In-situ Treatment of Mirror Lake Sediments to Reduce Uptake of Pollutants in the Food Chain

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1. EXECUTIVE SUMMARY

The St. Jones River has been contaminated from various historic sources of industrial pollutants from the watershed. Elevated concentrations of polychlorinated biphenyls (PCBs) in fish collected from the Saint Jones system first led to the issuance of a fish consumption advisory in 1988. Although PCB production was banned in the 70's and concentrations in environmental media are decreasing over the years, the rate of decrease is slow and recovery is expected to take many more decades based on current model predictions. Therefore, the Delaware Department of Natural Resources and Environmental Control (DNREC) is currently working with the City of Dover to evaluate alternatives for enhancing Mirror Lake in Dover, Kent County, Delaware.

Conventional approaches for remediation of contaminated sediments include isolating contaminated sediments (capping), or removing contaminated sediments from the environment (dredging) followed by disposal in an off-site hazardous waste landfill. However, both dredging and conventional capping have severe limitations such as the need for large-scale material handling, high cost, and disruption of existing ecosystem. A recent development in sediment remediation involves amending contaminated sediments with strong sorbents like activated carbon to reduce the bioavailability of toxic chemicals. Recent work in estuarine and river systems has demonstrated that uptake of PCBs can be greatly reduced by the amendment of activated carbon into sediments at a dose of 3-5% by weight. This proposal provides a background of the new technology, and a scope of work to apply the carbon amendment technology in the Mirror Lake system that can achieve reduction of pollutant uptake in the food web along with the planned ecological restoration effort being designed for the lake.

This proposal is focused on the submerged area shown in Figure 4 covered by Mirror Lake (141,509 sq. ft, shown in blue) and the channel between Loockerman Street and the wooden weir structure below Court Street (70,942 sq. ft. shown in purple). The main objectives of the proposed project include:

1) Reduction of the concentration of PCBs and mercury in fish so that consumption advisories can be relaxed or lifted;
2) Reduction of bioavailability of PAHs, PCBs, and mercury in Mirror Lake sediments to minimize ecotoxicological impacts on benthic and aquatic organisms; and
3) Restoration of the ecosystem with minimal off-site transport of contaminated media

The overall approach will involve diversion of flow to drain Mirror Lake using a temporary Porta-dam structure, re-grading sediments within Mirror Lake to create a sinuous channel with adjacent inter-tidal wetlands, integration of activated carbon in the top layer of the sediments to reduce residual contaminant bioavailability, removal of diversion structures, and monitoring over several years to evaluate remediation performance. The dose of activated carbon based on previous experience is 0.7 lb/sqft resulting in a total amount of 150,000 lb activated carbon for the treatment area. The cost to implement this proposal is $551,000. This includes: overall project planning and management; rental of the Porta-dam structure; purchase of activated carbon; monitoring the environment both before and after the application of carbon in order to evaluate the effectiveness of the remedy; and report preparation/data interpretation. This cost does not include preparation of engineering plans and specifications, processing of permits, purchase of wetland plants, and construction.

The primary criteria for the evaluation of remediation performance will be the reduction of PCB levels in fish caught in Mirror Lake. The goal is to reduce PCB concentrations in fish to allow lifting or easing of the current consumption advisories. Additional monitoring of upstream and downstream PCB total loads (suspended and dissolved) will provide an indication of the extent of ongoing sources of PCBs to Mirror Lake and whether the lake is serving as a source of PCBs or a trap of PCBs in the larger St. Jones River system pre- and post-remediation.

2. INTRODUCTION

The Saint Jones River and Mirror Lake became contaminated with polychlorinated biphenyls (PCBs) and a range of other toxic organics and metals as a result of releases from land-based sources within the watershed. The majority of the release occurred prior to strong Federal and State regulatory controls on PCBs beginning in the late 1970s. Release from upland sources has diminished since that time. This "peak and decline" is revealed through the analysis of deep sediment cores collected within the tidal waters of the Saint Jones watershed (Sommerfield, 2005; Velinsky, et. al., 2007). Despite the improvements, PCB levels are still high enough in the surface sediments and water column to cause elevated fish contamination. Elevated concentrations of PCBs in fish collected from the Saint Jones system first led to the issuance of a fish consumption advisory in 1988. Subsequent testing of water, sediment, and biota indicates that the PCB problem persists. Although having a fish advisory is expected to reduce the public's exposure to PCBs through voluntary avoidance, a fish advisory does not, in itself, eliminate the problem. PCBs continue to enter the Saint Jones system, albeit at lower loading rates than in the past. Further, PCBs already in the system from past releases will continue to exchange between the sediments and overlying water column. Because of the persistence of PCBs in sediments, exposure to the aquatic organisms will continue for years even if all of the remaining upland legacy sources could be eliminated. Thus, some intervention is necessary to address the exposure from legacy pollutants in sediments and shorten the time required for improvement in the fish tissue levels through natural attenuation, with the goal of eliminating or at least relaxing the existing fish advisory for PCBs in the Saint Jones. The Delaware Department of Natural Resources and Environmental Control (DNREC) is currently working with the City of Dover to evaluate alternatives for enhancing Mirror Lake in Dover, Kent County, Delaware.

A necessary first step in the remediation effort is the identification, and to the extent feasible, elimination of remaining release of legacy contamination from upland sources. However existing contaminated sediments in the system will continue to serve as a long-term source of bioaccumulative pollutants to the aquatic food web. Dredging of contaminated sediment from Mirror Lake and disposal at an off-site landfill is a possibility. However, dredging has a mixed track record of success, at least at large federal superfund sites (NRC, 2007). Another alternative is capping of the sediments with clean material to isolate the contamination. This option can also have its downsides including adding additional sediment to water bodies often already clogged with excess sediment, and significantly impacting the existing benthic community from burial under a cap. A third alternative is monitored natural attenuation to observe and wait for natural recovery of the site. However, preliminary modeling suggested that one may have to wait for several decades to see significant reduction in contaminant levels in fish in Mirror Lake.

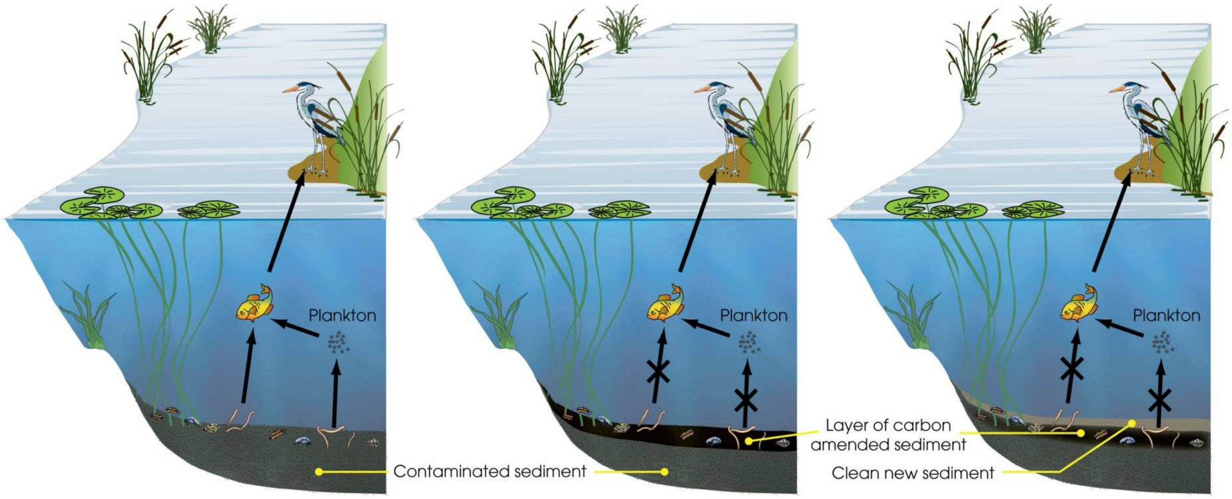
A recent development in sediment remediation involves amending contaminated sediments with strong sorbents like activated carbon to reduce the bioavailability of toxic chemicals (Ghosh et al. 2011). Recent work in estuarine and river systems has demonstrated that uptake of PCBs can be greatly reduced by the amendment of activated carbon into sediments at a dose of 3-5% by weight (Cho et al. 2010, Beckingham et al. 2011). This proposal provides a background of the new technology, and a scope of work to apply the carbon amendment technology in the Mirror Lake system that can achieve reduction of pollutant uptake in the food web along with the planned ecological restoration effort being designed for the lake.

