Impact of Particle Size on Activated Carbon Kinetics and Cap Modelling – Application of Study Data to a Great Lakes Legacy Act (GLLA) Site Model Using CapSim

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BACKGROUND

Activated carbon (AC) is a proven amendment for remediating sediments contaminated with hydrophobic organic compounds (HOCs) such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).[1] The successful implementation of AC in a sediment cap requires good understanding of the adsorption behavior of AC for the site-specific contamination conditions.

Predictive capping models, such as CapSim[2], utilize AC-HOC aqueous isotherms to determine the amount of AC required to achieve the desired effective life of the cap for the remedial design. A critical component of this approach is an agreement on the definition of AC equilibrium for the particle sizes – whether powder activated carbon (PAC) or granular activated carbon (GAC). This has been confounded by the practice of determining the equilibrium behavior of GAC by following a protocol that directs the pulverization of the GAC to the particle size of PAC. This introduces a particle size bias unrealistic to the expected behavior of GAC as compared to PAC.

Several studies with HOCs have shown that PAC reaches equilibrium much faster than GAC[3,4], underlining the need to consider the relative time to equilibrium, especially for GAC. When predictive models assume equivalent equilibrium behavior, the model results (and subsequent specified AC dosages) do not reflect the impact of transient behavior of the GAC as compared to PAC, raising a question related to the applicability of equilibrium behavior as an appropriate model assumption for field-scale conditions within transient, dynamic, and kinetic-driven environments, and areas with even relatively low groundwater upwelling rates.

This work provides new data regarding the impact of particle size on the time to equilibrium of AC adsorption of PAHs and PCBs and the subsequent impact of the transient adsorption on a representative CapSim model, using an initial cap design for a GLLA site.

OBJECTIVES AND GOALS

The objective of the work herein was to:
- Evaluate the effect of particle size on AC adsorption kinetics for environmentally relevant HOCs.

The goal of this work was to:
- Illustrate the implications of kinetic differences between PAC and GAC for Naphthalene in a representative CapSim Model based on an actual GLLA site modeling effort that utilized CapSim.

STUDY APPROACH

Three separate test programs conducted by industry-certified labs evaluated the performance differences between PAC and GAC for different HOCs as follows:

I. Naphthalene Aqueous Adsorption Study: A batch study assessing the kinetics of PAC & GAC sorption of Naphthalene in aqueous solution over 90 days,

II. PCB Aqueous Adsorption Study: A batch study assessing the kinetics of PAC & GAC sorption of a range of PCB congeners (from bi- to hexa-) in aqueous solution over 42 days as measured by passive samplers, and

III. PCB Sediment Mesocosm Study: Ex situ amendment of PAC & GAC with PCB-impacted site sediment over 10 weeks.

These tests also evaluated the differences between two particle sizes of the same AC and particles from different source materials – lignite and bituminous coal. The experimental data from the kinetics test were used to determine the first order kinetic rate. This was then used in a CapSim model that was compared to an early model developed for an actual GLLA site.

CAPSIM MODELLING

Implementing AC Kinetics using CapSim in an Early Capping Design for a GLLA Site

An early design of an activated carbon chemical isolation layer evaluated the use of a mixed sand-GAC or an AquaGate+PAC cap layer to limit porewater concentrations and transport of Naphthalene into the overlying sediments and surface water.

AC kinetics can be implemented into CapSim by inputting the first order kinetic adsorption rate into the model.

First, a representative model that reproduced the reference site early capping design was developed. This allowed us to run several model scenarios that evaluated the impact of AC kinetics on the expected performance of PAC and GAC.

Fitting the First Order Kinetic Parameter

The time series adsorption data from the Naphthalene and PCB aqueous adsorption studies were fit with a non-linear pseudo first order equation.

$$Q_t = Q_e(1 - e^{-k_1 t})$$

Where, Q_t is the adsorbed mass of the COC on AC at time t, µg/g.
Q_e is the equilibrium adsorbed mass of the COC on AC, µg/g.
k_1 is the first order kinetic rate, yr.[-1]
t is the time, yr.

