Bioaccumulation Control at Open Water Placement Sites by Dredged Material Amendment with Activated Carbon

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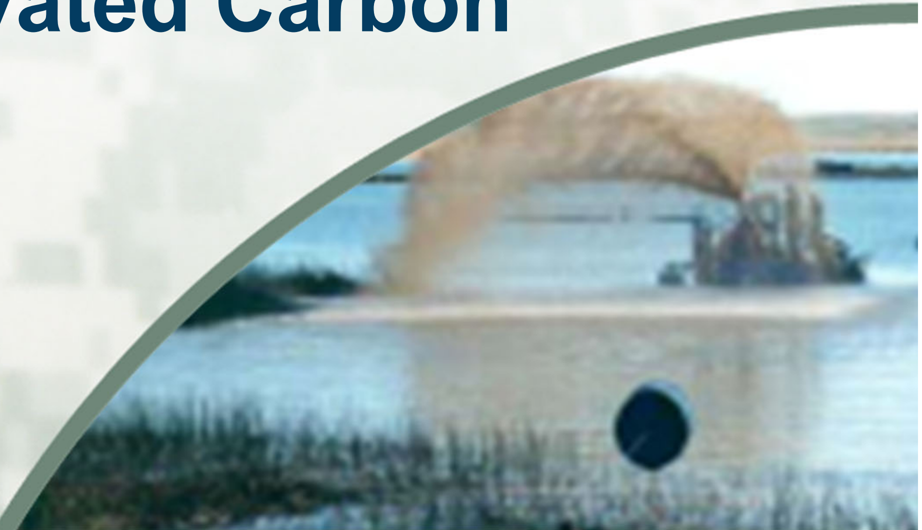

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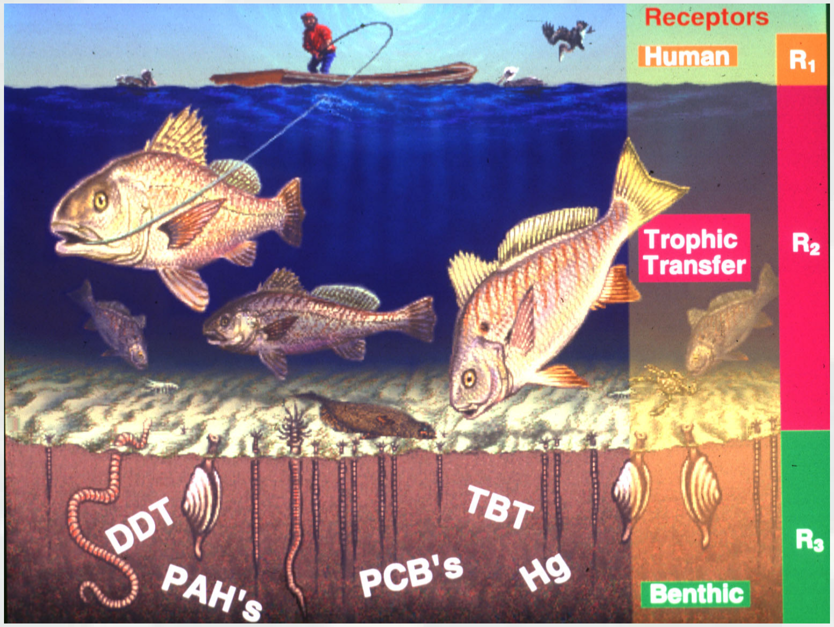
Outline

- Background
- Dosage Testing
- Field Demonstration
  - ► Implementation
  - ► Carbon Losses
  - ► Characterization
  - ► Bioaccumulation Reduction
  - ► Benthic Impacts

Problem

- Historic contamination poses ecological and human health concerns from potential bioaccumulation of contaminants placed dredged material placed in an aquatic environment for disposal or beneficial use
- Limiting placement alternatives and increasing costs
- Need for cost-effective, implementable bioaccumulation control technology



Past Applications of Activated Carbon in Sediments

- Activated carbon has been applied directly to sediment only about a dozen times, mostly in small pilot demonstrations
- Additionally, activated carbon has been applied in caps at contaminated sediment sites at about a dozen sites, also mostly in small field demonstrations
- Only a few of these applications were larger than our current demonstration and half of the applications were much smaller.
- All of the applications were intended to remediate in situ contaminated sediment by reducing contaminant exposure/flux and limiting bioaccumulation.

Past Applications of Activated Carbon in Sediments

- None of the applications used a technique similar to our method of applying activated carbon except two applications in Norway that applied carbon as a blended cover with clean dredged clay; however, the carbon was placed as pumped slurry from a hopper dredge with a tremie (Cornelissen et al. 2012 and Eek et al. 2012).
- Carbon has been applied directly to the surface of the sediment without mixing in test plots at Grasse River, and Upper Canal Creek near Aberdeen, MD (USEPA 2013) while activated carbon within a delivery system such as SediMite® and AquaGate™ have been applied at about a dozen sites (Patmont et al. 2015).
- Prior to this study, an application of activated carbon in a conventional mechanical dredging operation has never been demonstrated in a navigation dredging project.

Objectives for Dosage Testing

- Evaluate the dosage screening protocols and volume requirements for amended dredged material to adequately treat PCBs in the bioactive zone
- Examine the performance of low activated carbon dosages suitable for controlling widespread low-level contamination using laboratory testing
- Determine performance differences as a function of PCB homolog

Sediments Tested

Sediment	PCBs Conc. µg/kg	% Organic Matter			% Clay	% Silt	% Sand	% Solids
		Total	Soft	Refractory				
Ashtabula Harbor	43.7	3.4	0.8	2.6	21	69	10	60.7
Cleveland Harbor	110	4.1	1.6	2.5	20	69	11	58.6
Buffalo River	184	4.3	1.8	2.5	24	63	13	48.1

Unamended Bioaccumulation Results

Bioaccumulative properties for PCBs were characterized using 28-day tests with *Lumbriculus variegates*.

Sediment	% lipids	Total PCBs Conc. in Tissues (ng/g)	Lipid Normalized PCBs Conc. (µg/g)	Bioavailability, µg PCBs / g Lipid per µg PCBs / g OM (Refractory)
Ashtabula Harbor	0.49	41.1	8.40	6.5 (5.0)
Cleveland Harbor	2.19	129	5.87	2.2 (1.3)
Buffalo River	2.10	702	33.2	7.7 (4.4)

Laboratory Testing

- Mixed 6 gallons of sediment plus PAC at target dosage in 20-gallon stainless steel barrel
- Rolled at 10 rpm for a minimum of 7 weeks
- Performed 28-day bioaccumulation testing using *Lumbriculus variegates*

PAC Amended Bioaccumulation Results

Sediment	Treatment	% Lipids	Total PCBs Conc. in Tissues (ng/g)	Lipid Normalized PCBs Conc. (µg/g)	Reduction in Lipid Normalized Bioaccumulation
Ashtabula Harbor	3% PAC static	1.3	6.39	0.52	93.8%
	0.3 % PAC rolled	1.5	8.24	0.55	93.4%
	0.06% PAC rolled	1.5	17.8	1.21	85.6%
Cleveland Harbor	0.3 % PAC rolled	1.3	27.2	2.14	63.6%
	0.1% PAC rolled	1.7	32.5	1.97	66.4%
Buffalo River	0.3% PAC rolled	1.4	103	7.54	77.3%
	0.1% PAC rolled	1.6	130	7.91	76.2%

Target Lipid Normalized PCBs Conc. of 2 µg/g.
Reductions of 65 to 85%.

Treatment Effectiveness by Homolog

- Comparison of the homolog distributions in the tissues from the bioaccumulation testing of original unamended sediments and the sediments amended with 0.3% PAC dosages showed that activated carbon was effective in sequestering all of the dominant homologs in the Ashtabula and Cleveland sediments.
- The greatest reductions were for the tetra-PCBs and penta-PCBs.
- Similarly, penta-PCBs and less chlorinated PCB homologs were effectively sequestered by the PAC in the Buffalo River sediment, but the reductions in hexa-PCBs and hepta-PCBs were well below the overall reduction.
- The more chlorinated homologs were poorly sequestered, likely due to their low solubility.

Low Dosage Performance

- Typical activated carbon dosages that have applied at contaminated sediment sites range from 3 to 6% on a dry wt basis to achieve bioavailability reductions of 95% to 98%. These results show that dosages of about 0.1% can achieve reductions of about 75%, which may be sufficient for low level widespread contamination.
- The reduction for a given PAC dosage is a factor of the sediment's organic matter composition, and the composition/distribution and bioavailability of the PCBs. Reductions increase with bioavailability and decrease with higher chlorinated PCB homologs.

Low Dosage Performance

- Higher PAC dosages appears to yield diminishing returns; that is, doubling a PAC dosage yields a bioaccumulation reduction that is much smaller than half of the bioaccumulation. For example, tripling the PAC content in the Cleveland and Buffalo sediment yield nearly no difference. Similarly, if a linear response were to occur, when a 3 to 6% dosage is expected to yield a 95 to 98% reduction, then a 0.3% dose would be expected to yield a reduction of about 40% and a dose of 0.1% would be about 10%. The laboratory reductions were approximately 75%.

Objectives for Field Demonstration

- Place amended dredged material to reduce bioaccumulation
- Determine the efficacy of mixing activated carbon (both powdered and granular) within the barge using conventional dredging equipment
- Determine the potential loss of activated carbon (powdered and granular) during and after placement through 15 meters (50 feet) of water
- Determine the extent of replacement or coverage of the bioactive zone with activated carbon amended dredged material
- Determine the long-term reduction in PCB bioavailability and bioaccumulation in the bioactive zone of the demonstration site

Ashtabula Harbor Dredged Material Characteristics

- Classified as CL (lean clay of low plasticity)
- Liquid Limit of 37, Plastic Limit of 22 and Plasticity Index of 15
- Engineering water content ranging from 65 to 67%
- Solids content of 60%
- Liquidity Index ranged from 2.7 to 3.0
- Toughness Index ranged from 1 to 1.3
- Amended dredged material: 0.934 g/cc dry bulk density in barge
0.947 g/cc dry at placement site

Other Measurements

- PCBs in dredged material
- Bioaccumulation of PCBs from unamended dredged material
- Losses of PAC and fines in laboratory tank tests
- Carbon content at placement site after 1 year and 3 years
- Bioaccumulation of PCBs from amended dredged material from placement site 1 year and 3 years after placement
- Benthic community structure

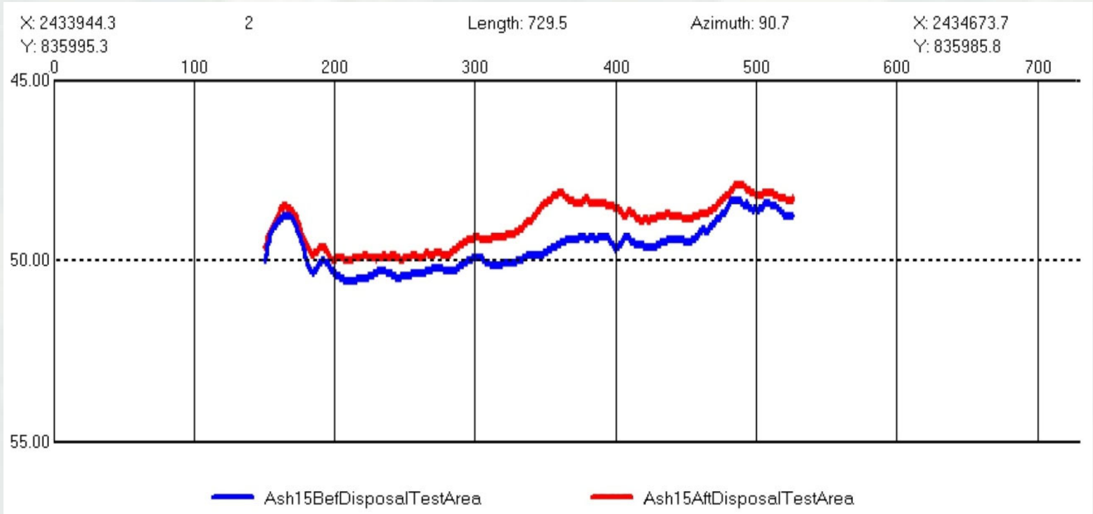
Approach

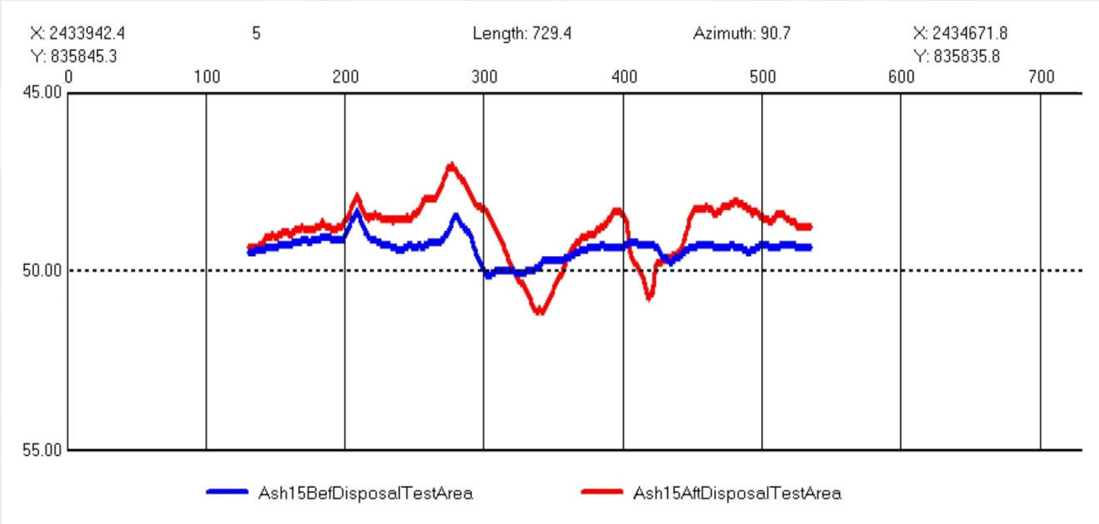
- Place four barges of unamended mechanically dredged material at a point in the open water placement site in 50 ft of water (about 6000 cy to form a 1-ft high mound); sample the barges to characterize the unamended dredged material in August 2015

Approach

- Mix both PAC and GAC in two layers of dredged material in the dump scow using a small conventional dredge bucket; sample the amended dredged material from each hopper of the dump scow to characterize the activated carbon distribution

Mound Dimensions





Carbon Addition

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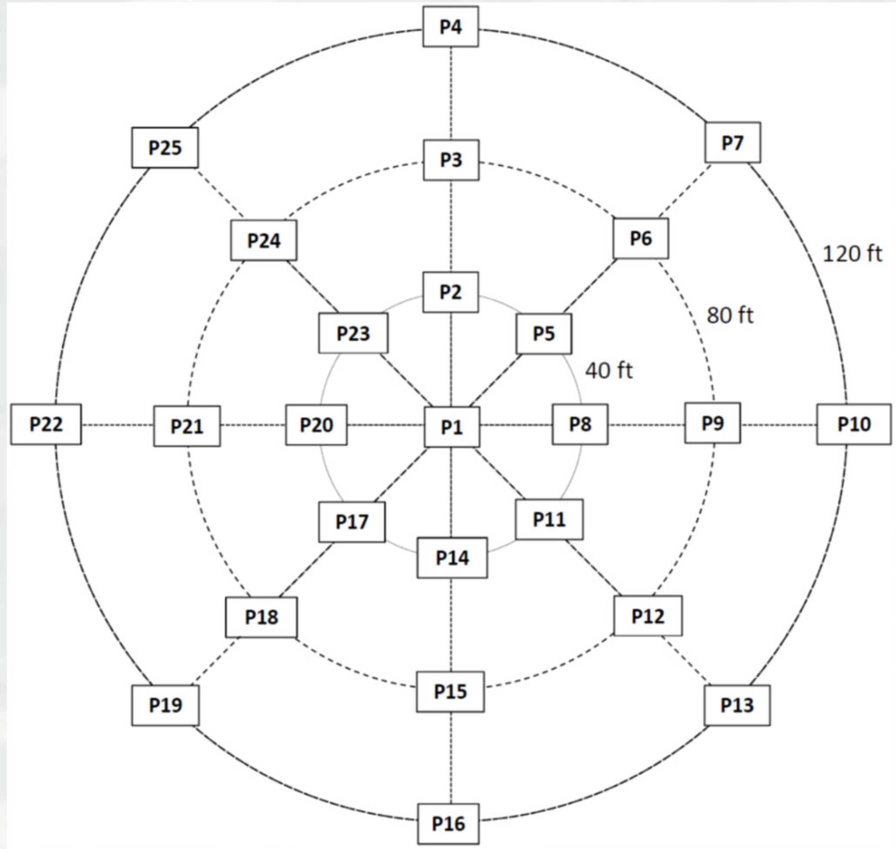
Barge AC Content

SAMPLE	PAC Content	GAC Content*	Total AC Content
Average	1.50%	2.20%	3.70%
Maximum	2.60%	4.00%	6.60%
Median	1.60%	2.10%	3.70%
Minimum	0.60%	0.80%	1.50%
Std. Dev.			1.10%
CV			32.00%

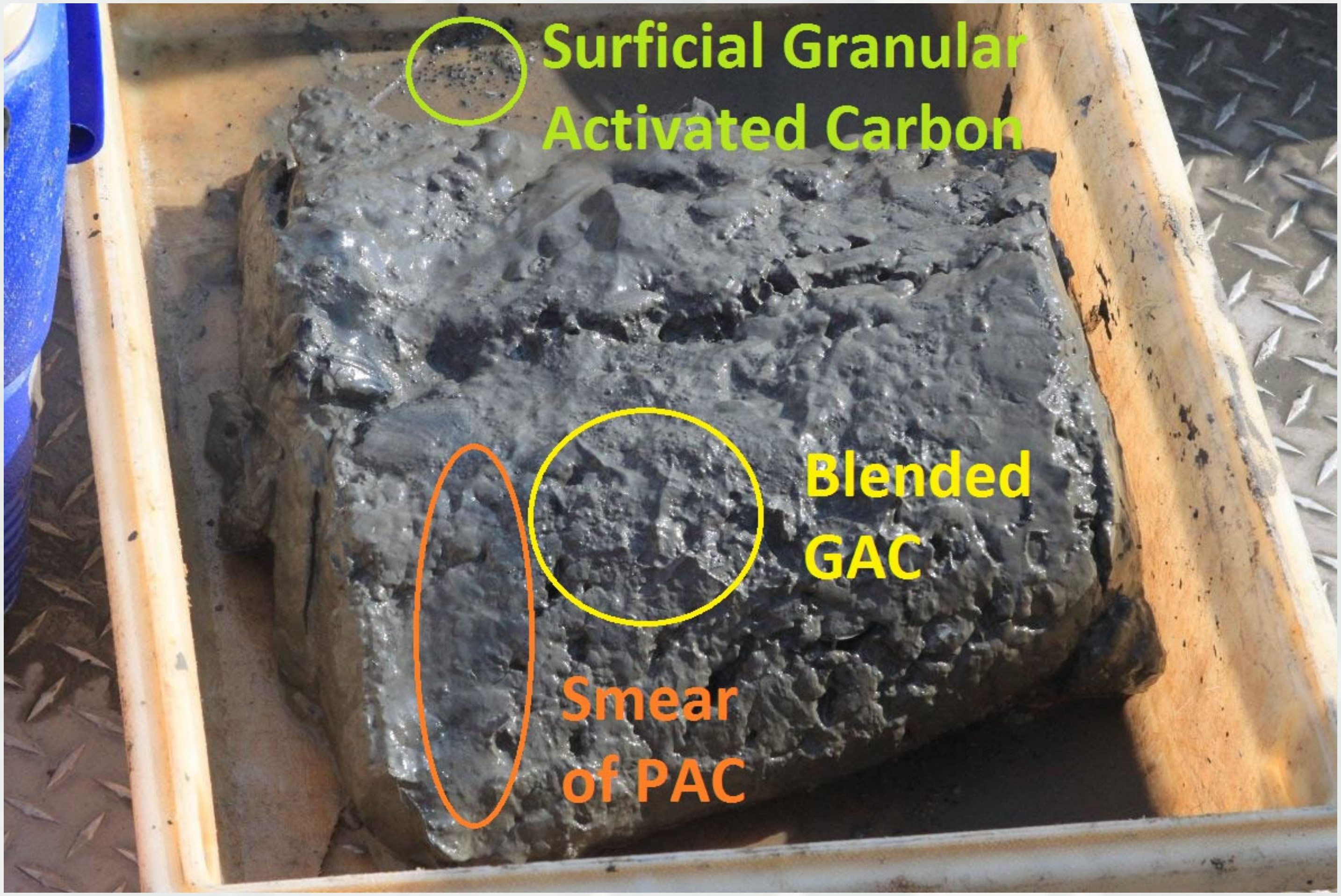
* 0.3% GAC added to surface also.

Approach

- Disperse GAC on the surface of the amended dredged material in the dump scow
- Bottom dump the amended dredged material on the placement mound
- Sample the top four inches of the placement mound to characterize the activated carbon distribution three weeks after placement at end of August 2015



Placement Site Sample



Placement Site AC Content

SAMPLE	PAC Content	GAC Content	Total AC Content*	Thickness of Amended Dredged Material	
				cm	inches
Average	0.47%	2.33%	2.69%	5	2
Maximum	0.99%	4.86%	5.12%	10	4
Median	0.42%	2.51%	2.80%	5	2
Minimum	0.01%	0.27%	0.56%	2.5	1
Std. Dev.	0.25%	1.09%	1.10%	2.5	1
CV	52.90%	46.70%	41.00%	48.40%	

* Measured by differential combustion and sieving

Placement Site AC Content

SAMPLE	PAC Content	GAC Content	Total AC Content*	Percent Loss	
				PAC	GAC
Barge	1.50%	2.20%	3.70%		
Initial	0.47%	2.33%	2.69%	70**	0**
1-Year	0.50%	1.18%	1.68%	0***	50***
3-Year	0.77%	0.37%	1.14%	-60***	80***

* Measured by differential combustion and sieving; normalize to 4-inch layer
** During placement
*** Following placement

1-Year Bioaccumulation Reductions

Sample	% GAC	% PAC	%AC	Effective % AC	Percent reduction in PCB concentrations in lipids after 1 year
No AC	0	0	0	0	0
Low AC	0.40	0.48	0.88	0.52	52
Medium AC	1.34	0.38	1.74	0.56	56
High AC	1.78	0.62	2.40	0.84	75

*Assuming GAC is about 10% as effective as PAC in the short-term due to distance between AC particles in the dredged material.

** TOC is 1.4% comprised of 0.4% carbon from soft labile organics and 1.0% carbon from hard refractory carbon.

3-Year Bioaccumulation Reductions

Sample	% GAC	% PAC	%AC	Effective % AC	Percent reduction in PCB concentrations in lipids after 3 years
No AC	0	0	0	0	0
Low AC	0.09	0.29	0.38	0.31	61
Medium AC	0.3	0.43	0.73	0.49	67
High AC	0.99	0.68	1.67	0.88	79

*Assuming GAC is about 10% as effective as PAC in the short-term due to distance between AC particles in the dredged material.

** TOC is 1.4% comprised of 0.4% carbon from soft labile organics and 1.0% carbon from hard refractory carbon.

Impacts on Benthos

- The abundance, richness, Shannon diversity, pollution tolerance and the relative abundance of tubificid worms were computed for each benthic sample (ten unamended and ten amended).
- The abundance (number of organisms) was greater, but not statistically significant ($p=0.059$), in the unamended samples compared to the AC-amended samples. GAC appeared to impact the abundance of pollution tolerant tubificid worms.
- The percent community composition of tubificids was statistically significantly larger ($p=0.011$) in unamended sediment, showing a less balanced community structure in the unamended sediment than in the amended sediment.

Impacts on Benthos

- The average pollution tolerance scores of the organisms in the unamended sediment were significantly greater ($p=0.011$) than that of organisms in the amended sediment.
- While the richness (number of genera) of the two sets of sediments were not statistically different, the diversity of organisms in the amended sediment was statistically greater, about 50% greater on average, using a 1-tailed t-test ($p=0.033$), due to more balance in the number of organisms in each genus, indicating a healthier community structure.

Conclusions

- These results show that PAC dosages of about 0.3% (and perhaps as low as 0.1%) can achieve reductions of about 75% in both laboratory and field applications, which may be sufficient for treating low level widespread contamination.
- Dredged material treatment is a viable option for placement marginally unsuitable dredged material in aquatic placement/ beneficial use settings rather than placement in CDFs.
- Benthos diversity improved slightly and included some less pollution tolerant species.
- PAC needs to be applied only to the bioactive zone to achieve the bioaccumulation reduction benefits.
- Bioaccumulation reductions are greatest in the tri-, tetra- and penta-chlorinated PCB homologs.

Acknowledgements

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