3. BACKGROUND

Remediation of contaminated sediments. Aquatic sediments form the ultimate repositories of past and ongoing discharges of hydrophobic organic compounds (HOCs) such as PCBs, as well as mercury. The cleanup process of contaminated sediment sites pose several unique challenges (USEPA 2005) including: 1) large number of sources, some of which can be ongoing and difficult to control, 2) environment is usually dynamic, and understanding the effect of natural forces and man-made (anthropogenic) events on sediment movement and stability as well as contaminant transport can be difficult, 3) cleanup work in an aquatic environment is frequently costly and difficult from an engineering perspective, 4) contamination is often diffuse and the sites are often large and diverse, 5) many sediment sites contain ecologically valuable resources or legislatively protected species or habitats.

In aquatic environments that are impacted by contaminated sediments, risk management strategies focus on interrupting potential exposure pathways by which contaminants might pose an ecological or human health risk over time. Conventional approaches achieve this goal by isolating contaminated sediments (capping), or removing contaminated sediments from the environment (dredging) (NRC, 1997). However, both dredging and conventional capping have severe limitations such as the need for large-scale material handling. In the case of dredging, these materials can be contaminated and require off-site transport. Dredging and capping are costly and tend to be largely destructive of the native benthic environment.
Dredging often has difficulty achieving risk reduction goals (i.e., low sediment contaminant concentrations) due to sediment suspension and redeposition during dredging. Off-site placement also tends to be problematic both because of the large-scale sediment handling requirements, and because the contaminated media is simply relocated, and contaminants are neither destroyed nor permanently sequestered. Sediment caps tend to be several feet thick in order to ensure cap stability and to minimize the potential for contaminant breakthrough over time. Such thick caps can alter surface water hydrogeology and significantly impact the benthic environment. In some regions, capping may be challenged by restrictions on filling natural water bodies. Other unresolved issues of sediment capping are the long-term efficiency of caps and their ability to permanently sequester contaminants, maintenance requirements, enhanced contaminant advection due to wave and tidal pumping, and organisms that can burrow into the caps and impair their efficacy. These challenges have led to new initiatives in developing in-situ approaches of management of contaminated sediments.

In-situ remediation of sediments. Bioaccumulative contaminants in sediment can be taken up by pelagic or benthic organisms through ingestion and dermal absorption, and subsequently passed on to higher organisms and humans as illustrated in Figure 1. For both of these pathways, the uptake exposure depends on the bioavailability of contaminants in sediment (Luthy et al. 1997; NRC 2003). Work in the last two decades has demonstrated that black carbonaceous particles in sediments such as soot, coal, and charcoal very strongly bind HOCs, and their presence in sediments (both natural and anthropogenic) reduces exposure (Ghosh et al. 2000), often by one order of magnitude or more compared to natural organic matter. “Natural” contaminant sequestration in native carbonaceous particles can be greatly enhanced by the addition of clean, manufactured carbonaceous materials into sediments, such as activated carbon (AC) as illustrated in Figure 1 (Ghosh et al. 2011).



Legacy contaminants in exposed sediment contaminate the food chain through bioaccumulation in benthic organisms, flux into the water column, and uptake in the pelagic food web.

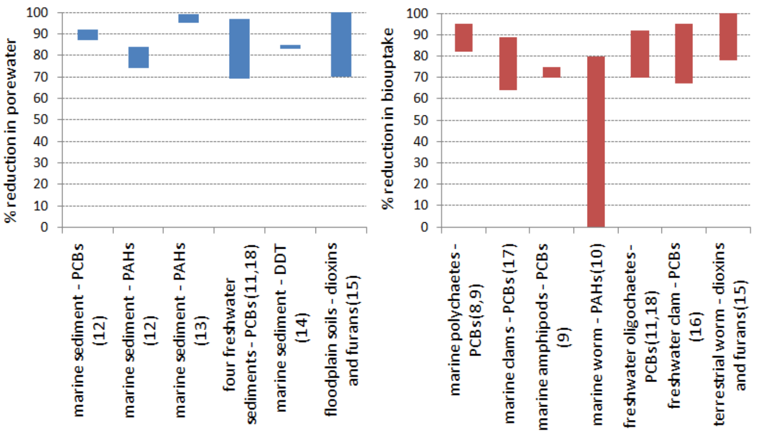
Activated carbon amended to surficial bioactive sediments reduces contaminant exposure to food chain through reduced bioaccumulation in benthic organisms and reduced flux into water column and uptake in the pelagic food web.

In the long term (>5 years), the carbon amended layer is covered with clean new sediment deposit and continues to serve as a barrier to the release of legacy contaminants to surficial sediments and water column.

Figure 1*. Conceptual model of how sorbent amendment of sediment reduces contaminant exposure pathways of benthic organism accumulation and flux from the sediment bed. (Ghosh et al. feature article, ES&T 2011).*

Laboratory tests with contaminated sediment aged over decades in the field show proof-of-concept through reductions in HOC bioavailability (Figure 2). Tests with a range of field sediments showed that AC amendment in the range of 2-5% reduces equilibrium porewater concentration of PCBs, PAHs, DDT, dioxins, and furans in the range of 70-99%, thus reducing the driving force for the diffusive flux of HOCs into the water column and transfer into organisms. Most of the studies using benthic organisms show a reduction of biouptake of HOCs in the range of 70-90% compared to untreated control sediment (Figure 2). These studies have been generally successful in demonstrating that contaminant bioavailability in sediments can be altered by engineered amendments.

Figure 2*. Percent reduction ranges of aqueous equilibrium concentration and contaminant biouptake in different laboratory studies of activated carbon amendment to sediments and soils from the field. These studies range from freshwater to marine sediments and cover a wide range of benthic organisms. The dose of activated carbon used in these laboratory experiments typically ranged from 1-5 % by dry sediment weight (Ghosh et al. 2011).*



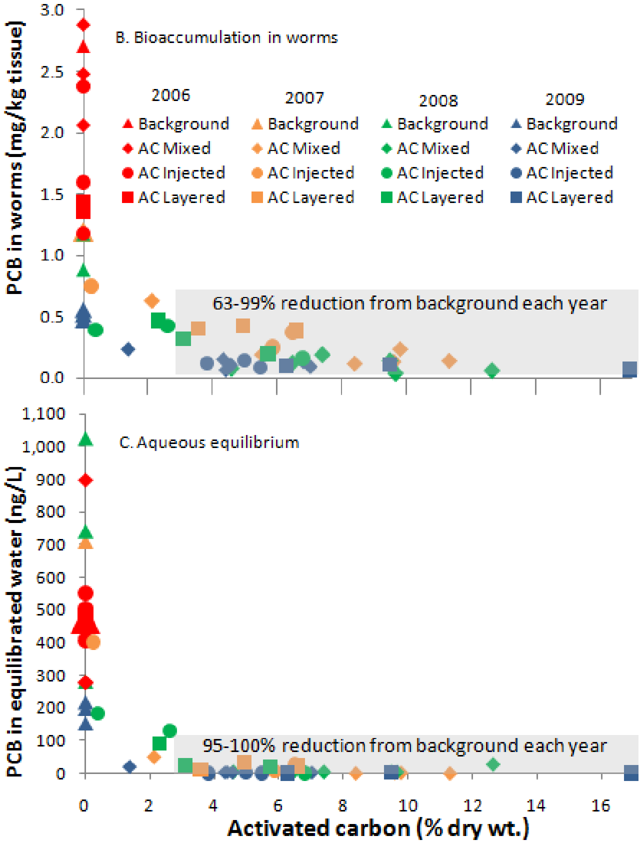


***Figure 3.** Effect of activated carbon dose achieved in sediments in the field treatment plots on bioaccumulation in worms (top) and aqueous equilibrium concentration (bottom) in each year show increasing effectiveness with dose.*

