Effects of Activated Carbon Dosage for Aquatic Bioaccumulation Control

Paul R. Schroeder, PhD, PE

Environmental Laboratory
U.S. Army Engineer Research and Development Center
Vicksburg, Mississippi

Battelle Tenth International Conference on Remediation and Management of Contaminated Sediments

New Orleans, LA

13 February 2019

U.S.ARMY

US Army Corps of Engineers®

ERDC
Engineer Research and Development Center

Background

- Sediments in Great Lakes and other urban harbors often exhibit elevated levels of bioaccumulation, particularly PCBs
- Limits suitability for aquatic or wetland placement, depleting limited upland storage capacity
- Need inexpensive way to treat sediments to expand placement alternatives
- Activated carbon may provide a viable treatment alternative for widely dispersed contamination

Objectives

- Examine the performance of low activated carbon dosages suitable for controlling widespread low-level contamination
- Examine the effects of sediment properties on reductions in bioaccumulation by activated carbon
- Examine the effects of PCBs characteristics on bioaccumulation and its reduction by activated carbon
- Examine the effects of activated carbon size on bioaccumulation reduction and kinetics
- Examine a low technology approach in a conventional dredging operation to replace or cover 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

Approach

- Examine three sediments from Great Lakes harbors at several activated carbon concentrations in the laboratory under near equilibrium conditions
- Characterize the sediments PCBs concentration, grain size distribution and organic carbon
- Characterize the bioavailability/bioaccumulation of PCBs homologs in both unamended and amended sediment in the laboratory
- Examine the effects of activated carbon size on kinetics under static conditions in the laboratory
- Examine activated carbon performance under the non-ideal conditions of a field demonstration project

Sediment Characteristics

Sediment	PCBs Conc. µg/kg	% Organic Matter*			% Clay	% Silt	% Sand	% Solids
		Total	Soft	Refractory				
Ashtabula Harbor	110	3.4	0.8	2.6	21	69	10	60.7
Cleveland Harbor	43.7	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

* Measured by differential combustion, 325 ºC and 525 ºC

Bioaccumulation without Activated Carbon

Tissue PCBs concentrations of *Lumbriculus variegatus* after 28-day exposure to unamended sediments in triplicates.

Sediment	Sediment PCBs Conc. ug/g	% OM, Total *(Refractory)*	% lipids	Total PCBs Conc. in Tissues (ng/g)	Lipid Normalized PCBs Conc. (µg/g Lipids)	Bioavailability, µg PCBs / g Lipid per µg PCBs / g OM *(Refractory)*
Ashtabula Harbor	0.110	3.4 *(2.6)*	0.49	41.1	8.40	2.6 *(2.0)*
Cleveland Harbor	0.044	4.1 *(2.5)*	2.19	129	5.87	5.6 *(3.4)*
Buffalo River	0.184	4.3 *(2.5)*	2.10	701.7	33.2	7.7 *(4.4)*

Activated Carbon Addition

- Activated carbon was dried and then added to about 20 liters of sediment at the desired dosage based on dry weight (g AC/g solids) in a 75-liter stainless steel barrel with about 2 liters of water to ensure that the mixture is fluid enough to allow thorough mixing.
- The barrel was then placed on a barrel roller and rolled for seven weeks to facilitate rapid adsorption and approach equilibrium.

- AquaCarb S Series reactivated spent, coconut- and coal-based powdered activated carbon (PAC) was used in the testing.

Bioaccumulation of PCBs from Amended Sediments

Sediment	Treatment	% Lipids	Total PCBs Conc. in Tissues (ng/g)	Lipid Normalized PCBs Conc. (µg/g)	Reduction in Lipid Normalized Bioaccumulation
Ashtabula Harbor	0.3 % PAC rolled	1.5	8.24	0.92	93.3% 16-fold
	0.06% PAC rolled	1.5	17.8	1.21	85.6% 7-fold
Cleveland Harbor	0.3 % PAC rolled	1.3	27.2	2.14	63.6% 2.7-fold
	0.1% PAC rolled	1.7	32.5	1.97	66.4% 3-fold
Buffalo River	0.3% PAC rolled	1.4	103	7.54	77.3% 4.4-fold
	0.1% PAC rolled	1.6	130	7.91	76.2% 4.2-fold

PCBs Homologs and Reductions

Homologs	Ashtabula Sediment	Cleveland Sediment	Buffalo Sediment	Ashtabula Reduction by 0.3% PAC	Cleveland Reduction by 0.3% PAC	Buffalo Reduction by 0.3% PAC
Mono-PCBs	0%	0%	0%	NQ*	NQ	NQ
Di-PCBs	1%	2%	4%	NQ	NQ	94%
Tri-PCBs	8%	13%	19%	91%	68%	95%
Tetra-PCBs	29%	26%	33%	95%	78%	90%
Penta-PCBs	27%	24%	21%	96%	71%	75%
Hexa-PCBs	19%	28%	13%	92%	66%	25%
Hepta-PCBs	11%	5%	8%	92%	40%	12%
Octa-PCBs	3%	1%	2%	89%	NQ	NQ
Nona-PCBs	1%	0%	0%	NQ	NQ	NQ
Deca-PCBs	1%	1%	0%	NQ	NQ	NQ
Overall				93.3%	63.6%	77.3%

Observations

- Ashtabula sediment had the lowest bioavailability despite the lowest quantity of organic matter, although its refractory organic matter was slightly greater than the other sediments.
- Ashtabula Harbor has a coal rehandling facility that likely contributes to the refractory content of the sediment and a higher refractory carbon content than the other sediments, causing its lowest bioavailability.
- Percent reductions are greater for less chlorinated PCB homologs, particularly tri-, tetra- and penta-chloro biphenyls.
- Percent reductions tend to be greater for higher PCBs concentrations.
- There was not a significant difference between 0.3% and 0.1% dosages of PAC; even lower dosages need examination. There are diminishing returns with increasing dosages.

Kinetic Test under Static Conditions

- A study was performed to compare the bioaccumulation reduction as a function of time for a 3% dosage of PAC and granular activated carbon (GAC) by dry weight using the Ashtabula Harbor sediment at its *in situ* solids concentration in a 25-liter stainless steel boxes without mixing after the initial blending of the sediment and activated carbon.

- The mixtures were sampled for bioaccumulation testing after 9 and 21 months.

Kinetic Test Results

Dosage	Treatment	% Lipids	Total PCBs Conc. in Tissues (ng/g)	Lipid Normalized PCBs Conc. (µg/g)	Reduction in Lipid Normalized Bioaccumulation
3 % GAC	Static 9 months	1.3	19.8	1.61	83.8% 6-fold
	Static 21 months	1.3	15.2	1.21	87.8% 8-fold
3% PAC	Static 9 months	1.3	6.39	0.52	93.8% 16-fold
	Static 21 months	1.1	2.50	0.23	97.7% 43-fold

Reduction is greater and more rapid with PAC.

Ashtabula Field Demonstration

- 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.
- Discharge amended dredged material in 50 feet of water.
- Sample placement site to characterize the deposit.

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*
Initial	0.47%	2.33%**	2.69%
1-Year	0.50%	1.18%***	1.68%
3-Year	0.77%	0.37%****	1.14%

* Measured by differential combustion and sieving; normalize to 4-inch layer
** Considerable GAC is located loose on the surface
*** Surface GAC is largely absent
**** GAC is breaking down to smaller particle size causing an increase in PAC

Bioaccumulation Reduction

Table 3. Bioactive Zone (10-cm depth) Characteristics

Sample	%GAC	%PAC	%AC	Effective %AC*	Percent Reduction in PCBs Concentration in Lipids after 1 year
No AC**	0	0	0	0	0
Low AC	0.20	0.24	0.44	0.26	52
Med AC	0.67	0.19	0.87	0.28	56
High AC	0.89	0.31	1.20	0.42	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.

Low and Med AC may not be mixed throughout the full depth of 10-cm samples and therefore may underestimate the actual reduction in the bioactive zone.

Conclusions

- Amending sediments with PAC greatly reduced bioaccumulation of the less chlorinated PCB homologs, generally hexa- and less chlorinated biphenyls, in all three sediments tested.
- Hepta- and more chlorinated biphenyls are more slowly and poorly reduced due to their low solubility and slow migration into the inner pores of the activated carbon due to large size.
- Dosages of 0.1% PAC reduced bioaccumulation by 3- or 4-fold in all sediments tested and even greater in one of the sediments.
- Comparable results were obtained with a PAC dosage of about 0.3% where less thorough mixing was achieved.
- The kinetics and performance of PAC are considerably more favourable than GAC.

Acknowledgements

- Support was provided by the USACE Buffalo District
- Additional on-going support is being provided by the USACE Engineering with Nature (EWN) Program and the Dredging Operations and Environmental Research (DOER) Program