Naphthalene Aqueous Adsorption Study	K_1 (yr.[-1])
Calgon F400 GAC	32
Calgon F400 PAC	13,185
Cabot SedimentPure PAC	14,899

PCB Aqueous Adsorption Study	K_1 (yr.[-1])
AC 1 (GAC)	8.4
AC 1 (PAC)	156.5*
AC 2 (GAC)	13.9
AC 3 (PAC)	123.3*

* PAC data were poorly fit as first data point was already at >99% reduction

Model Scenario	#	Cap Material	Layer Thickness (cm)	AC Application Rate (g/cm²)	Darcy Velocity (cm/yr.)	Porewater Concentration (µg/L)	Kinetic Mode
1 – Reproduced Site Example	1A	Sand-GAC-0.75%	7.57	0.089	10	6666	Equilibrium
	1B	AquaGate+PAC	2	0.24	10	6666	Equilibrium
	1C	Sand-GAC-0.75%	7.57	0.089	0	6666	Equilibrium
	1D	AquaGate+PAC	2	0.24	0	6666	Equilibrium
2 – Implementing Transient Kinetics	2A	Sand-GAC-0.75%	7.57	0.089	10	6666	Transient
	2B	AquaGate+PAC	2	0.24	10	6666	Transient
	2C	Sand-GAC-0.75%	7.57	0.089	0	6666	Transient
	2D	AquaGate+PAC	2	0.24	0	6666	Transient
3 – AC dose to meet project objectives	3A	Sand-GAC-5%	45	3.2	10	6666	Transient
	3B	AquaGate+PAC	1	0.12	10	6666	Transient
4 – Comparing equal AC dose and layer thickness of PAC and GAC	4A	Sand-GAC-9.1%	30	3.6	10	6666	Transient
	4B	AquaGate+PAC	30	3.6	10	6666	Transient
	4C	Sand-GAC-9.1%	30	3.6	0	6666	Transient
	4D	AquaGate+PAC	30	3.6	0	6666	Transient

DISCUSSION OF MODELLING RESULTS

- The attempt to reproduce the modeling output for the reference GLLA site was relatively successful. The reproduced results showed a concentration profile that was similar enough to support further analysis of transient vs. equilibrium behavior as outlined in the additional model runs presented above.

- There was no significant difference between the model output of transient and equilibrium kinetics for the AquaGate+PAC case, suggesting that for PAC-based approaches, equilibrium kinetics can be assumed/adopted in the model.

- The implementation of kinetics in the model showed that the slower uptake rate of GAC negatively impacted the predicted performance of the reference site cap. At the dose of 7.57 cm of sand-GAC at 0.75% AC, the sand-GAC cap did not achieve the goals for the porewater concentrations at the cap compliance point.

- Additional model scenarios were investigated to determine the sand-GAC dose and thickness necessary to meet the break-through objectives. These scenarios showed than an increase to 5% AC and to 45 cm thickness was required for the sand-GAC approach. These changes resulted in **a 36x increase in the GAC dose required to meet the desired levels when** the transient kinetics of GAC were considered.

- The fast kinetics of the PAC also resulted in more efficient use of AC (i.e., lower quantity required). A 1 cm thick layer of AquaGate+PAC, a constructible nominal thickness, still resulted in reducing porewater concentrations beyond the objective at the cap compliance point. This lower impedance resulted in an equivalent PAC dose that was **21x lower than the equivalent performing dose of GAC** (45 cm of sand-GAC at 5% GAC).

- For an equal 30 cm cap thickness and AC application rate of 3.6 g/cm², the AquaGate+PAC approach resulted in better cap performance.

A — Sand-GAC at 10 cm/yr. upwelling B — AquaGate+PAC at 10 cm/yr. upwelling C — Sand-GAC at 0 cm/yr. upwelling D — AquaGate+PAC at 0 cm/yr. upwelling

