



Cabot NORIT[®] SedimentPure[™] Activated Carbon Calculator Tool

SEDIMENT REMEDIATION APPLICATION

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Sediment Remediation Activated Carbon Calculator Tool

Background - Sediment Remediation Application Overview

Sediments accumulated on the bottom of waterbodies can become sinks for toxic, bio-accumulative chemicals that can create an environmental risk as contaminants are passed from the benthic community residing in the sediments to fish and other species via food webs. Due to recognized technical and cost issues associated with more invasive remedial methods, such as dredging, engineers and practitioners are turning to in situ methods such as capping for treatment of contaminated sediments as alternatives. Approximately fifteen years of research has provided evidence to support the use of activated carbon and other amendments to reduce the ecological and human health risks posed by contaminants. The approach, using activated carbon for in situ treatment involves applying the treatment amendments onto the surface of sediments either mixed with sand or other inert materials (reactive capping), or directly onto the sediment surface (in situ treatment).

Activated Carbon Job-To-Be-Done

Activated carbon is deployed underwater in a variety of product formats to decrease: 1) sediment pore water concentrations of contaminants; and 2) bioavailability and biological uptake of contaminants into food webs. Target contaminants are primarily persistent, hydrophobic organic contaminants (HOCs), including PCBs, PAHs, pesticides, dioxin and furan, as well as metals such as mercury and tri-butyl tin (TBT), the latter of which comes from anti-fouling paints used on ships. To be effective, activated carbon must have a blend of mesoporosity and microporosity to adsorb the target contaminants in the presence of high natural organic matter (NOM) concentrations (5-100 mg/l).

Objective

To support the further growth and understanding of remediation using amendments, such as activated carbon, Cabot has developed a calculator tool to assist interested parties on the potential performance of Cabot NORIT® SedimentPure™ powdered and granular activated carbon in these sediment remediation applications. The tool is intended to simplify the complexity of utilizing the CAPSIM Model under a set of field scenarios. It also provides instruction regarding factors that influence the performance and efficacy of activated carbon in different forms under a range of typical site conditions.

About the Calculator

This calculator was developed solely to predict performance of NORIT SedimentPure powdered and granular activated carbon (PAC, GAC). The application of PAC can be in the form of sand/AquaGate® with PAC or AquaGate with PAC only, while GAC is mixed into sand. The tool applies to pore water with NOM concentrations ranging from zero to 25 ppm. The adsorption of PCBs and PAHs on NORIT SedimentPure activate carbon does not change within this NOM range.

The calculator has incorporated the output of over 500 CapSim (version 3.5) simulations into a series of interactive plots using a statistic program (JMP 12 Flash Profiler). The overall R-Squared statistic for the validation set is 0.93, signifying that the tool is highly predictive of the CapSim Model. The summary of the input parameter values for CAPSIM simulations are in **Table 1**. The output is the contaminant breakthrough concentration at the top of the remediation cap layer.

ACTIVATED CARBON – IMPORTANT BACKGROUND INFORMATION

Adsorption Process with Activated Carbon

In water treatment applications with activated carbon, including sediment remediation, the adsorption process occurs because of the mass transport of impurities in water to the activated carbon particle surface, diffusion of impurities into the activated carbon pores and, finally, the adsorption of impurities onto the activated carbon pore wall. Adsorption is both a physical-chemical process that relates to the size of the pores and the size and polarity of the impurities targeted for removal.

In potable water, wastewater treatment and in sediment remediation, it is critical for the activated carbon to have the right blend of micro-, meso- and macro-porosity. Micro-pores are required to adsorb the smaller, lower molecular weight contaminants, while meso- and macro-pores are required to handle high concentrations of larger, high molecular weight, non-target organics (e.g., humic acids, fulvic acids) present in the water matrix. These large, non-target organics are typically referred to as Total Organic Carbon (TOC) or Natural Organic Matter (NOM) and can be present in natural water bodies in the 5 – 100 ppm range. NOM (or TOC), depending on the carbon source, can partially or completely block the pores of the carbon particles which drastically reduces its adsorptive capacity. For example, coconut-shell-based activated carbon is highly micro-porous and is ineffective in water matrices with even low concentrations of NOM. This is one reason why coconut shell-based activated carbons are almost never used in potable water or wastewater treatment.