Grasse River Activated Carbon Pilot Study. The field site for this study was the lower Grasse River in NY which has been impacted by historic releases of PCBs from an industrial facility and is currently under a fish-consumption advisory. Total PCB concentrations in sediments in the study area were measured in the range of 2.1 to 3.9 µg/g dry wt. In 2006, granular activated carbon (particle size: 75-300 µm) was added to sediments at a target dose of 3.75% by dry weight as a slurry by three modes of amendment: 1) mixed (using an enclosed tilling device), 2) layered (without mixing), and 3) injected (injection into surficial sediments using two rows of hollow tines). An upstream background area did not receive any carbon amendment and served as a control site. Monitoring of effectiveness carried over four years at several sites within each treatment area included sediment distribution of activated carbon, bioaccumulation from sediments in a freshwater oligochaete worm, *Lumbriculus variegatus*, and measures of aqueous equilibrium, a surrogate for direct pore water measurements. Compared to baseline bioaccumulation measurements at each site, total PCB concentration in worms from sediment exposures in 2009 were reduced by 85-97% (field exposures) and 89-98% (laboratory exposures) in sites where the AC was mixed with the sediment (Figure 2). Similar bioaccumulation reductions were observed at the layered application sites (92-96%), and injection application sites (90-96%). Aqueous equilibrium concentrations were reduced by more than 90% compared to background sites for all treatment sites receiving AC at the target dose or higher. Reduction in equilibrium aqueous PCBs demonstrates the effectiveness of activated carbon amendment to reduce pore water concentrations, and subsequently the driving force for diffusive flux of PCBs from sediments to the water column. Measures of success evaluated in this study were PCB uptake pathways to fish such as sediment porewater, PCB release into the water column, and accumulation in benthic organisms.

Amendment with AC will be most effective at sites that are depositional in nature, less prone to sediment erosion, where native bioavailability of contaminants is high, and ongoing contribution from upstream and terrestrial sources have been controlled. AC amendment provides several advantages over traditional remediation methods, including less disruption to benthic habitats in sensitive rivers and wetlands, amenability to shallow or constricted locations, and potential for lower cost.

Potential impact of activated carbon on benthic organisms. The effect of activated carbon amendment on benthic organisms has been evaluated in several laboratory and field experiments. Activated carbon itself is not toxic and does not release any toxic chemicals and is used widely in drinking water treatments, aquarium filters, and as an antidote to human poisoning. However, addition to sediments may have some unintended ecological effects. While some studies in closed laboratory systems observed low organism survival at high carbon doses, especially when administered in the powered form (Jonker et al., 2009), other studies of activated carbon amendment in the granular form directly into sediments observed little impacts on benthic organisms (Sun et al. 2007, Cornelissen et al., 2006). Most importantly, field studies have demonstrated no impact on benthic community in activated carbon treated sediments (Cho et al., 2009).

4. PROPOSED REMEDIATION AT MIRROR LAKE

4.1. Contaminants in Mirror Lake and their relationship to fishing advisories and ecological risk to benthic aquatic life. The St. Jones River is plagued by contaminant issues from various historic sources throughout the watershed. As a result, fish consumption advisories have been issued for the entire Saint Jones River, including Mirror Lake, for PCBs, dioxins, and mercury (DNREC, 2011). PCBs are thought to be the primary risk driver associated with consumption of fish from the River and Mirror Lake. Therefore, a major focus of the proposed study will involve assessing the tracking of PCB fate and biouptake in Mirror Lake pre- and post-remediation. The average total PCB concentration in the surface sediments (0-2”) of Mirror Lake measured in 2004 was 144 ng/g dry weight (ppb dw), while the average in the subsurface sediments (>2”) was 478 ppb dw (Greene, 2011). Based on modeling forecasts, Greene (2011) predicts it will take 30 to 50 years for the concentration of PCBs in Mirror Lake fish to drop to the point where an advisory will no longer be needed. Indeed, one of the primary reasons that DNREC is considering carbon sequestration is to reduce that time horizon.

In addition to the fish contamination problem, polyaromatic hydrocarbons (PAHs) are also at levels in the sediments of Mirror Lake that represent a risk to aquatic life that reside in and on the sediments (Cargill, 2010). The average total PAH concentration in the surface sediment of Mirror Lake is 45,800 ppb dw and the average in the subsurface sediments is 10,310 ppb dw (Cargill, 2010).

This proposal is focused on the submerged area shown in Figure 4 covered by Mirror Lake (141,509 sq. ft, shown in blue) and the downstream channel from Loockerman Street down to the wooden weir structure (70,942 sq. ft. shown in purple). The area downstream of the wooden weir structure (shown in green) is also known to be contaminated (Velinsky, et. al., 2007) but that area is beyond the immediate scope of this proposal. DNREC has reached out to the U.S. Environmental Protection Agency (EPA) to explore possible collaboration on a sediment remediation project in that part of the Saint Jones River as part of the Dover Gas Light Superfund Site.

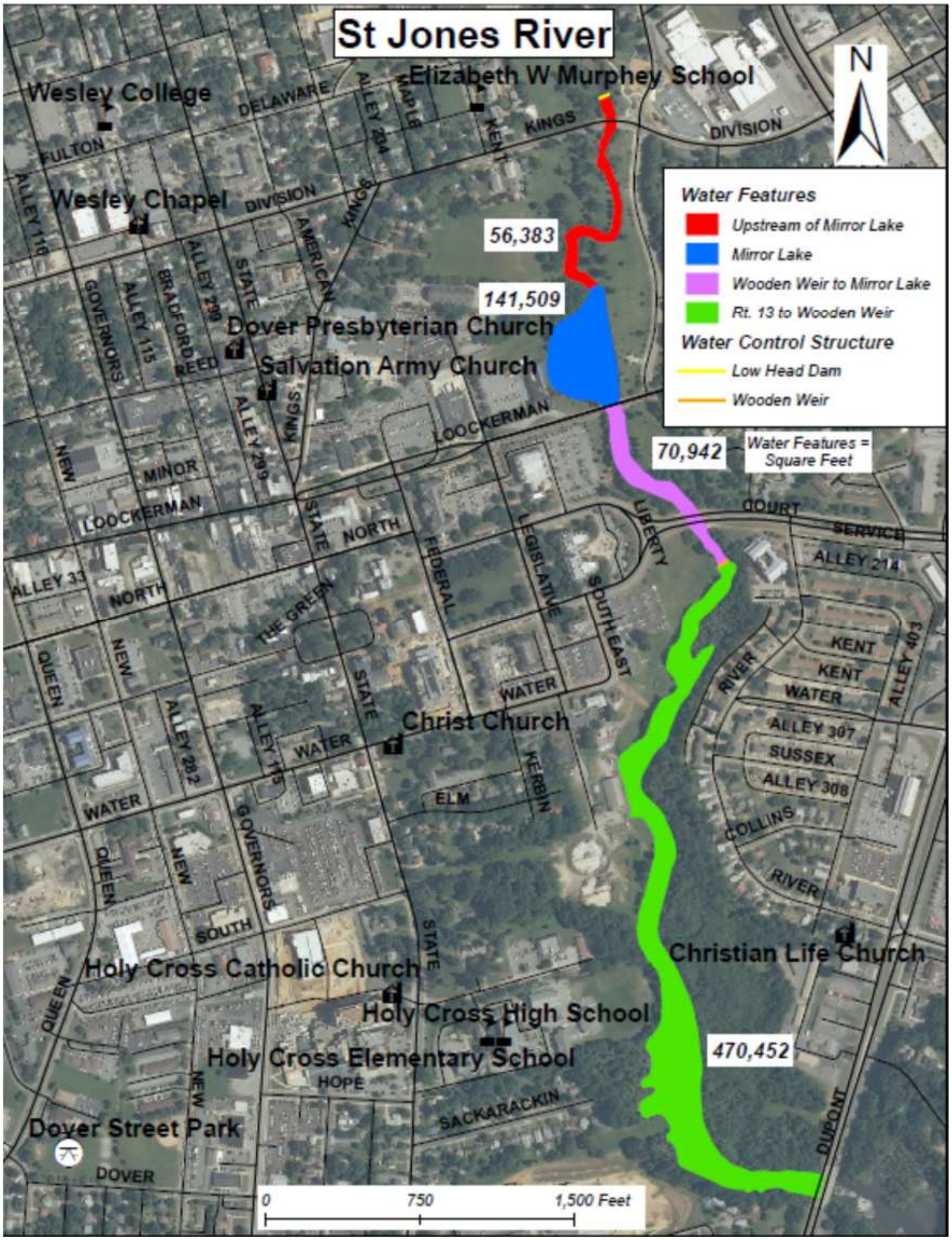


Figure 4. *Proposed remediation area for carbon sequestration. The area to be treated with activated carbon includes Mirror Lake (shown in blue) and the Saint Jones River between Loockerman Street and the wooden weir structure downstream of Court Street (shown in purple). The area in red is hard bottom, is not expected to accumulate contaminants, and will not be treated with carbon. The area in green has elevated contaminants in sediments but is beyond the scope of this proposal.*