Ref. Site Examples

1 Reproduced Site Examples
2 With Transient Kinetics
3 Target AC dose
4 Equal AC dose
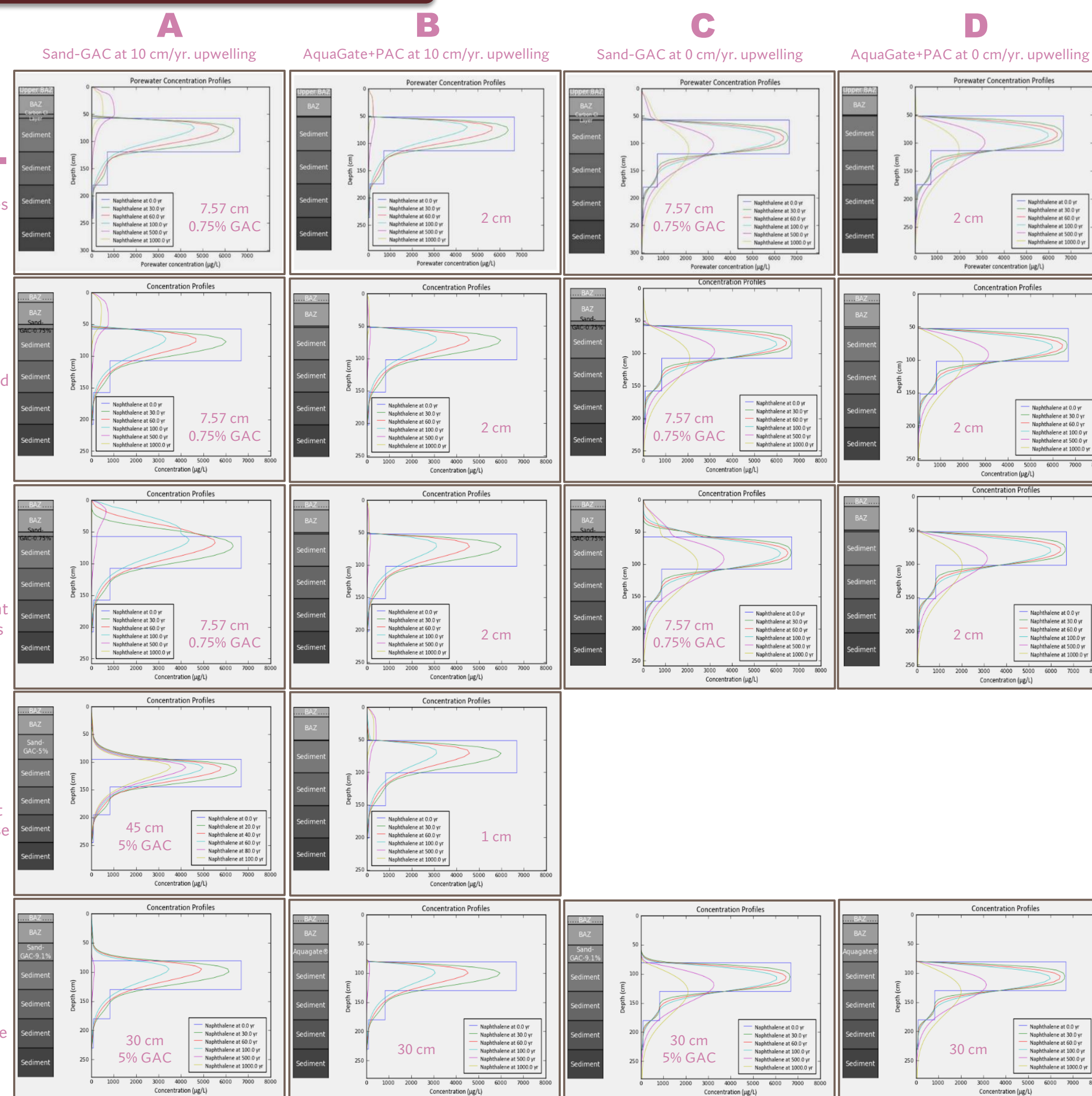
FINDINGS AND RECOMMENDATIONS

- This work investigated the impact of particle size on the adsorption kinetics of activated carbon by evaluating adsorption of PAHs and PCBs by PAC and GAC in aqueous batch systems and in a sediment mesocosm study. These studies were designed to be representative of real-world sediment scenarios. The batch kinetic study was used to develop first order kinetic parameters for implementing transient kinetics in CapSim. The particle size kinetic effect on AC capping was evaluated using a representative CapSim model based on an early capping design of an actual GLLA site.

- The effect of particle size on adsorption kinetics was clearly expressed in all three adsorption tests. The time to equilibrium of PAC was much shorter than for GAC. The different kinetic rates of the two particle sizes will have an impact on the transient adsorption of contaminants to AC when implemented in a sediment cap.

- The adsorption of rate of Naphthalene (a low MW PAH with Log K_{ow} of 3.29) by either form of AC was faster than for PCB-18 (a low MW PCB with Log K_{ow} of 5.6), suggesting the adsorption speed correlates with solubility expressed as octanol-water coefficient, which has been reported by others.[5]

- The kinetic rate of PAC was 400x and 20x faster than GAC for Naphthalene and PCB-18. Based on the model results, the use of a PAC-based approach resulted in a 21x reduction of AC dose compared to a similarly performing GAC-based approach when groundwater upwelling rate was 10 cm/yr.

- When the same amount of AC is implemented, the PAC will remove the COC at a faster rate and likely to a greater degree than GAC.

- When considering the implementation of a cap layer, the additional dredging required to accommodate a thicker cap can result in a more expensive remedial design, which may also present a greater risk of remedy.

- This work showed that even under conditions of low or limited groundwater upwelling, it is erroneous to assume equilibrium kinetics for a GAC-based approach.

