Predicting Reduction in Sorption Capacity of In Situ Activated Carbon Amendments Due to Fouling

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In-Situ Activated Carbon Applications for Contaminated Sediment Remediation

- In-situ containment (capping)
  - Placing a layer of Activated Carbon (AC) or AC mixed with sand (or other diluent capping media) over contaminated sediments
- In-situ treatment
  - Applying to surface of sediments
  - Injecting in surficial sediments
  - Mechanically mixing in surficial sediments

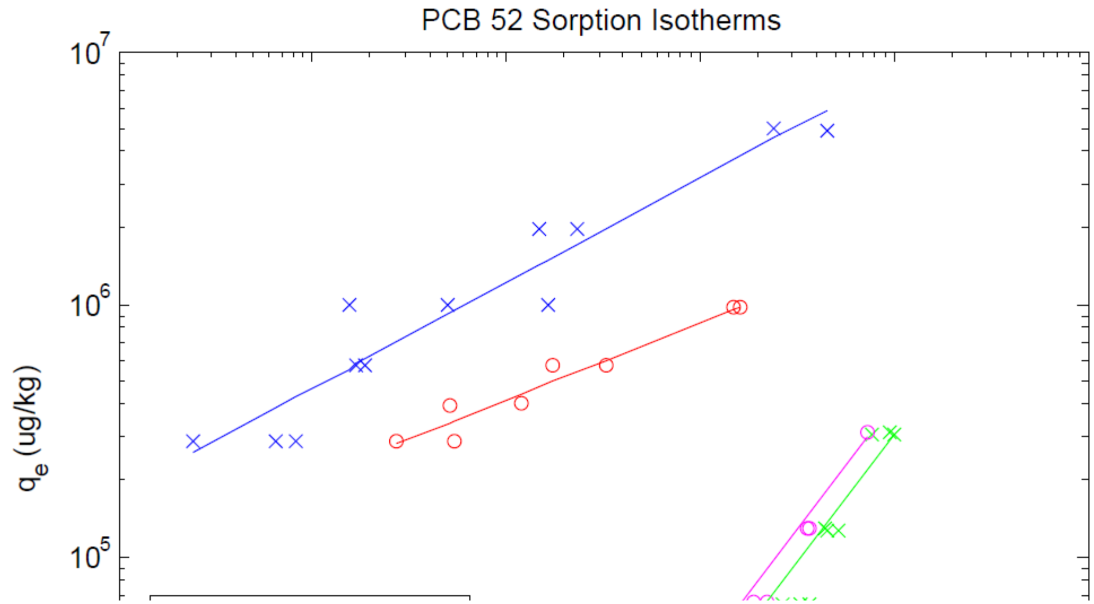
Activated Carbon Amendments

- Extensive research exists on the use of AC as an amendment
- AC has widespread application as an adsorptive material for hydrophobic organic compounds
- Adsorption is a surface process → ACs ideal adsorbents due to their high surface areas and porosities
- Susceptible to competitive adsorption in the presence of NOM → adsorption capacity decreases

PCB Sorption Experiments

- Batch isotherm tests using two types of water
  - Manistique Harbor porewater
  - Laboratory water – no organic matter
- Amendment materials
  - Calgon granular activated carbon
  - CETCO organoclay PM-199
- PCBs 18, 52, 77, 101, and 118 analyzed to represent range of hydrophobicities and planarities

Reduction in AC Sorption Capacity due to Fouling



- Site porewater is less sorbing than laboratory water for AC
- K_d about the same order of magnitude as K_{ow} for organoclay

Fouling Mechanisms

- Natural organic matter (NOM) competes with the target contaminant or chemicals at active adsorption sites
- Size of NOM molecules ≈ contaminant molecule size → Direct sorption onto AC surface
- Size of NOM molecules > contaminant molecule size → Pore blocking

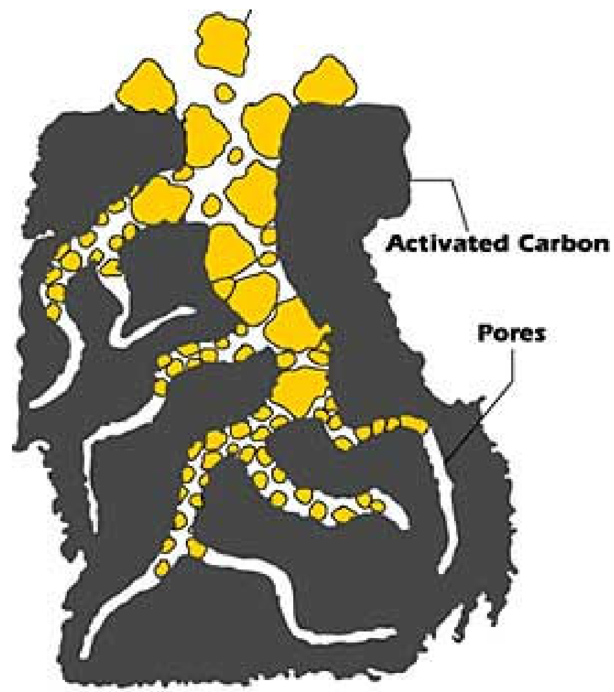


Image source: https://electrocorpairpurification.wordpress.com/2010/06/29/why-activated-carbon-works-so-well/