4.2. Remediation objectives.

The main objectives of this remediation effort include:

1) Reduction of the concentration of PCBs and mercury in fish so that consumption advisories can be relaxed or lifted;

2) Reduction of bioavailability of PAHs, PCBs, and mercury in Mirror Lake sediments to minimize ecotoxicological impacts on benthic and other aquatic organisms; and

3) Restoration of the ecosystem with minimal off-site transport of contaminated media

The overall approach will involve diversion of flow to drain Mirror Lake using a temporary Porta-dam structure, re-grading sediments within Mirror Lake to create a sinuous channel with adjacent inter-tidal wetlands, integration of activated carbon in the top layer of the sediments to reduce residual contaminant bioavailability, removal of diversion structures, and monitoring over several years to evaluate remediation performance. Several tasks are involved in carrying out this restoration effort and are detailed below.

4.3. Task 1: Obtain necessary permits for the restoration project.

The Mirror Lake restoration project will need several Federal and State permits. We have made preliminary contact with the Philadelphia District Office of the US Army Corps of Engineers to discuss the project and have tentatively determined that Nationwide Permit 27 (Aquatic Habitat Restoration, Establishment and Enhancement) and Nationwide Permit 38 (Cleanup of Hazardous and Toxic Waste) may both be needed for this project. Since the Mirror Lake is not considered a Critical Resource Water, the two nationwide permits do not require the State to issue Water Quality Certification or Coastal Zone Consistency determinations. However, the project will require a State Subaqueous Lands Permit (issued by DNREC) and a Sediment and Erosion Control Permit (issued by the Kent County Conservation District).

To support the permit applications, detailed design plans will be prepared for the project. The plans will include a site survey, pre- and post-construction cross-sections, a longitudinal profile of the channel, cut and fill quantities, construction sequence, unit quantities of materials, location of construction entrance, LOD, location of temporary structures and equipment needed to dewater Mirror Lake, types and locations of “hard” and “soft” restoration structures, and types of locations of wetland plantings. The design plans and permit applications will be prepared by a separate DNREC contractor with close oversight by DNREC personnel. The design costs are not included in this proposal.

It is important to note that the Mirror Lake Project is immediately downstream from another stream restoration project that is just getting underway. That project is located between the dam at Silver Lake and Division Street and involves stream bank stabilization and other enhancements. The Mirror Lake project would extend the benefits associated with restoration further downstream in the Saint Jones watershed.

4.4. Task 2: Detailed monitoring of contaminant levels in sediment, water, and biota.

Past work has evaluated levels of contaminants in sediment, water and fish in the Mirror Lake (DNREC 2011). However, much of the data are from more than seven years ago. So, there is a gap in the understanding of the current levels of pollutants in the surficial sediments, water, and fish. To evaluate performance of the remediation effort, it is important to have a more current and accurate understanding of the level of pollution. The following measurements are proposed in early fall of the year of application.

i) PCBs in fish and a representative worm (possibly an oligochaete). Resident fish samples will be collected from Mirror Lake in the Fall of 2012 or 2013 before initiation of remedial activities. Largemouth bass, catfish, and crappie are present in Mirror Lake, have small home ranges, are easy to catch, and are moderate to high in the aquatic foodchain. Depending on availability, one of these species will be used to monitor PCB levels in adult fish. To account for trophic transfer, we will also collect and analyze small (prey) fish and benthic organisms (as described below). The common mummichog *Fundulus heteroclitus* is expected to be present in sufficient numbers but we will consult with local fisheries experts on alternative prey species. We propose to collect 3 composite samples of large fish and 3 composite samples of prey fish from Mirror Lake prior to remediation. In addition to the fish species, grab samples of sediment will be collected from 10 locations within the lake and sieved to collect native benthic organisms, preferably an oligochaete. At least 1g quantity of worm tissue will be collected from each location for PCB analysis in the laboratory. If native worm abundance is not sufficient, the sediment samples will be used for laboratory bioaccumulation studies as described in Beckingham et al. (2010).

To account for possible contaminant transport into Mirror Lake, both an upstream control site (upstream of Division Street) and a downstream control site (below the wooden weir near Court Street) will also be monitored prior to remediation. We propose to collect 1 large fish composite sample and 1 small fish composite sample at both the upstream control site and the downstream control site. Our goal is to retain the same fish species from the two control stations and Mirror Lake.

ii) PCBs in surficial 4" of sediment. Sediment samples will be collected using a petite ponar from 10 locations evenly distributed in Mirror Lake. Surficial sediment samples will be collected before the application, and 1, and 2 years after the application. In addition, one set of surficial sediment samples will be collected after re-grading the surface and immediately before AC amendment to evaluate changes in PCB levels in sediment from the pre-application condition. These sediment samples will be analyzed for PCBs.

iii) PCBs in surface water and sediment porewater. PCBs in surface water and sediment porewater will be measured in the field using in-situ passive samplers. The passive samplers in sediment and water column will be located at the five sites where worms will be collected. In addition, two passive samplers will be positioned in the upstream and downstream channels to monitor the concentration of dissolved PCBs entering and leaving the lake. The method of passive sampling is described in the appendix.

iv) PAHs in sediment porewater. PAH concentration in surficial sediments of Mirror Lake are elevated. The primary concern from PAHs in these sediments is toxicity to benthic invertebrates. Recent work by Hawthorne et al. (2006) has demonstrated that PAH toxicity to benthic invertebrates can be directly related to sediment porewater concentrations. In-situ porewater PAH concentrations will be measured using similar passive samplers used for porewater PCB measurement.

v) Total PCBs in water column entering and leaving Mirror Lake. Loading of PCBs to the Lake from upstream and export of PCBs downstream will be monitored before and after the remediation to better understand recovery with time. These measurements will be performed using traditional large volume water sampling, filtration of suspended solids on a filter paper, and capture of dissolved PCBs in an adsorbent resin trap as described in the appendix. Duplicate samples will be collected once in the summer and once in fall. Stream velocity will also be measured during the water sampling events to keep track of changes in suspended solids load as a function of river flow.

4.5. Task 2: Draining of Mirror Lake, re-grading to shape and deepen river channel and create tidal wetlands.

Mirror Lake is subject to base flow and stormwater flow from the upper part of the Saint Jones watershed and tidal flows from the lower part of the watershed. How to manage those flows and dewater Mirror Lake are important considerations. When to dewater Mirror Lake is also an important consideration. As planned, the dewatering work is to be carried out in November of 2012 or 2013, after permits and funding have been secured and after baseline sampling has been completed. November is the best time to perform the work because: i) it avoids the peak of the Atlantic hurricane season (Greene, 2012); normal base flow in the Saint Jones watershed is still relatively low (see Figure 5); iii) it avoids spawning runs of fish; (iv) local recreational fishing activity is tapering off by then; and v) new wetland plantings will experience less heat stress at that time of year.