- The higher effectiveness of PAC-based approaches demonstrated that AC based sediment cap should have different specified doses for PAC vs GAC – for equivalent performance. That is to say, these two forms of AC should be treated differently, as they will perform differently. Testing of PAC and GAC should occur in a manner representative of how they will be applied based on a similar set of assumptions for anticipated site conditions.

- These results support the conclusion that particle size has a significant impact on activated carbon adsorption, especially where higher flux rates may be present. It is therefore important to understand the site-specific characteristics and to ensure that sufficient data exists to support appropriate material selection for a given set of site conditions.
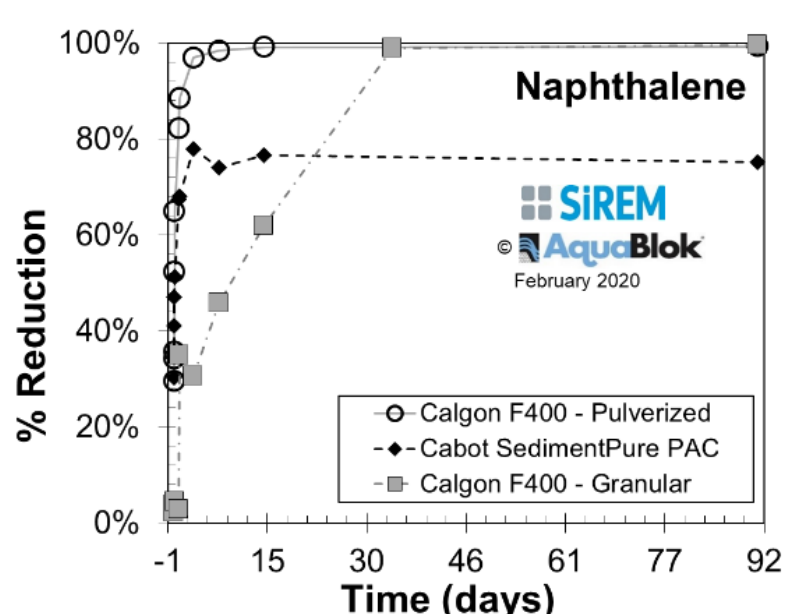
Naphthalene Aqueous Adsorption

Experimental Overview:

10 mg of GAC and PAC were added to 100 mL of Gowanus Canal surface water spiked to a concentration of 20 mg/L Naphthalene and 20 mg/L humic acid. Naphthalene concentrations were measured over a 92-day period by GC-MS.

Results:
- PAC reached equilibrium within days (3 days) compared to weeks (>4 weeks) for GAC.
- When the same activated carbon was tested as PAC and GAC, the PAC absorbed Naphthalene 10x faster than the GAC, directly illustrating the effect of particle size.
- The first order kinetic rate of Naphthalene adsorption was 412x higher for PAC than GAC.

Naphthalene

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- Calgon F400 - Pulverized
- Cabot SedimentPure PAC
- Calgon F400 - Granular

PCB Aqueous Adsorption

Experimental Overview:

4 mg of GAC and PAC were added to 240 mL artificial surface water spiked with several PCB congeners and Suwanee River NOM. PCB concentrations were measured by passive samples between 14 – 42 days.

Results:
- PAC was already at equilibrium (<14 days), while GAC did not reach equilibrium by test end at 42 days.
- When different sources of AC were tested, significant differences were attributable to particle size than to carbon source. The GAC forms only reached ~60% of the PAC adsorption.
- The first order kinetic rate of PCB-18 adsorption was 19x higher for PAC than GAC.

PCB-18

- AC 1 (GAC)
- AC 1 (PAC)
- AC 2 (GAC)
- AC 3 (PAC)
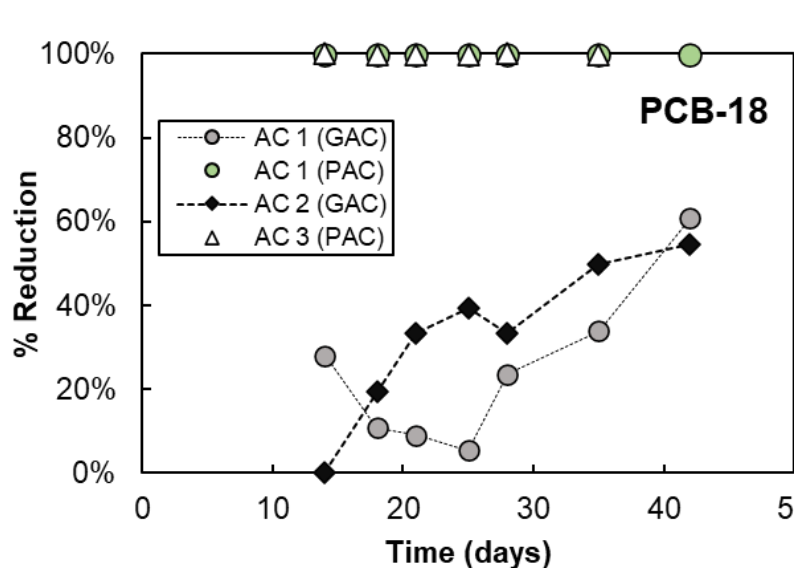
PCB Sediment Mesocosm