Product Formats

Powdered activated carbon (PAC) and granular activated carbon (GAC) are used in this application. For example, PAC is deployed in the form of an amendment in which it is added to a binder and affixed to an aggregate (AquaGate) which acts as an anchor to sink the PAC-based amendment through the water column to its intended location on top of contaminated sediments. PAC cannot be placed directly onto a water body as it would neither sink through the water column, nor stay in its intended location. Granular activated carbon is either placed directly on contaminated sediments, added to a sand mixture to form a reactive cap layer, or deployed in a geotextile mat (e.g., CETCO, Huesker).

Numerous commercial and pilot studies have proven the efficacy of activated carbon in treating the most challenging contaminated sites, those at the water's edge or underwater. Activated carbon, even in small percentages, has proven to dramatically reduce pore water concentration of contaminants and decrease contaminant concentrations in benthic organisms at the bottom level of food webs.

Cabot Norit Research & Development – Design Data Needs

Cabot Norit set out to develop a product offering and to generate specific performance data that would provide the right information to engineering firms to enable them to assess and approve Cabot Norit activated carbons for use in sediment remediation projects. Cabot Norit investigated several key areas to guide our product development:

1. Relative performance of PAC vs. GAC
2. Adsorption capacity vs. kinetics of PAC and GAC
3. Relative performance of different feedstocks (e.g., coconut shell, lignite coal, re-agglomerated bituminous coal)
4. Impact of NOM on activated carbon performance

Cabot Norit performed all the work on PAHs at our global R&D site in Billerica, MA. Cabot partnered with Professor Danny Reible to perform the work on PCBs at Texas Tech University.

INFORMATION REGARDING THE CALCULATOR TOOL

Designing Reactive Caps Using NORIT Activated Carbon and the CAPSIM Model

To evaluate the potential performance of various reactive cap remedy designs using activated carbon, engineering firms frequently use the CAPSIM model developed by Dr. Danny Reible (Texas Technical University). To accomplish this, the model requires specific activated carbon grade performance data, namely the partition coefficient, which can be calculated from a Freundlich adsorption isotherm equation at a given equilibrium concentration of the contaminant in pore water.

$$C_{\text{carbon}} = k f C_{\text{water}}^{1/n}$$

C_{carbon} = mass of HOCs adsorbed on carbon

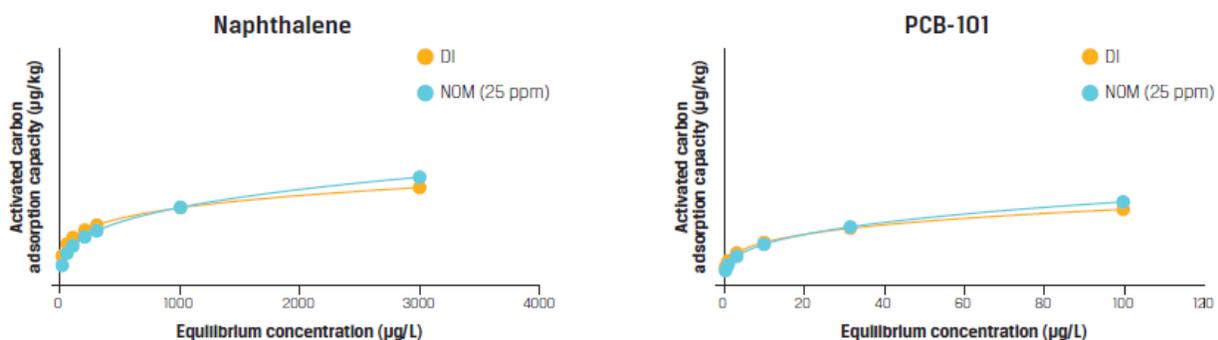
C_{water} = Equilibrium concentration of HOCs in sediment pore water

K and n are constants for a given HOC and AC at room temperature

Partition coefficient ($C_{\text{carbon}}/C_{\text{water}}$) can be calculated from Freundlich equation at a given equilibrium concentration of contaminant in pore water.