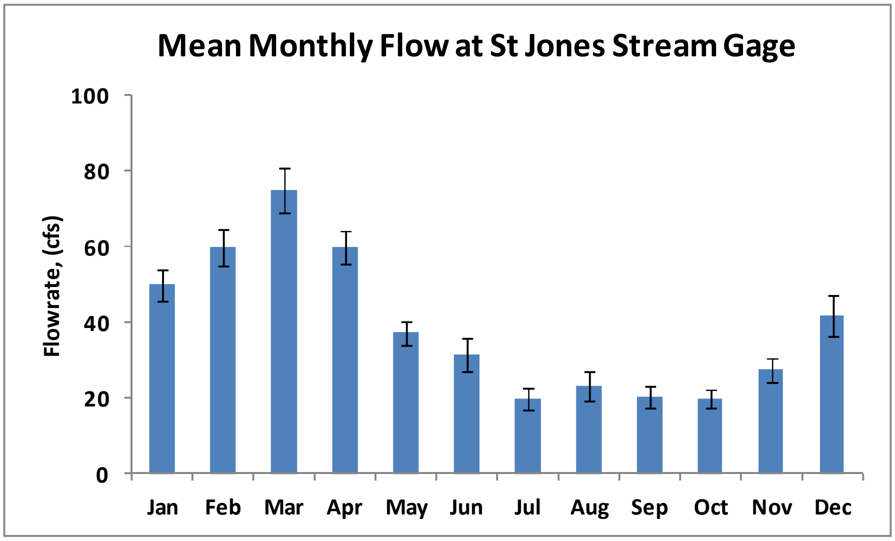


Figure 5. *Mean monthly flow of St. Jones River.*

To minimize the amount of base flow and potential storm water entering Mirror Lake, the water level in Silver Lake, upstream of Mirror Lake, will be drawn down prior to the start of the Mirror Lake project. This will be done by opening a gate in a control structure located immediately upstream of the Silver Lake dam. Opening the gate will allow large volumes of water to be released from discharge pipes located at the base of the dam, thereby lowering the water level in Silver Lake. After the water in Silver Lake is drawn down several feet, the gate in the control structure will be closed and work will begin in Mirror Lake shortly thereafter. The drawdown will provide a buffer against large surges of storm flow being delivered downstream to the Mirror lake project area during construction.

To prevent tidal water from flowing upstream into Mirror Lake during construction, a temporary Porta-dam structure will be placed in Mirror Lake parallel to the Park Drive side of the Lake, approximately 50 feet off shore (Figure 6). This will leave a temporary channel on the Park Drive side of Mirror Lake to allow for water to move upstream in response to tidal forcing and downstream in response to base flow and storm flows. Once the Porta-dam is in place, water in the main part of Mirror Lake will be drawn down using large capacity pumps and sumps. This dewatering operation is expected to take a few days based on preliminary pumping calculations. Although we had considered dewatering the Saint Jones River downstream of Mirror Lake between Loockerman Street and Court Street using a Porta-dam, close examination of the physical constraints in that reach lead us to abandon the idea. We will still be able to incorporate activated carbon into the sediments in that reach, but the carbon will need to be broadcast on top of standing water (to be described in Section 4.6 Task 3).

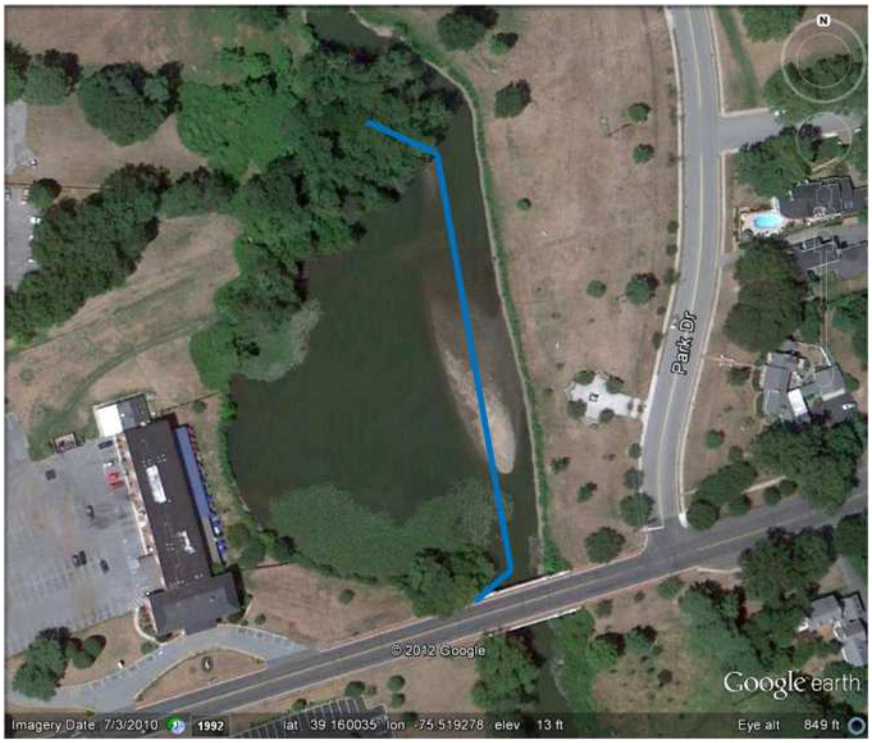


Figure 6. *Proposed placement of Porta-dam structure to isolate a major portion of Mirror Lake for restoration.*

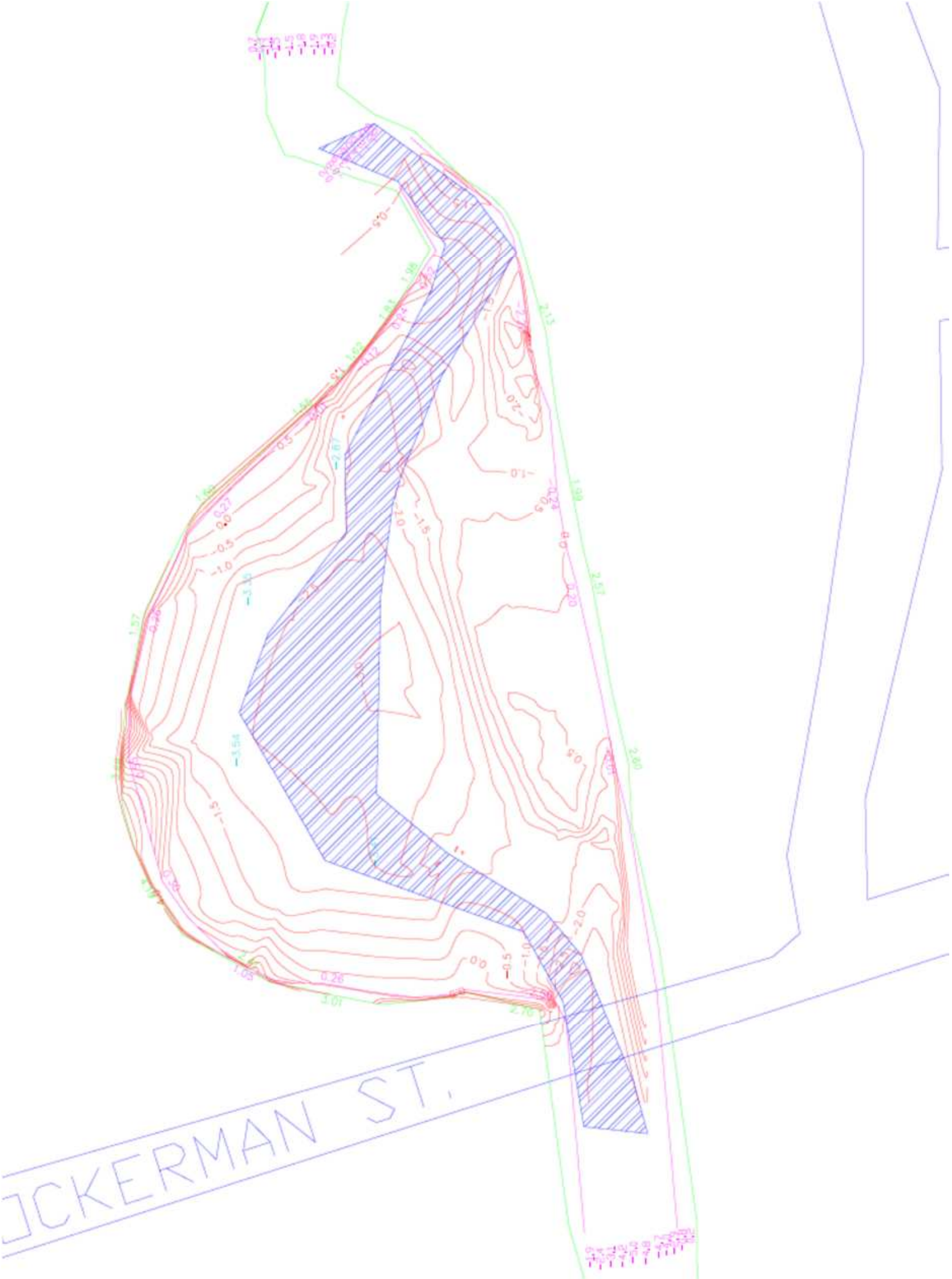


__Figure 7__. Bathymetry map of Mirror Lake

Once Mirror Lake is dewatered, surface sediments within Mirror Lake will be re-graded on either side of the original main channel (shown in blue in Figure 7) to create intertidal wetland zones with native plantings. Before the plantings go in however, the new intertidal areas and the channel will be treated with activated carbon. If necessary, the new intertidal areas will also be covered with appropriate fill. This will provide the substrate needed for the plantings and prevent erosion of contaminants sequestered in the sediments below.

