as PCBs, that they pose health risks to humans and wildlife. Clean up costs for PCBs in sediment are extremely high. For example, remediation of PCBs in the Hudson River will cost an estimated \$700 million. General Electric, the company responsible for the contamination, has already spent over \$500 million on the project.

EPA and state requirements are driving the market for PCB cleanup in the U.S. Although PCB cleanup represents only a portion of the total remediation market, the overall market size is estimated at \$7.7 billion per year. Over 50 U.S. companies, approximately one in five of all remediation...

ANTICIPATED BENEFITS

To the nation: (CONT'D)

companies, offer services to clean up PCB-contaminated sediments. The remediation industry has historically employed either dredge-and-haul (followed by treatment) or capping methods to address PCB-contaminated sediments. Dredge and haul, which involves removing the sediment, is extremely disruptive to aquatic ecosystems. Capping, which involves placing a barrier such as sand between the contaminated sediment and the water column, does not destroy the PCBs nor does it guarantee long-term containment of contamination. A single flood event has the potential to eliminate any capping protection. The GPRSSs technology offers the a passive, re-usable remediation system capable of removing and degrading the PCBs from the contaminated sediments in a safe and cost competitive manner.





TECHNOLOGY TRANSFER OPPORTUNITY

In Situ Removal of PCBs from Sediment Systems

Scientists at NASA's Kennedy Space Center (KSC) have developed a novel method for the *in situ* removal of PCBs found in sediment systems. The technology consists of a redeployable polymer blanket that attracts and absorbs PCBs.

The Problem

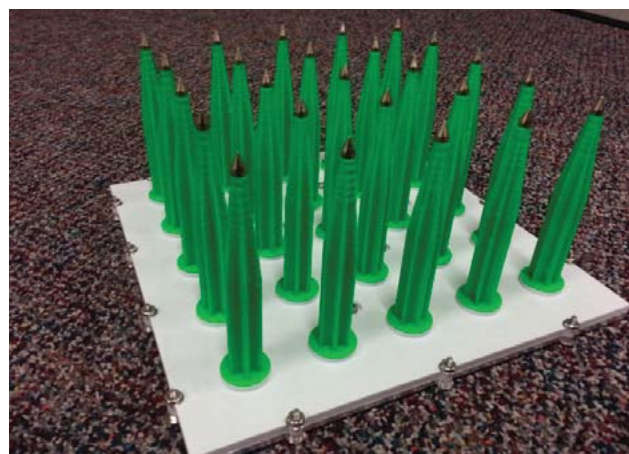
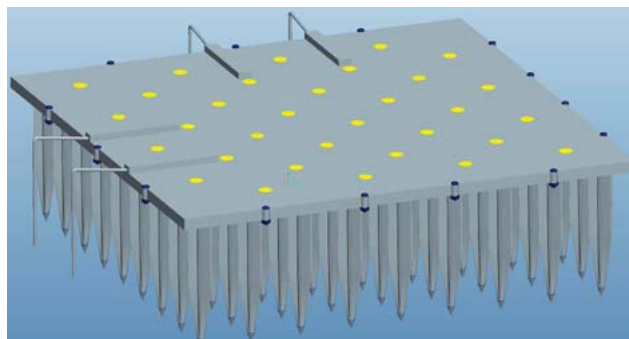
Current methods for addressing PCB contamination in sediments are severely limited. Dredging the sediment and disposing of it in a landfill compliant with the Toxic Substances Control Act (TSCA) is an expensive option with long-term liability implications because it implements a waste transfer remedy rather than a waste destruction alternative. In addition, it is possible for a landfill to reintroduce contaminants into the water table. There is also a high risk of rereleasing PCBs into the water table during the dredging process. Transport and incineration of dredged sediment is costly and requires high-temperature facilities to avoid forming dioxin. Another alternative, sealing contaminated sediment in place using impermeable capping material, does not treat the source of contamination, and it runs the risk of reintroducing contaminants into the local water table if the cap fails.