Predict Reduction in Sorption Capacity due to Fouling

- Reduction in AC capacity directly defines its performance as an in-situ amendment
- Polanyi-Dubinin-Manes (PDM) Model
  - Could be used as tool for performance prediction based on physico-chemical properties of adsorbent and adsorbate
  - Basic concept – Can reduction in micropore surface area predict sorption isotherm changes?
  - Trying to predict equilibrium, not kinetics

PDM Model – Governing Equations

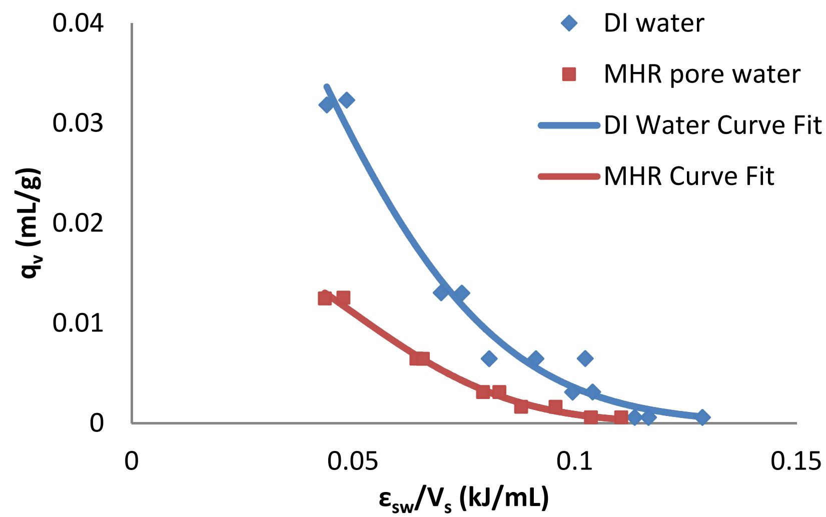
$$\log q_v = \log Q_v + a\left({}^{\varepsilon_{sw}}/_{V_s}\right)^b$$

- q_v is the adsorbed solute volume per unit mass of adsorbent (cm^3/g)
- Q_v is the adsorption volume capacity at saturation (cm^3/g)
- V_s is the molar volume of solute (cm^3/mol)
- a and b are fitting parameters
- ε_{sw} is effective adsorption potential (kJ/mol)

$$\varepsilon_{sw} = RT\ln\left({}^{C_s}/_{C}\right)$$

- C_s and C are saturation and bulk concentrations at temperature, T and R is the universal gas constant

PDM Characteristic Curves (Isotherms)



- PCB 18 characteristic curves show that PDM model provides a good fit for the experimental isotherms
- Manistique porewater shows lower sorption compared to its corresponding isotherm in DI water

Modified PDM Model

- Long et al. (2008) study shows that adsorption of a contaminant on different sorbents can be defined by a single correlation curve by normalizing with micropore volume of the respective adsorbents
- This would result in an equation of the form:

$$log\frac{q_v}{V_{micro}} = logQ_v + a\left({}^{\varepsilon_{sw}}/_{V_s}\right)^b$$

- Due to the structural differences in fouled vs. virgin AC it may be treated as two different sorbents