This effort will restore Mirror Lake to a tidal river with a fringing intertidal wetland system. This will complement a larger effort in the Saint Jones River system to restore and enhance aquatic habitat, reduce pollutant outflows, meet TMDL requirements, and beautify the landscape. Although not an intrinsic part of this proposal for in-situ remediation of pollutants, work proposed in this document will need to be coordinated with this larger ecosystem restoration effort described in Tasks 2.

4.6. Task 3: Addition and blending of activated carbon on the top 4” of recreated wetland bed and river channel.

After sediment re-grading and filling are completed to achieve the desired profile, activated carbon will be incorporated into the top 4” of sediment. The total area to be treated with activated carbon is 212,451 sq ft, which includes Mirror Lake (141,509 sq ft) and the downstream channel between Loockerman Street and the wooden weir structure (70,942 sq ft).

i) Dose of activated carbon to be added. Based on previous experience with AC application in sediment sites, a recommended dose of activated carbon is 5% of sediment dry mass in the top 4” of sediment layer. Making an assumption of dry bulk density of sediment of 0.5kg/L, the areal dose is 3.1kg/square meter or 0.7 lb/square foot.

ii) Type and method of activated carbon amendment and cost. A range of activated carbon types are available for direct application of carbon to sediments. These activated carbons include low cost regenerated carbons and specialized virgin carbons that can be expensive. For the proposed remediation we suggest the following types of carbon application:

a) *Application of AC directly into sediment after dewatering*. For areas in Mirror Lake that can be dewatered and accessed by heavy equipment for re-grading (71,000 sq. ft.), the most economical method of application will involve direct placement of the activated carbon and tilling into the top 4” of surface sediment. The activated carbon can be either made into a water slurry and spread on the sediment surface to achieve the target dosing rate (0.7lb/sq. ft.) or applied in the dry form. Application in a slurry form may be better than dry application to minimize carbon dust generation during application. To achieve a uniform distribution, the treatment area will be divided into segments and a calculated quantity of activated carbon distributed evenly onto each segment.

For this application the most suitable and low cost activated carbon will be regenerated AC made from carbon previously used for drinking water treatment. This type of AC is available from Siemens at a cost of approximately $1/lb plus shipping. Lower cost alternatives are biochars that are not activated. However, the effectiveness in sequestering pollutants is also low in biochars.

Because the placement will be performed after dewatering, the required dose of carbon in this area will be placed all in one time. The total amount of activated carbon required will be 50,000 lb. The anticipated cost of regenerated activated carbon with shipping is $55,000.

b) *Application of AC in pelletized form (SediMite™) in areas that will not be or cannot be dewatered safely*. Another potential application method, especially in areas that do not dewater well, remain soft, and are difficult to operate heavy equipment in, is the use of the commercial product SediMite™. These areas will include approximately half of Mirror Lake where the sediments are known to be soft and fine-grained. (71,000 sq. ft.) and the downstream area between Loockerman St. and Court St. (71,000 sq. ft.). In this application, activated carbon is blended with clay and sand and made into pellets that can be broadcasted on the water surface from a distance. The SediMite™ pellets fall through the water column and deposit on the sediment surface and slowly releases the carbon over time which is integrated into the surficial sediment through natural bioturbation activity (See appendix). Because application of SediMite™ does not require dewatering, it is proposed that the required dose be added in two instances over two years. Splitting the application will allow a more even spatial distribution of the carbon, and allow us to evaluate the effect of the first application before augmenting with another dose. Also, splitting the applications helps spread the cost over two years. The total amount of SediMite™ required for the first application (immediately after re-grading) is 100,000 lb. The anticipated cost for this amount of SediMite made of virgin activated carbon is $200,000. A determination will be made one year after application based on results of carbon analysis of surficial sediments and sediment porewater PCB concentrations if a second dosing of SediMite™ is required for the treated areas.

4.7. Task 4: Removal of diversion structures and evaluation of activated carbon levels in sediments.

After amendment of the sediment surface with activated carbon, the lake will be slowly allowed to fill in with water by opening the control structure at Silver Lake and removing the Porta-dam structure in Mirror Lake. This will have to be managed in a way to minimize any large-scale movement of unconsolidated sediment produced after re-grading and mixing. A key component of success of this remediation effort will involve physical stability of the sediments and amended carbon in the surface layer. Disruption of the surface treated layer will expose contaminated sediments lying underneath. It is expected that sediment movement driven by water flow will be minimal.

After 1 week of resuming flow in the system and allowing the sediments to reach a new stable state, sediment cores will be taken at 5 distributed locations within the lake and 2 points along the channel in the upstream and downstream sections. These sediment cores will be sectioned to measure activated carbon in 0-2”, 2-4”, and 4-10” sections. These measurements will provide us with a starting point for activated carbon distribution within the treated sediments which will be tracked over the subsequent years of sampling to evaluate any erosion or deposition of new sediments in the treated area.

4.8. Task 5: Post remediation performance monitoring.

Success of the remediation will be monitored through detailed assessment of contaminant levels in water, sediment porewater, native benthic organisms, and resident fish in the lake. A major focus will be on understanding fate/transport and bioaccumulation of PCBs. Monitoring will be performed 1-year and 3-years after remediation and will follow the measurements performed in Task 2 for baseline assessment as illustrated in Table 1.

Table 1. Pre- and post- carbon application monitoring.

Monitoring task	**Pre-application baseline**	**After re-grading before carbon amendment**	**1-year after application**	**2-year after application**
1. PCBs in fish (predator and prey)	**X**		**X**	**X**
2. PCBs in worms	**X**		**X**	**X**
3. PCBs in top 4" of sediment	**X**	**X**	**X**	**X**
4. PCBs in surface water by passive sampling	**X**		**X**	**X**
5. PCBs in sediment porewater by passive sampling	**X**		**X**	**X**
6. PAHs in sediment porewater by passive sampling	**X**		**X**	**X**
7. Activated carbon in sediment core samples	**X**		**X**	**X**
8. PCBs in water column entering and leaving lake	**X**			**X**

Selected split samples of sediment and fish tissue will be sent to a commercial laboratory for analysis and confirmation of results from UMBC laboratory. PCB congener analysis will be performed at the commercial laboratory using method 1668 (HRGC/HRMS) on a subset of the pre-application and post-application samples. Roughly 3 fish, 3 bulk sediment, 3 pore water, and 3 water column samples will be analyzed pre-application and the same post-application in the commercial laboratory. Additionally, selected fish samples before and after remediation will be sent to a commercial analytical laboratory for the measurement of Hg and MeHg in fish tissue.

4.9. Task 6. Data interpretation and evaluation of remediation performance.

The primary criteria for the evaluation of remediation performance will be the reduction of PCB levels in fish caught in Mirror Lake. Comparisons will be made of PCB levels in fish tissue before remediation and after 1 and 3 years after remediation. The goal is to see reduction of PCB concentrations in fish to levels that would allow lifting or easing of the current consumption advisories. Several secondary criteria will be assessed to evaluate remedy effectiveness in reducing sediment porewater concentrations of PCBs and PAHs, and surface water concentrations of PCBs. Reduction of porewater concentrations of PCBs and PAHs after remediation will indicate successful containment of the pollutants in sediments and reduction of bioavailability of these chemicals to the aquatic food chain. Additional monitoring of upstream and downstream PCB total loads (suspended and dissolved) will provide an indication of the extent of ongoing sources of PCBs to Mirror Lake and whether the lake is serving as a source of PCBs or a trap of PCBs in the larger St. Jones River system pre- and post-remediation.