In support of this, Cabot generated **partition coefficients** to enable engineering firms to design reactive caps using NORIT activated carbon grades using the CAPSIM Model. These are all published in the Cabot Infosheet “HIGHLY EFFECTIVE NORIT ACTIVATED CARBON FOR SEDIMENT REMEDIATION.”

Partition coefficients were generated for three types of activated carbon (coconut, lignite, bituminous) in both deionized water and water with 25 ppm NOM. Lignite-based activated carbon (both PAC and GAC) was superior to coconut shell and re-agglomerated bituminous activated carbon as it was highly effective at adsorbing PCBs and PAHs while also being highly resistant to fouling (pore blocking) from NOM. In fact, there was no meaningful difference in performance for lignite-based activated carbon in DI water or water with 25 ppm NOM.



In contrast, coconut shell based and re-agglomerated bituminous activated carbons had significant to meaningful degradation in performance in the presence of NOM. For this reason, Cabot Norit developed two products for sediment remediation:

Grade	Parameter	Product Specifications	UOM
SedimentPure™ PAC	Mesh Size (U.S. Sieve Series) < 325 mesh (45 µm)	90% min.	%
	Moisture	12 max.	% as packed
SedimentPure™ GAC	Particle Size Distribution: 8x40 mesh < 40 mesh > 8 mesh	65% min.	%
		15% max.	
		25% max.	
	Moisture	12 max.	%

SedimentPure Activated Carbon Calculator

As a result of the research effort to develop the extensive list of partition coefficients, it became clear that the information could be used to develop a ‘calculator’ that could take advantage of both the adsorption information and the CAPSIM modeling performed. The Cabot R&D team ran over 500 CAPSIM Model simulations using a range of real life scenarios for the key parameters that influence the efficacy of activated carbon reactive cap layers. With the guidance of Dr. Danny Reible and several engineers who are thought leaders in this application, Cabot R&D assessed the following:

Parameter	Description	Parameter range analyzed in this project		
		Low	Medium	High
Reactive cap	Sand + activated carbon	Used for all scenarios (15 cm cap + 30 cm sediment)		
% Activated Carbon	Mass % of activated carbon in cap	1%	5%	10%
Upwelling rate	Fresh water up-flow in sediment (cm/day)	0	1	3
PAH concentration	PAH concentration in pore water (µg/l)	100	--	3000
PCB concentration	PCB concentration in pore water (ng/l)	1	--	100
NOM	Natural organic matter in pore water (ppm)	0	--	25
Half-life rate	Mass transfer rate of contaminant to AC	Local equilibrium	1 day	30 days

Cabot R&D analysed three PAHs (naphthalene, phenanthrene, and pyrene) and several PCB congeners (PCB-18, PCB-52, PCB-77, PCB-101, PCB-151). After running over 500 CAPSIM simulations, we used regression and neural networking to show the correlation between the key parameters and the long-term efficacy of the remedial design in a simple-to-use calculator. The calculator output has an R² value of 94%, indicating that it is highly predictive of the CAPSIM Model for the selected activated carbon and parameter range of the key variables listed in the table above. As a result, the SedimentPure Calculator is a robust, easy-to-use tool that can provide early guidance to engineers for the potential solution set for a contaminated site using Cabot NORIT SedimentPure activated carbons.

The SedimentPure Calculator allows the user to run “what if” scenarios by changing the key variables to determine the contaminant concentration in the pore water at the top of the cap at the designed cap life. The calculator has six dynamic window panes, including:

1. Contaminant Type (select one)
2. Activated Carbon Type (select PAC or GAC)
3. Activated Carbon % (pick the % carbon you want to assess from 0% to 20%)
4. Upwelling Rate in cm/day (select a rate between 0% and 3.5%)
5. Cap Thickness (select a number between 15 cm and 30 cm)
6. Designed life of the cap in years - no contaminant breakthrough (15-105 years)

R&D Study Conclusions

Before you begin using the SedimentPure Calculator, please review the following key conclusions from our R&D study:

Investigation	Conclusions
Capacity vs. Kinetics	<ul style="list-style-type: none"> • Adsorption capacity is the same for PAC and GAC although GAC may adsorb less due to slower kinetics of sorption • HOCs have low solubility and migrate slowly, so kinetics is not important if the upwelling rate is low
PAC vs. GAC	<ul style="list-style-type: none"> • Adsorption rate of HOCs is much faster with PAC • PAC is a better solution than GAC for PCBs when there is a high upwelling rate because kinetics become very important
Impact of NOM	<ul style="list-style-type: none"> • Lignite carbon is a better solution than coconut in the presence of NOM • NOM at 25 mg/L has negligible impact on performance of lignite carbon • NOM at 25 mg/L reduces performance of coconut carbon by up to a factor of 5
Feedstocks	<ul style="list-style-type: none"> • All carbons perform about the same for PAHs and PCBs when there is no upwelling • All GACs perform the same (quick breakthrough) when there is very high upwelling

Technical Documentation Background

At the Ninth International Conference on Remediation and Management of Contaminated Sediments in January, 2017, Cabot published NORIT SedimentPure Activated Carbon (PAC and GAC) adsorption data for PCBs and PAHs required for the design of caps and in-situ treatments for the management of contaminated sediments remediation caps using the CapSim Model¹. Cabot research also compared the adsorption kinetics between granular and powdered activated carbon on the uptake of PCBs and PAHs. Further, the results demonstrated that SedimentPure Activated Carbon is “resilient” to the natural organic matter (NOM) impact on adsorption for PCBs and PAHs.

How to Access Online Calculator

On line registration for the SedimentPure Calculator can be located at www.cabotcorp.com/calculator . Once you have completed the registration, an access code will be emailed to you allowing access to the tool and you will see the image displayed in **Figure 1**.

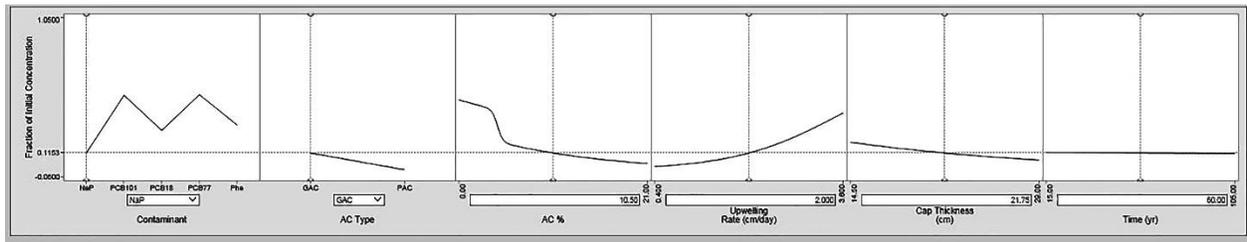


Figure 1. Cabot Sediment Remediation Activated Carbon Calculator Tool.

The HTML5 implementation of the JMP Profiler (Figure 1) displays two-dimensional views of six variables as X factors (Contaminant, AC type as GAC or PAC, AC% by weight, Upwelling Rate, Cap Thickness, and Simulation Time). A detailed description on the X factors are listed below.

X Factor	Descriptions
Contaminant*	Left to Right: NaP (Naphthalene); PCB 101; PCB 18; PCB 77; Phe (Phenanthrene)
AC Type	GAC (granular carbon) vs. PAC (powdered carbon)
AC %	Activated carbon dose by weight applied in the cap layer
Upwelling Rate (cm/day)	Groundwater seepage Darcy Velocity
Cap Thickness (cm)	Mixture of: Sand+ GAC or Sand + Aquagate; or Aquagate only
Time (yr)	Simulation period of time

* The five contaminants were selected to cover a broad range of molecular weight, which is highly correlated to the bioavailability in sediment. For preliminary purposes, the selected contaminants can also represent other similar contaminant forms such as dioxin, DDX, a range of PAHs, SVOCs, metals, etc.

These cross-sectional views enable you to explore the model space by changing one X factor and examining the effect on the predicted response, namely the predicted normalized concentration on the examined contaminant. The predicted breakthrough concentration can be obtained by multiplying the predicted normalized concentration by the initial pore water concentration provided in **Table 1**.

- At the top left, the menu button displays actions you can take in this application.
- At the top right is the Help link. At the bottom left is an icon that links to the jmp.com web site.
- The profiler displays a two-dimensional grid of graphs. Dependent variables (responses) are on vertical (Y) axes. Independent variables (factors) are on horizontal (X) axes.
- Each graph displays a curve, or profile trace, that is the predicted response as one factor is changed while others are held constant.
- Vertical dashed lines show the current values of each X factor. Adjusting any X factor changes the predicted responses in all other graphs.
- Horizontal dashed lines show the current predicted values of each Y response for the current values of the X factors.

Adjust X Value:

- To change an X value, click in the graph, or drag and slide the triangle in the graph. The vertical reference line moves to the new location. The horizontal reference line moves to show the current predicted response value.

- Or, click on an X value and type a new X value
- Click on the red X factor to edit the current value. Press the “enter” or “tab” key to confirm your change. If you enter a value outside the valid range, it will be ingored.

Table 1. Summary of Input Parameter Values for CAPSIM Modeling

Model Input Parameter	Value	Data Source
Chemical-Specific Properties		
Organic carbon, partition coefficient, log Koc (log L/kg)	Material Dependent	CapSim built in database (version 3.4)
Water diffusivity (cm ² /s)		
Chemical Biodegradation Rate (yr ⁻¹)	0	Assumed no decay
Chemical Initial Porewater Concentration (ug/L)	Material Dependent	NaP: 500µg/L; Phe: 100µg/L; PCB101: 0.1µg/L; PCB77: 0.1µg/L; PCB18: 1µg/L
Activated Carbon Properties (Lignite)		
Isothermic Coefficient	Material Dependent	Measured in Cabot lab, values provided in Cabot product datasheet
Cap Type		
Carbon Fraction of Sand + Granular Activated Carbon	Variable 1%-20%	Design parameter: altered to reduce contaminant breakthrough at the cap, and to increase the time to breakthrough of contaminant
Carbon Fraction of Sand + Aquagate	Variable 1%-20%	Design parameter: altered to reduce contaminant breakthrough at the cap, and to increase the time to breakthrough of contaminant
Carbon Fraction of Aquagate only	Variable 5%-10%	Design parameter: altered to reduce contaminant breakthrough at the cap, and to increase the time to breakthrough of contaminant
Cap Properties		
Total Cap Thickness (cm)	Variable	Mixture of: Sand + Granular Activated Carbon; or Sand + Aquagate; or Aquagate only
Sediment Thickness (cm)	30	Design parameter
Particle Density (g/cm ³)	Material Dependent	Based on the following pure materials: Sand: 1.25; GAC: 0.4; PAC: 0.4; Aggregate: 1.25
Effective Particle Density (g/cm ³)	Material Dependent	Calculated by CapSim based on pure materials
Total Porosity	Material Dependent	Calculated by CapSim based on the following pure materials: Sand: 0.5; GAC: 0.6; PAC: 0.6; Aggregate: 0.5
Effective Porosity	Material Dependent	Calculated by CapSim based on pure materials
Fraction Organic Carbon (foc) of bioturbation zone (filter layer) (%)	0	Only evaluating cap performance, not bioturbation impact
Mass Transport Properties		
Benthic Layer Mass Transfer Coefficient (cm/hr)	0.01	Recommended by Reible
Groundwater seepage Darcy Velocity (cm/day)	0.5, 1, 3	Design parameter
Depositional velocity (cm/yr)	0	Assumed no net sedimentation
Dispersion length (cm)	Variable	Calculated by CapSim based on cap thickness
Bioturbation Layer Thickness (cm)	0	Only evaluating cap performance, not bioturbation impact
Biodiffusion coefficients (cm ² /yr)	0	No bioturbation impact, no biodiffusion

References:

1. CAPSIM Model:

<https://www.depts.ttu.edu/ceweb/groups/reiblesgroup/downloads.html>

“A model for contaminant fate and transport in surficial sediments to support site conceptual model development, natural recovery assessment and remedial response is also available. The model has unique capabilities for describing processes at the sediment-water interface including the interface specific processes of bioturbation, benthic mass transfer, consolidation, and deposition as well as advection, diffusion, linear and nonlinear sorption and reaction. The model can simulate behavior in multiple sediment layers or sediment caps, including active caps.”