NASA'S Approach

Seeking to avoid the pitfalls of current methods for handling PCB-contaminated sediments, NASA researchers

developed a two-step approach for removing and treating the PCBs. Step one involves placing a unique polymer blanket filled with an environmentally green solvent (e.g., ethanol) into the contaminated sediment. Projecting into the sediment, the blanket's spikes attract PCBs through the polymer into the solvent until equilibrium is achieved.

Step two consists of removing the blanket from the sediment, followed by extracting the now PCB-laden solvent from the blanket. Following extraction, the solvent is treated *ex situ* using a derivative of a patented NASA PCB treatment technology (Activated Metal Treatment System) to break down the PCBs into benign by-



products. The blanket can then be decontaminated, refilled with fresh solvent, and deployed again.

The Design

The invention is designed to be deployed in individual rectangular segments that can be hooked together to form a blanket. The bottom piece of a segment is molded from polymer and contains numerous hollow star-shaped spikes. Metal tips can be added to the spikes to help penetrate the sediment. The top piece of the segment is solid, except for a hermetically sealed opening through which the solvent is introduced into and extracted out of the segment. Gaskets on edges of the top and bottom pieces of a segment provide a hermetic seal when the pieces are fastened together. The blanket is designed so that if one segment develops a leak, the solvent loss is limited to that one segment.

Laboratory Testing

Initial lab studies focused on determining how well various polymers handled PCB absorption. Using PCB-spiked sediment vials, experiments carried out over several months determined that certain polymers (butyl rubber, Norprene, gum rubber/foam) were better at removing PCBs. Follow-up studies were conducted to determine if PCB removal could be increased by using an interior solvent. Researchers determined that such a solvent opens the polymer lattice for easier transport as well as extends the concentration gradient and increases the capacity for storage of PCBs. One study showed Nitrile polymer filled with acidified ethanol recovered ~70% of the PCBs (see chart below).

Sample ID	% PCB Removal	
	3 Weeks	7 Weeks
Nitrile Glove A	19.19%	66.13%
Ethanol Interior A	4.99%	2.47%
EtOH Interior + Glove A	24.18%	68.61%
Nitrile Glove B	19.42%	70.13%
Ethanol Interior B	4.34%	2.49%
EtOH Interior + Glove B	23.76%	72.62%

Demonstration Units

KSC scientists developed small-scale test demonstration units to test the invention's mechanical functioning and physical properties before producing a high-cost mold. Initial testing using river sediment helped determine how various spacing between spikes (2.0, 1.75, and 1.5 inches) would affect the amount of force needed to insert the blanket into the sediment. As expected, the direct force required to insert the test blankets increased as the spacing between spikes was decreased. Testing also revealed that gentle vibration of the blanket greatly reduces the amount of force required for insertion.

Field Testing

Small-scale field testing of prototype blankets is planned for the summer of 2013. This effort will examine the initial PCB extraction efficiency of the polymer blankets, whether the blankets can be reused, and how effectively they remove PCBs when used multiple times. KSC will also test the effectiveness of the derivative PCB treatment technology in treating the extracted PCB-laden solvent.

Partnership Opportunities

NASA's Kennedy Space Center is offering licensing or partnering opportunities in the development and commercialization of this innovative remediation technology. If your company is interested in the Green PCB Removal from Sediment Systems (GPRSS) technology, please make reference to Case Number KSC-13579 and contact:

Lew Parrish
Technology Transfer Office
Mail Code: ESC-22
Kennedy Space Center, FL 32899
Telephone: (321) 867-5033
Fax: (321) 867-2050
Lewis.M.Parrish@nasa.gov
Website: <http://technology.ksc.nasa.gov>

National Aeronautics and Space Administration

John F. Kennedy Space Center
Kennedy Space Center, FL 32899
www.nasa.gov/centers/kennedy

www.nasa.gov