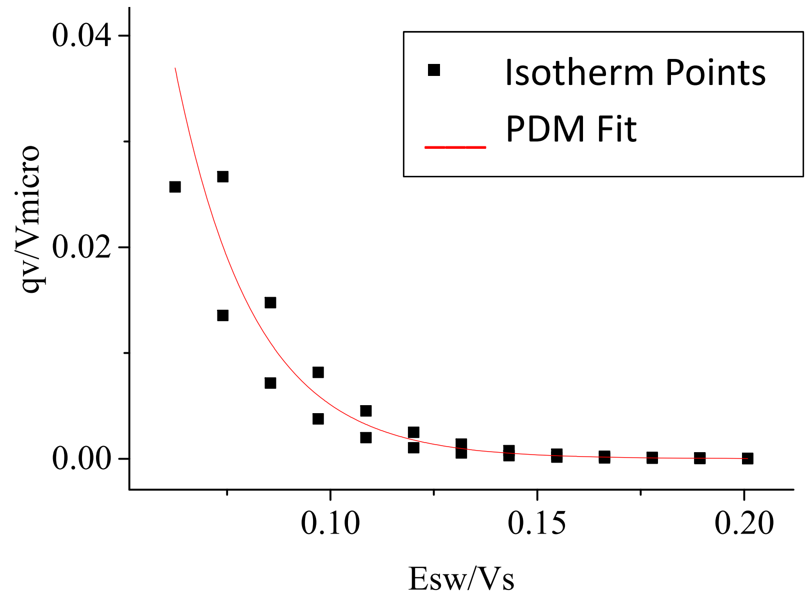
Material Characterization

	Units	Virgin		MHR		SRL	SRH
		TOG	F400	TOG	F400	TOG	TOG
BET Surface Area	(m^2/g)	1035	1101	829	662	876	825
Micropore Volume	(cm^3/g)	0.385	0.372	0.304	0.223	0.323	0.305
Total Pore Volume	(cm^3/g)	0.435	0.655	0.358	0.400	0.373	0.350

- Both carbons equilibrated with NOM waters
  - Manistique Porewater (MHR), 14 mg/L DOC
  - Suwannee River Low (SRL), 14 mg/L DOC
  - Suwannee River High (SRH), 25 mg/L DOC
- Reduction in SRH > SRL

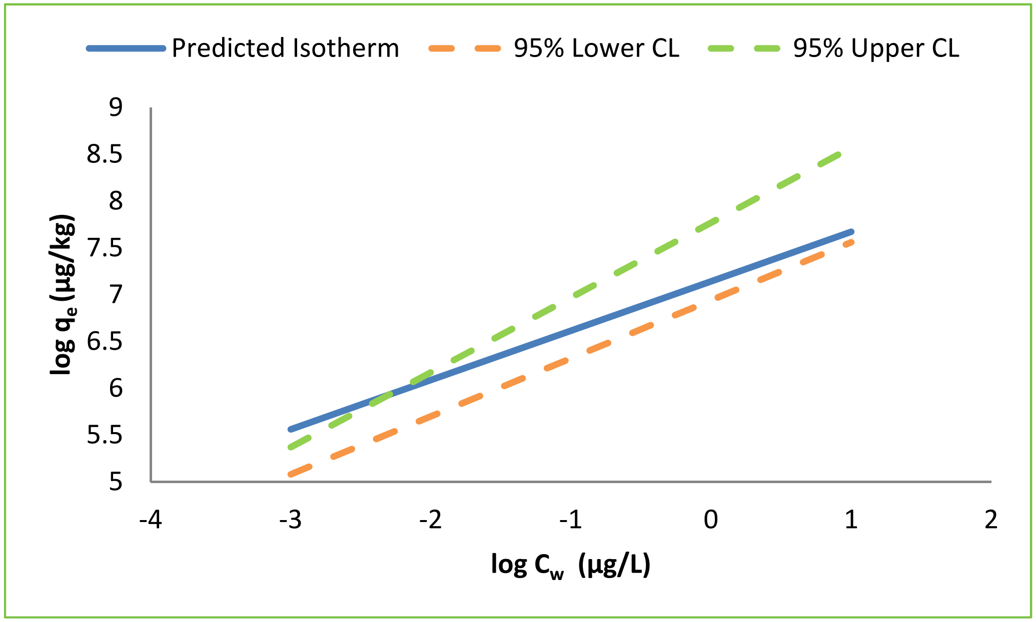
PDM Correlation Curve

$$log\frac{q_v}{V_{micro}} = log1.025 - 22.61\left({}^{\varepsilon_{sw}}/_{V_s}\right)^{.992}$$



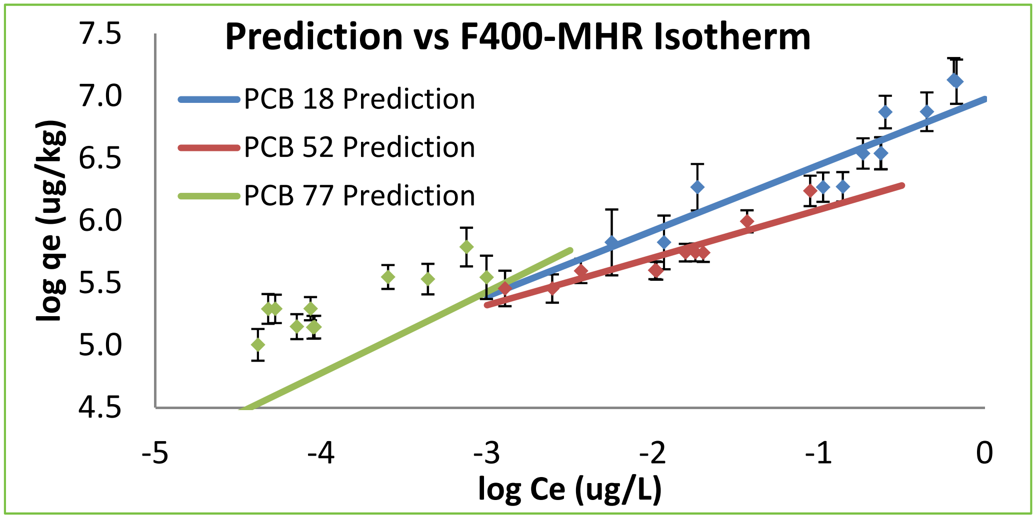
- Correlation curve obtained by normalizing Polanyi isotherms of lab and MHR site water with micropore volume of virgin and DOM-loaded TOG AC
- Non-linear curve fitting function was used to obtain this modified PDM correlation curve for PCB 18