Experimental Overview:

GAC and PAC were mixed with site sediment at 5% and 15% dose levels. PCB concentrations were measured at 1 week, 3 weeks, and 10 weeks.

Results:
- The GAC appeared to reach equilibrium within 3-10 weeks, but only showed a 33% reduction in concentrations.
- The PAC had reduced concentrations to below detection limits by the first sampling time of 1 week.

Data from original presentation by Matt Vanderkooy, Geosyntec Consultants. "Evaluation of Powdered vs Granular Forms of Amendments for In Situ Sequestration of Sediment Contamination."
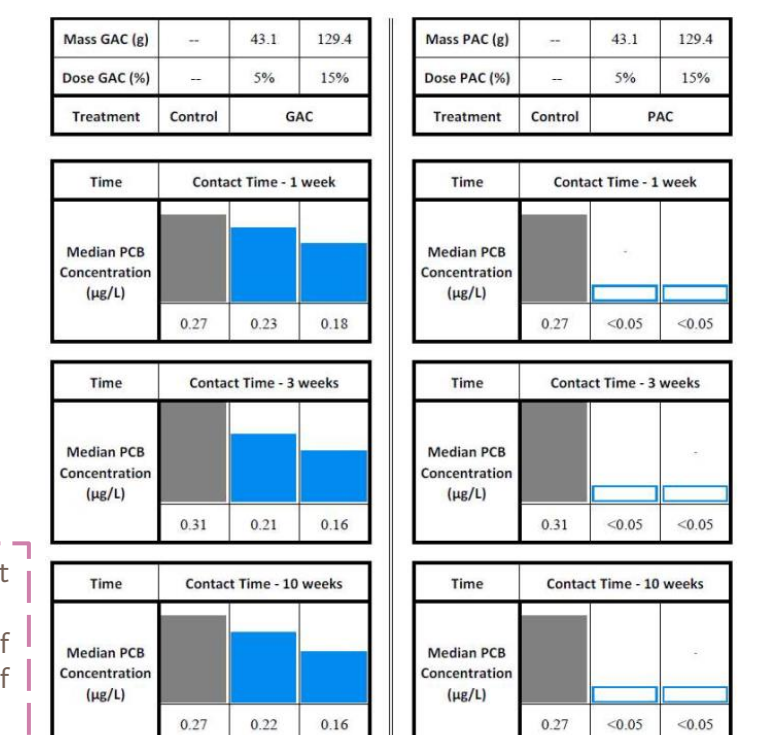
REFERENCES

1. Patmont CR, Ghosh U, LaRosa P, et al. In situ sediment treatment using activated carbon: A demonstrated sediment cleanup technology. *Integr Environ Assess Manag*. 2015;11(2):195-207. doi:10.1002/ieam.1589
2. Shen X, Lampert D, Ogle S, Reible D. A software tool for simulating contaminant transport and remedial effectiveness in sediment environments. *Environ Model Softw*. 2018;109(August):104-113. doi:10.1016/j.envsoft.2018.08.014
3. Zimmerman JR, Werner D, Ghosh U, Millward RN, Bridges TS, Luthy RG. Effects of dose and particle size on activated carbon treatment to sequester polychlorinated biphenyls and polycyclic aromatic hydrocarbons in marine sediments. *Environ Toxicol Chem*. 2005;24(7):1594-1601. doi:10.1897/04-368R.1
4. Rakowska MI, Kupryianchyk D, Harmsen J, Grotenhuis T, Koelmans AA. In situ remediation of contaminated sediments using carbonaceous materials. *Environ Toxicol Chem*. 2012;31(4):693-704. doi:10.1002/etc.1763
5. Shen X, Hussain T, Reible D, Mitchek M. Evaluating the Sorption Kinetics of HOCs in Activated Carbon by Batch Experiments Using Polydimethylsiloxane Passive Samplers. Conference Presentation, SETAC North America 42nd Annual Meeting. 14-18 November 2021. Virtual Conference.