5. ANTICIPATED COST OF REMEDIATION WITH ACTIVATED CARBON AMENDMENT AND MONITORING

The primary cost categories for this remediation effort are material cost of activated carbon and SediMite™, cost of application in the field, and monitoring cost. There is some uncertainty in the cost of the application of activated carbon, but some estimates are provided based on calculations done previously for another application. The application cost will need to be finalized by consultation with the chosen contractors. The performance monitoring is proposed to be done at UMBC with selected split samples sent to EPA certified commercial laboratories. It is also anticipated that in-kind manpower support will be provided by DNREC for the field application and also for field sampling efforts.

The costs in this table do not include the preparation of detailed plans and specifications for the overall restoration project, nor incremental costs associated with re-grading, filling, installation of structural and non-structural BMPs, and plantings.

Table 2. Cost itemization for Mirror Lake in-situ remediation project

Porta-dam installation and pumping		$80,000
Thin layer backfill of AC only, no excavation, with tiller mixing		$76,000
Activated carbon cost	*$55,000*	
Broadcast carbon using tractor spreader	*10,000*	
Soil tilling twice using D3 doser with tiller attachment (2x 20 hr @ $200/hr)	*5,000*	
Forklift to move bulk bags of activated carbon	*3,000*	
Decontamination	*1000*	
Spare doser with tiller and tractor	*2000*	
SediMite (100,000 lb)		$200,000
SediMite application cost using a salt spreader on a boat		$10,000
Professional labor management (@ 33% of application costs)		$10,000
UMBC (Planning, data interpretation, initial, year 1 and year 3 monitoring)		$150,000
Commercial lab (selected Initial and long-term monitoring of split samples)		$25,000
TOTAL		**$551,000**

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7. APPENDIX

7.1. Passive samplers. Passive samplers are used as devices that accumulate chemicals of interest from the air or water phase by chemical diffusion into the sampler matrix. Used correctly, such samplers can yield measurements of very low concentrations of hydrophobic organic chemicals that can be extremely difficult to measure directly. Polyoxymethylene-solid phase extraction (POM-SPE) method has been used to measure low aqueous concentrations of PAHs and PCBs in sorption isotherm studies with strong sorbents (Jonkers et al. 2001). Recent work by Cornelissen et al. (2007) developed calibrations for thin POM strips that achieves equilibrium more readily than some of the other SPE devices, and used the approach to measure in-situ porewater and overlying water concentrations of PAHs in Oslo Harbor sediments. Work at UMBC has extended the calibration of the POM samplers for a larger range of PCB congeners (Sun and Ghosh 2008; Hale et al., 2009). The advantages of using passive samplers for water quality analysis include: 1) low cost of deployment and analysis compared to direct water sampling, 2) higher rate of recovery of deployed samplers compared to live organisms, 3) cleaner matrix for PCB analysis compared to water, sediment, or tissue samples, 4) at least an order of magnitude improved detection limits compared to typical large volume water sampling, 5) an integrated measurement of water phase concentration over the period of deployment. Disadvantages include the need for accurate calibration of the passive sampler in the laboratory. Recent deployments of the passive samplers in the field at Grasse River, NY gave values of ambient PCB levels in the water column that were close to independently measured water column PCB concentration measurements (unpublished data). As illustrated below in Figure 4, we find using passive samplers deployed in the field at Grasse River that gradients of freely dissolved PCB concentrations in the field (deeper sediments, sediment-water interface, and overlying water) can be measured directly. A revealing interpretation of such measurements is that for untreated sediments (right side of Figure A1), the driving force for PCB mass transport is from sediment to the surface water, whereas for the small plot treated with activated carbon, the porewater concentrations are depressed due to strong sorption and the direction of PCB flux is reversed where the treated sediments are no longer a source of contamination of the water column. Validation and use of such measurements at the sediment-water interface can provide valuable interpretation on the long-term recovery potential of contaminated sediment sites, especially after in-situ treatment with sorbents.

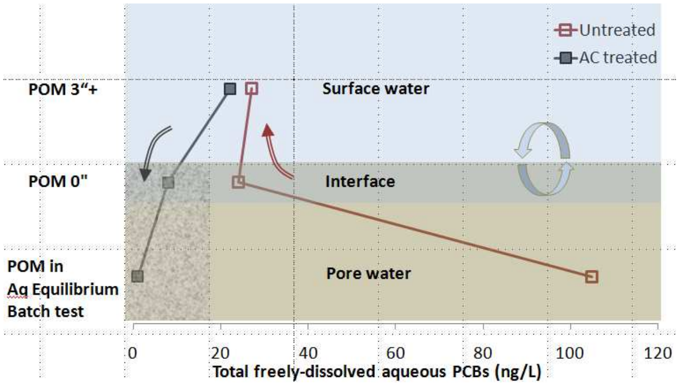

Figure A1. PCB porewater and surface water concentrations measured using passive samplers for Grasse River with and without amendment of activated carbon to sediments in the field as part of a pilot-scale demonstration project. Porewater PCB concentration in treated sediment is depressed reversing the flux from sediment.

7.2. Water sampling for measuring dissolved and suspended solids associated PCBs

The sample collection involves pumping 40-50L of water through a pre-combusted glass fiber filter in a stainless steel filter holder to trap suspended particles followed by passing the filtered water through a XAD-2 resin trap in a glass column. The method is similar to the surface water sampling method used in the EPA Lake Michigan Mass Balance Study (http://www.epa.gov/glnpo/lmmb/methods/field96.pdf). Some modifications will be made to the method to suit the unique field conditions of the sampling. Due to the shallow water over the sampling area, a peristaltic pump will be used to deliver the water to the in-line filter holders and XAD traps. Teflon tubings will be used to collect water samples and will be pre-equilibrated with field water by passing about 5 liters of water before the start of PCB sampling. The inlet of the Teflon sampling tube will be tied to a wooden stake and positioned at 0.5 ft above the sediment surface and will remained submerged under water during sampling. The water sample will be passed through a pre-combusted glass fiber filter paper with a nominal pore size of 0.7 microns, and through a pre-cleaned XAD-2 resin adsorbent column. The filter and resin media will be prepared for sampling following the method used in the EPA Lake Michigan Mass Balance Study (http://www.epa.gov/glnpo/lmmb/methods/). The clean filters will be wrapped in clean aluminum foil and stored in polyethylene bags until used. After sampling, the filter papers will be folded into quarters and stored in clean 8 oz. wide mouth glass bottles with Teflon-lined caps. The ends of the XAD columns will be closed using Teflon-lined nylon end-caps during transport before and after sampling. The filter papers containing suspended particulates and the XAD-2 resin columns containing trapped dissolved PCBs will be shipped in a cooler to the UMBC Chemical, Biochemical, and Environmental Engineering Laboratory for extraction and PCB analysis.

All filters and resin columns will have adhesive labels attached which identified the batch number, sampling site, sample number, date, and time of sampling. Processed samples will be kept chilled in an ice chest until refrigerated in the laboratory. PCB extraction, cleanup, and analysis followed EPA standard methods described below.

7.3. Sample processing and storage at UMBC.

The composite fish samples received from DDNR will be stored in a -20 ^{o}C freezer in a room dedicated for the fish sample storage and processing. The samples will be analyzed for PCBs within a period of 6 months of receiving. The fish samples will be thawed in a refrigerator at 4^{o}C and homogenized in the laboratory in a clean blender (Osterizer 16 speed blender). The homogenized tissue will be divided into 10g portions and stored in 2 oz glass jars with Teflon lined caps and frozen at -20 ^{o}C until analysis. The blender will be cleaned with soap water, isopropanol rinse, and DI water rinse between samples.