PDM Prediction of Literature Data



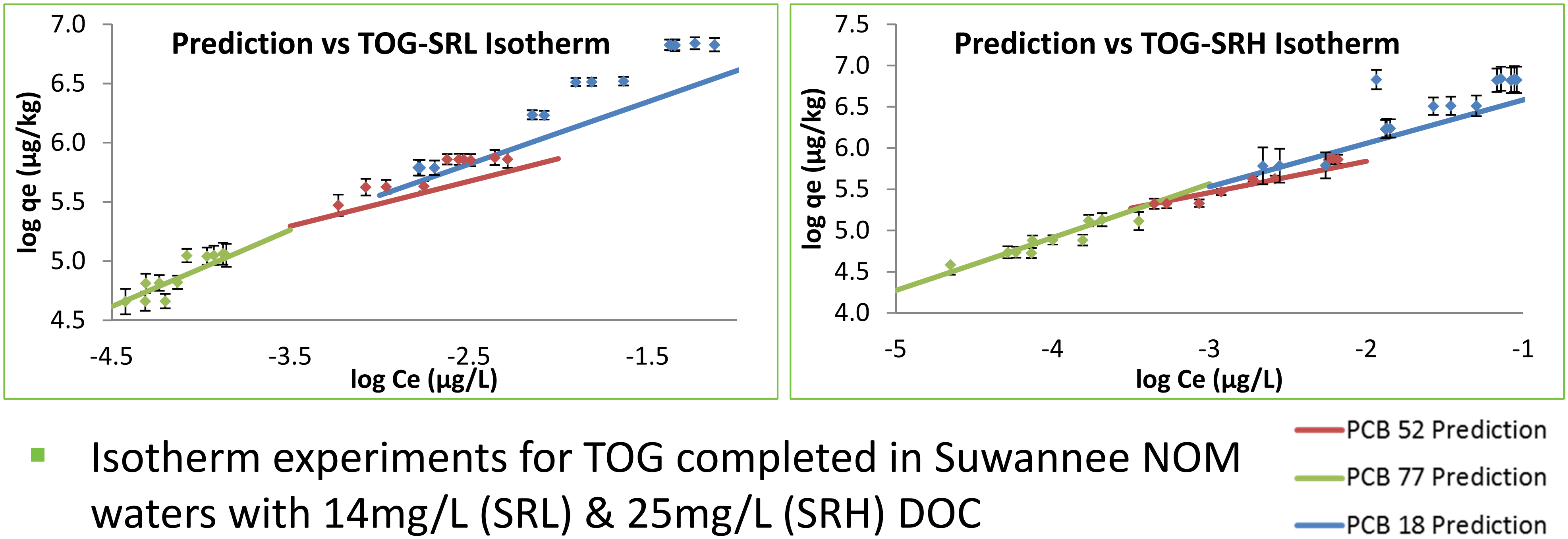
- Using micropore volume (V_{micro}) of AC from McDonough et al., 2008 in equation from the last slide, a predicted PCB 18 isotherm (blue) was compared with the experimental data from the study

Effects of Type of AC



- PCB isotherm experiments for F400 type AC completed in MHR porewater
- TOG-MHR based correlation described above was used with measured F400 V_{micro} in MHR porewater

Effects of DOC Variation



- Isotherm experiments for TOG completed in Suwannee NOM waters with 14mg/L (SRL) & 25mg/L (SRH) DOC
- Predictions used previous TOG-MHR based correlation was used with measured TOG V_{micro} in each SR water

Conclusions

- Treating fouled and virgin AC as different sorbents led to a modified PDM model
- Fouled and unfouled PDM curves normalized with fouled and virgin AC micropore volumes provide single correlation curve
- Correlation equation obtained by a non-linear curve fitting function was used as an adsorption prediction tool

Conclusions

- Modified PDM model successfully predicts effects of NOM on adsorption isotherms
- Experimental data confirms accuracy of prediction for different type of AC and at different DOC concentrations
- This modified PDM model presents an alternative for predicting adsorption potential of AC amendments at a site:
  - When limited sorption information is available
  - When the decrease in sorption capacity due to NOM needs to be estimated

Questions?