Equipment used in processing samples for organics analysis should be of stainless steel, anodized aluminum, borosilicate glass, polytetrafluoroethylene (PTFE), ceramic, or quartz. Polypropylene and polyethylene (plastic) surfaces, implements, gloves, and containers are a potential source of contamination by organics and should not be used. If a laboratory chooses to use these materials, there should be clear documentation that they are not a source of contamination. Filleting should be done on glass or PTFE cutting boards that are cleaned properly between fish or on cutting boards covered with heavy duty aluminum foil that is changed after each filleting. Tissue should be removed with clean, high quality, corrosion-resistant stainless steel or quartz instruments or with knives with titanium blades and PTFE handles. Fillets or tissue homogenates may be stored in borosilicate glass, quartz, or PTFE containers with PTFE-lined lids or in heavy duty aluminum foil. Prior to preparing each composite sample, utensils and containers should be washed with detergent solution, rinsed with tap water, soaked in pesticide-grade isopropanol or acetone, and rinsed with organic-free, distilled, deionized water. Work surfaces should be cleaned with pesticide-grade isopropanol or acetone, washed with distilled water, and allowed to dry completely. Knives, fish scalers, measurement boards, etc., should be cleaned with pesticide-grade isopropanol or acetone followed by a rinse with contaminant-free distilled water between each fish sample.

Composite homogenates should be prepared from equal weights of individual homogenates. The same type of individual homogenate (i.e., either single fillet or combined fillet) should always be used in a given composite sample. If individual homogenates have been frozen, they should be thawed partially and rehomogenized prior to weighing and compositing. Any associated liquid should be kept as a part of the sample. The weight of each individual homogenate used in the composite homogenate should be recorded, to the nearest gram, on the sample processing record (Figure 5-10.) Each composite homogenate should be blended as described for individual homogenates. The composite homogenate may be processed immediately for analysis or frozen and stored at -20 °C. The remainder of each individual homogenate should be archived at -20 °C with the designation "Archive" and the expiration date recorded on the sample label. The location of the archived samples should be indicated on the sample processing record under “Notes”. It is essential that the weights of individual homogenates yield a composite homogenate of adequate size to perform all necessary analyses. The total composite weight required for intensive studies may be less than that for screening studies if the number of target analytes is reduced significantly. The recommended sample size of 200 g for screening studies is intended to provide sufficient sample material to (1) analyze for all recommended target analytes at appropriate detection limits; (2) meet minimum QC requirements for the analyses of laboratory duplicate, matrix spike, and matrix spike duplicate samples; and (3) allow for reanalysis if the QC control limits are not met or if the sample is lost. However, sample size requirements may vary among laboratories and the analytical methods used. Each program manager must consult with the analytical laboratory supervisor to determine the actual weights of composite homogenates required to analyze for all selected target analytes at appropriate detection limits.

7.4. PCB extraction and cleanup in the laboratory.

Ten grams of homogenized fish sample will be used for extraction. The tissue sample will be thawed and dried using 50 g anhydrous sodium sulfate. The mixture will be transferred to a 150 ml glass beaker and surrogate PCB #14, 65, and 166 will be added and and Soxhlet extracted for 24 hours using 1:1 hexane: acetone. The extract will be concentrated to approximately 5 ml using a Buchi Rotavapor R-200 and a nitrogen evaporator, followed by solvent exchange to hexane. Concentrated sulfuric acid will be used for removal of lipids. 5 ml of concentrated sulfuric acid will be added to the sample and vortexed for 1 min and then allowed to stand for at least 1 min for phase separation. If the hexane layer remains colored another treatment with 5 ml of concentrated sulfuric acid will be performed. Two additional volumes of 2 ml of hexane each will be added to the vial and vortexed to ensure quantitative transfer of the PCBs. The pooled volume of hexane will be reduced to 1ml under a gentle stream of nitrogen and then treated with activated copper (EPA SW846 Method 3660B) for removal of sulfur. Further clean-up of the sample will be done using deactivated Florisil.

Florisil (60-100 mesh size) will be activated by baking at 550°C in a shallow borosilicate container for at least 4 hours and then deactivated by adding 2.5% by mass deionized water and placed on a roller overnight. A 1cm diameter chromatography column will be plugged with glass wool and 8g of deactivated Florisil will be poured on top. The Florisil layer will be capped with a 1 inch layer of anhydrous sodium sulfate. After quantitative transfer of the sample to the column, the PCB fraction will be eluted with 30 ml of hexane. The volume of hexane will be concentrated to approximately 1 ml for analysis.

7.5. Fish PCB analysis.

PCB congener specific analysis is performed using a modified EPA Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m x 0.25 mm inner diameter) and an electron capture detector is used for analysis. PCB standards for calibration are obtained from the EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, Michigan and also from Ultra Scientific. A 4-level PCB calibration table is prepared using a known PCB mixture containing 250 μg/L of Aroclor 1232, 180 μg/L of Aroclor 1248 and 180 μg/L of Aroclor 1262 yielding a total PCB concentration of 610 μg/L. Concentrations of individual PCB congeners in the mixture are obtained from Mullin (1994). Two internal standards are used: PCB 30 (2,4,6-trichlorobiphenyl) and PCB 204 (2,2',3,4,4',5,6,6'-octachloro biphenyl), which are not present in commercial Aroclor mixtures. Using this protocol, 92 PCB congeners or congener groups can be identified and quantified. With this analytical method, there are some coeluting PCB peaks in the analysis. Where this occurs, coeluting peaks are calibrated as sum of congeners. Details of the PCB extraction, cleanup, analysis, calibration, and QAQC plan are provided later in this document.

Analytical QA/QC

(See attached UMBC PCB analysis QA/QC document)

7.6. Application of activated carbon in the form of SediMite.

Laboratory and pilot-scale work has been completed to develop an agglomerate (*SediMite*^{TM}) that serves as a low-impact delivery system for in-situ treatment materials (Figure A2). See: www.sedimite.com

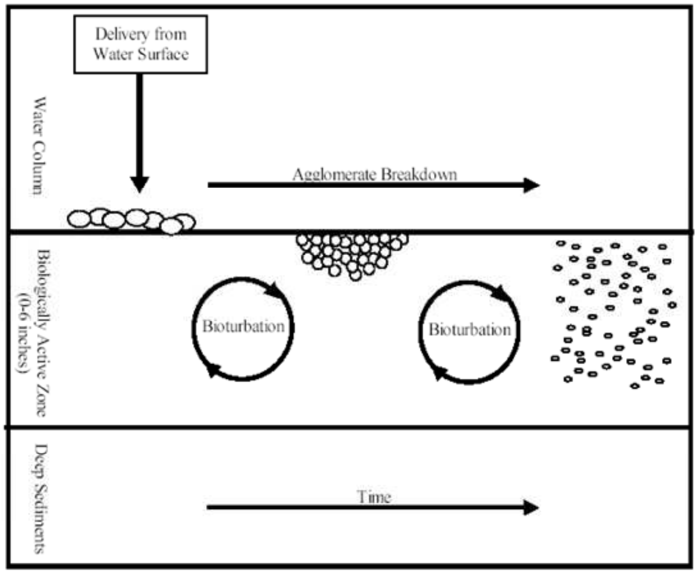

Figure A2. SediMite^{TM} is worked into the sediment by the benthic organisms present in the system, and breaks down over time, releasing treatment materials.

The approach relies upon incorporation of the small particle amendments into a larger, denser, and more manageable particle as a carrier for the fine materials. The agglomerated material can be transported on barges in bulk and delivered directly to the water surface. The agglomerate particles are designed to sink readily, without loss to the water column, and spread over the contaminated sediment surface or as part of a thin cap layer. Once spread, the aggregate particles fall apart and deliver the finer active material, typically activated carbon. Because the agglomerate is easily handled and controlled, it can also be mixed as slurry with a sand/sediment capping material. *SediMite* has been developed under an EPA SBIR and DoD SERDP grant and is being transitioned to the field at PCB, DDT, and mercury contaminated sites with support from NIH and DoD ESTCP programs (Figure A3). The product is now commercially available through a university startup company named Sediment Solutions.

Figure A3. Application of SediMite™ in a contaminated tidal wetland using an air blown applicator minimizes adverse impacts to existing vegetation and benthic organisms while reducing contaminant uptake in the food chain.

Conflict of interest disclosure:

"Dr. Ghosh is a co-inventor of two patents related to the in-situ sorbent amendment technology described in this proposal for which he is entitled to receive royalties upon commercialization. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, Dr. Ghosh is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC."