

Removal of PFAS Precursor Compounds Using GAC



Eric Forrester

Development Engineer, Drinking Water Solutions

E: fforrester@calgoncarbon.com

P: 412-787-6821

RESEARCH GOALS



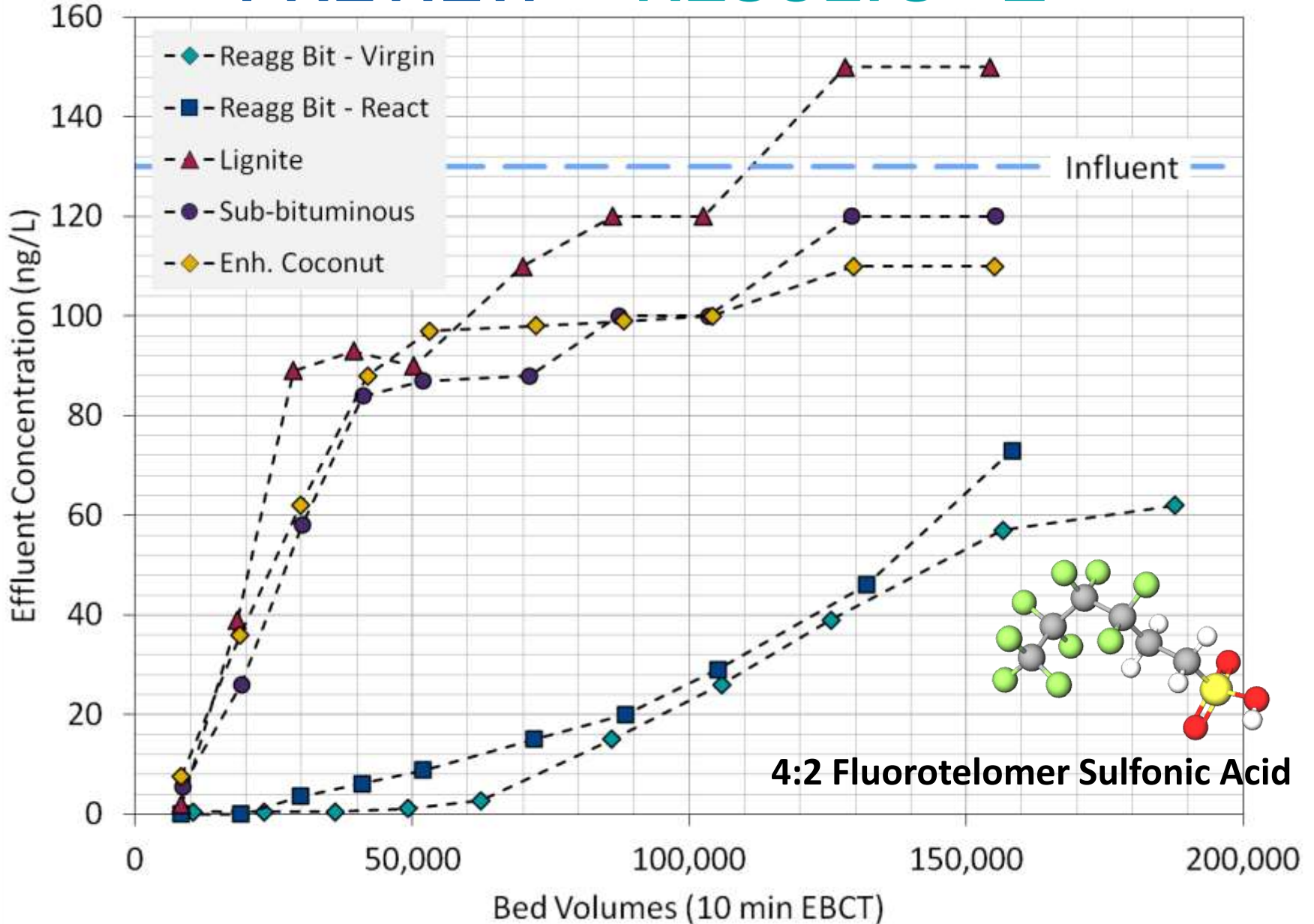
DEVELOP DATA SET FOR PFAS PRECURSOR REMOVAL

- RSSCTs – well-established method, relatively quick to run
- Target compounds: 4 fluorotelomers & 1 sulfonamide
- Compare multiple carbon types (5)
- PFOA & PFOS included in “background”

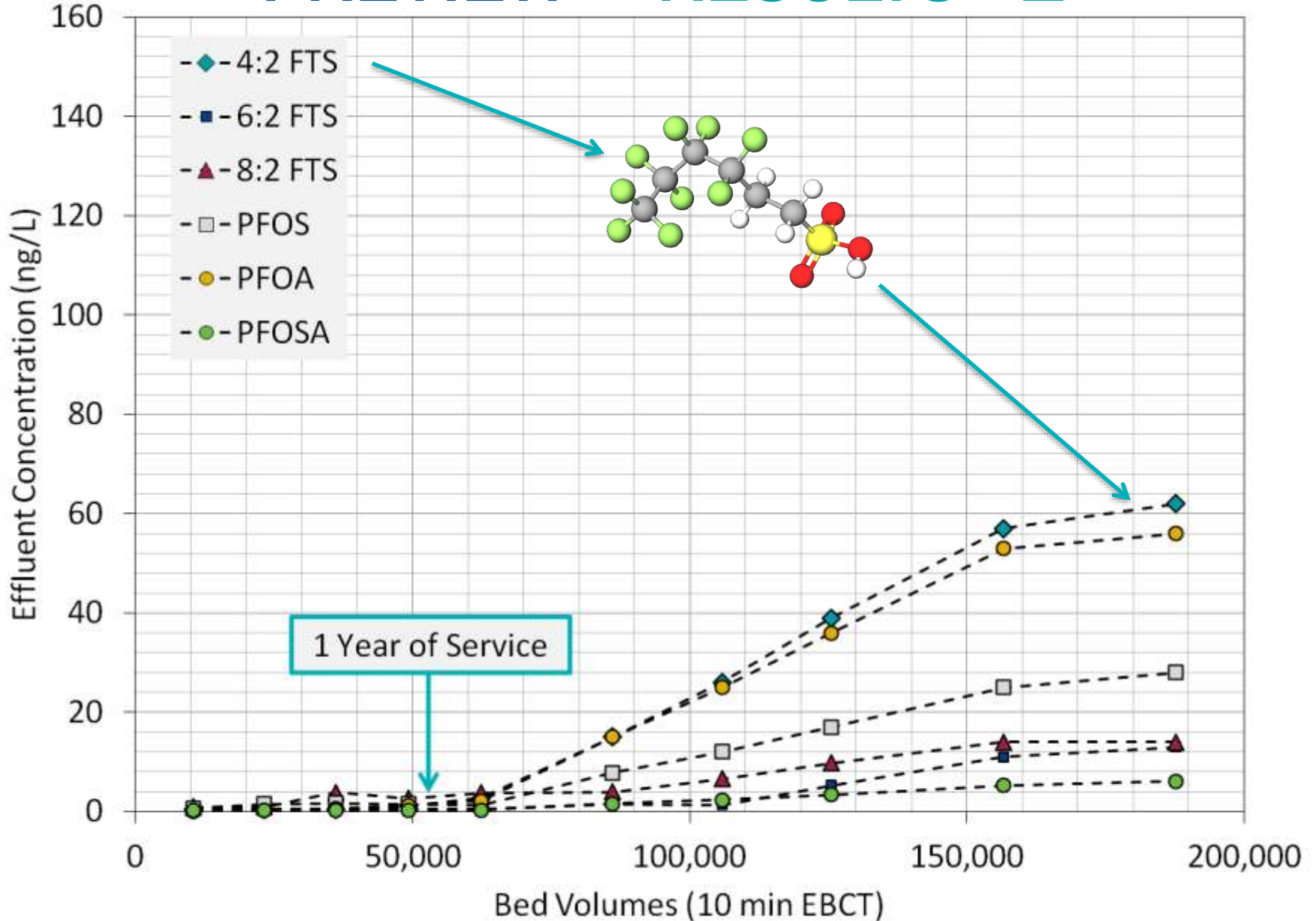
BETTER UNDERSTAND ROLE OF CARBON PROPERTIES

- Can pore volume distribution explain results?
- Can more “simple” test methods correlate to results?

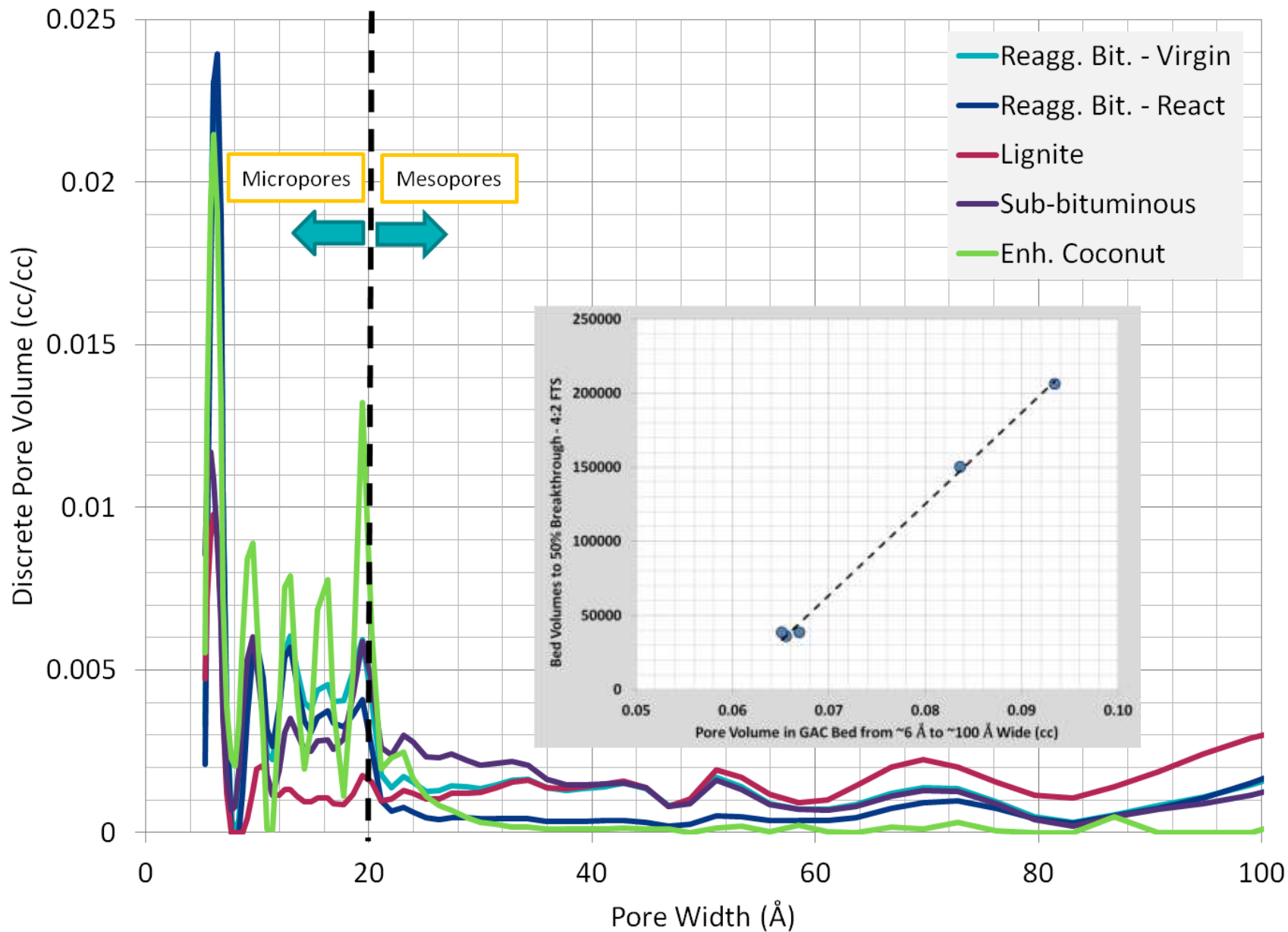
PREVIEW – RESULTS - 1



PREVIEW – RESULTS - 2



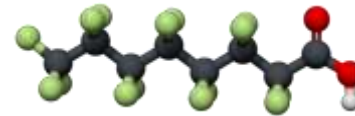
PREVIEW – RESULTS - 3



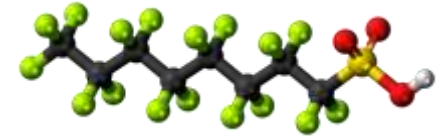
PFAS OVERVIEW

WHAT ARE PFAS?

- Poly- and perfluoroalkyl substances
- Class of man-made fluorinated compounds



PFOA Molecule



PFOS Molecule

Health Advisory:
70 ppt
Combined
PFOA / PFOS



WHY ARE THEY A PROBLEM?

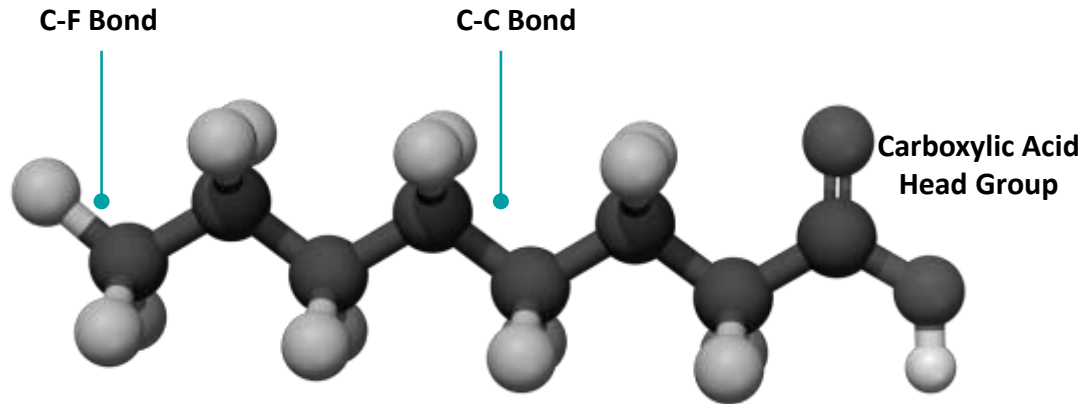
- Contaminates drinking water and food
- Highly persistent / resistant to degradation
- Accumulate in the body

WHERE DO THEY COME FROM?

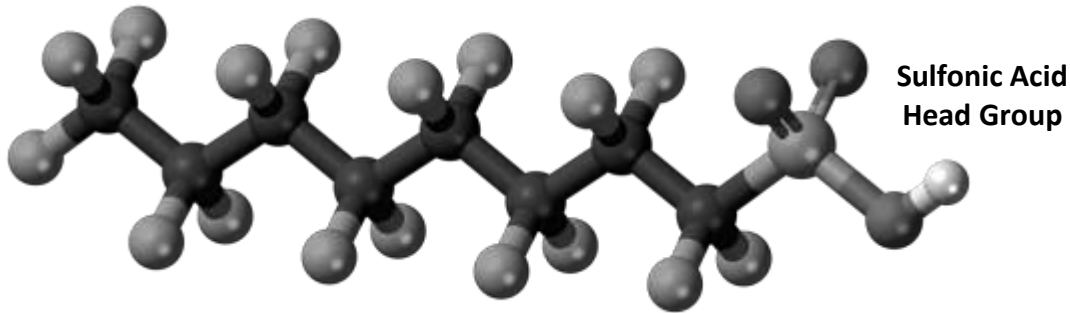
PFAS are used in a variety of products as a surface-active agent



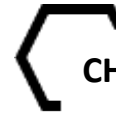
PFAS Molecular Characteristics



PFOA MOLECULE



PFOS MOLECULE

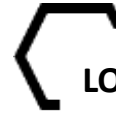


CHEMICALLY STABLE

- Carbon Chain backbone
- C-F Bond



RELATIVELY HIGH MOLECULAR WEIGHT



LOW VAPOR PRESSURE

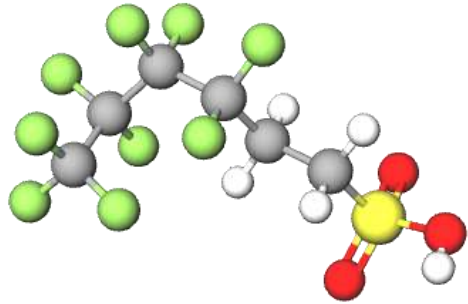


EASILY INFILTRATES INTO GROUNDWATER & SOIL

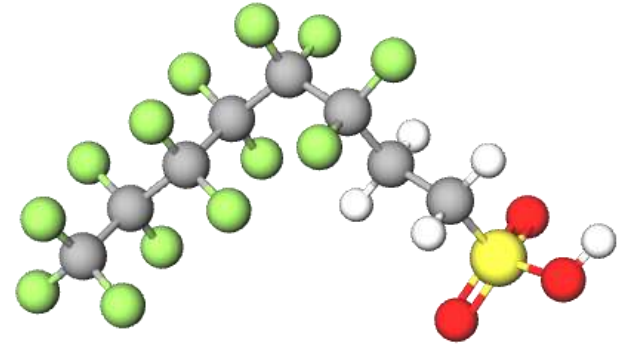


BIOACCUMULATES IN ORGANISMS

PFAS PRECURSORS



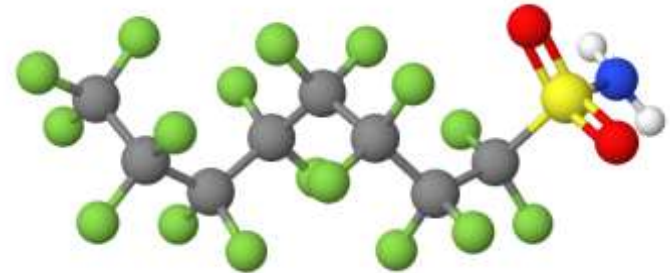
4:2 Fluorotelomer Sulfonic Acid
(4:2 FTS)



6:2 Fluorotelomer Sulfonic Acid
(6:2 FTS)



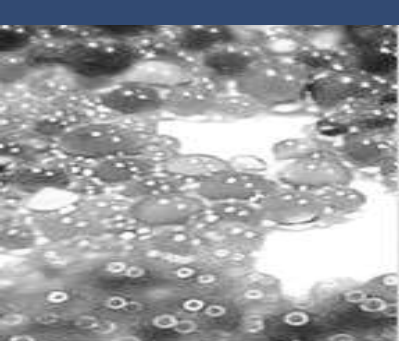


8:2 Fluorotelomer Sulfonic Acid
(8:2 FTS)



Perfluorooctane Sulfonamide

PFAS TREATMENT TECHNOLOGY

TREATMENT OPTION	PROS	CONS
	<ul style="list-style-type: none"> • Significantly lower capital costs • Significantly lower O&M costs • Reactivation saves cost, destroys PFASs, & removes liability • Established BAT for a long list of organic contaminants 	<ul style="list-style-type: none"> • High Natural Organic Matter (NOM) can increase use rates • Removal efficacy varies by size/weight/solubility of contaminant
	<ul style="list-style-type: none"> • Removes salts / inorganics that GAC cannot 	<ul style="list-style-type: none"> • Concentrated waste water disposal liabilities & costs • More energy / CO₂ intensive • High maintenance cleaning and replacement of fouled membranes • Removes healthy minerals
	<ul style="list-style-type: none"> • Resin can be regenerated • May be more economical at high concentrations of PFAS (generally much higher than drinking water applications – primarily remediation applications only) 	<ul style="list-style-type: none"> • High cost of media • Regeneration produces disposal liabilities & costs • Regeneration requires both brine and a solvent (e.g. methanol)

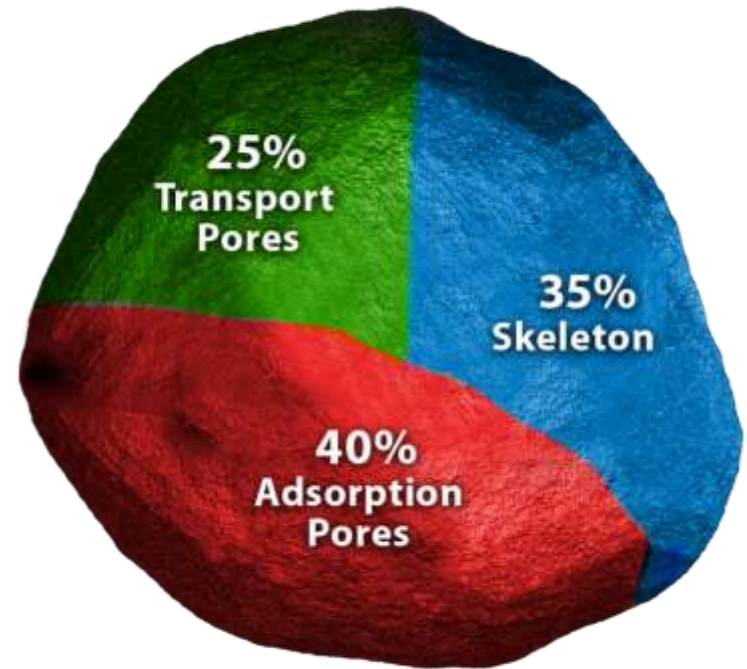
STRUCTURE OF ACTIVATED CARBON

Adsorption Pores

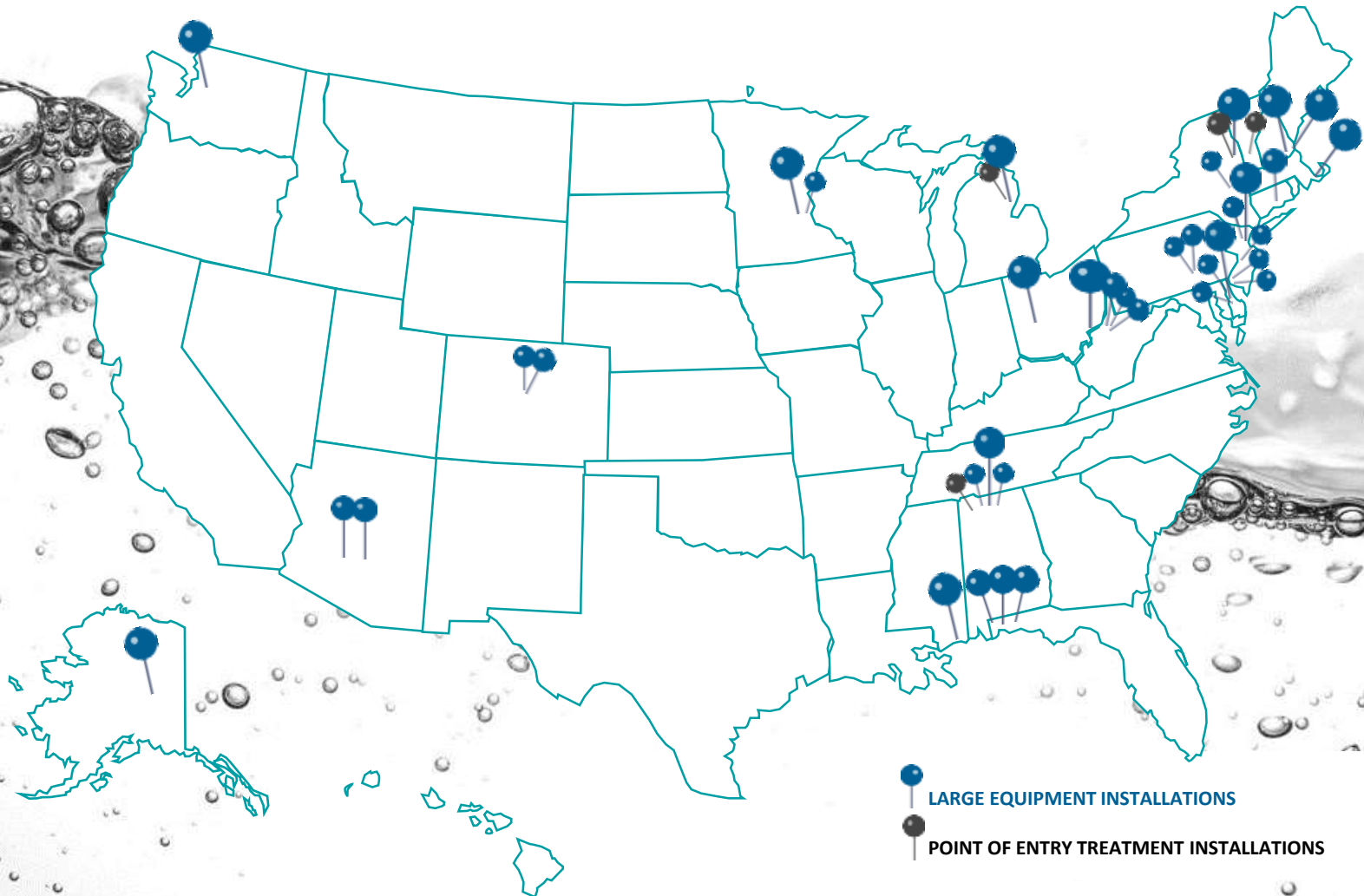
- Finest pores in structure
- Termed “micropores”
- $<20\text{\AA}$ diameter

Transport Pores

- Diffusion pathways to transport adsorbates
- Termed “mesopores”
- $20\text{\AA} - 500\text{\AA}$ diameter



CALGON CARBON PFAS TREATMENT LOCATIONS



40+ INSTALLATIONS ACROSS THE US

TREATMENT METHODOLOGY



DUAL VESSEL TREATMENT

- Maximize carbon loading
- Simplify carbon exchange logistics
- Redundancy

SUFFICIENT CONTACT TIME IS CRITICAL FOR EFFECTIVE REMOVAL

- Kinetics and Thermodynamics of adsorption must be considered
- 10 minutes EBCT per vessel minimum

REMOVAL STUDY

RSSCTs

Five GAC products evaluated under identical equivalent full-scale operating conditions and influent water quality

GAC DETAILS

GAC Source Material	Full-Scale Mesh Size	Apparent Density	Iodine Number (mg/g)	Xylenol Orange Dye Number (mg/g/hr)	Molasses Number
Reagglomerated Bituminous Coal - Virgin	12 × 40	0.543	1030	13.5	189
Reagglomerated Bituminous Coal – React.	12 × 40	0.546	905	13.4	236
Lignite Coal	12 × 40	0.377	605	17.4	416
Sub-Bituminous Coal	12 × 40	0.350	1015	21.7	154
Coconut Shell	12 × 30	0.414	1290	13.5	288

GAC COMPARISON

TEST CONDITIONS - 1



OPERATING PARAMETERS

- 10 minutes empty-bed contact time (EBCT).
- Pennsylvania groundwater spike with PFAS.

Compound	Abbreviation	Avg. Influent Concentration (ng/L)
4:2 Fluorotelomer Sulfonic Acid	4:2 FTS	130
6:2 Fluorotelomer Sulfonic Acid	6:2 FTS	43
8:2 Fluorotelomer Sulfonic Acid	8:2 FTS	56
Perfluorooctanesulfonic Acid	PFOS	153
Perfluorooctanoic Acid	PFOA	177
Perfluorooctane Sulfonamide	PFOSA	39

GAC COMPARISON

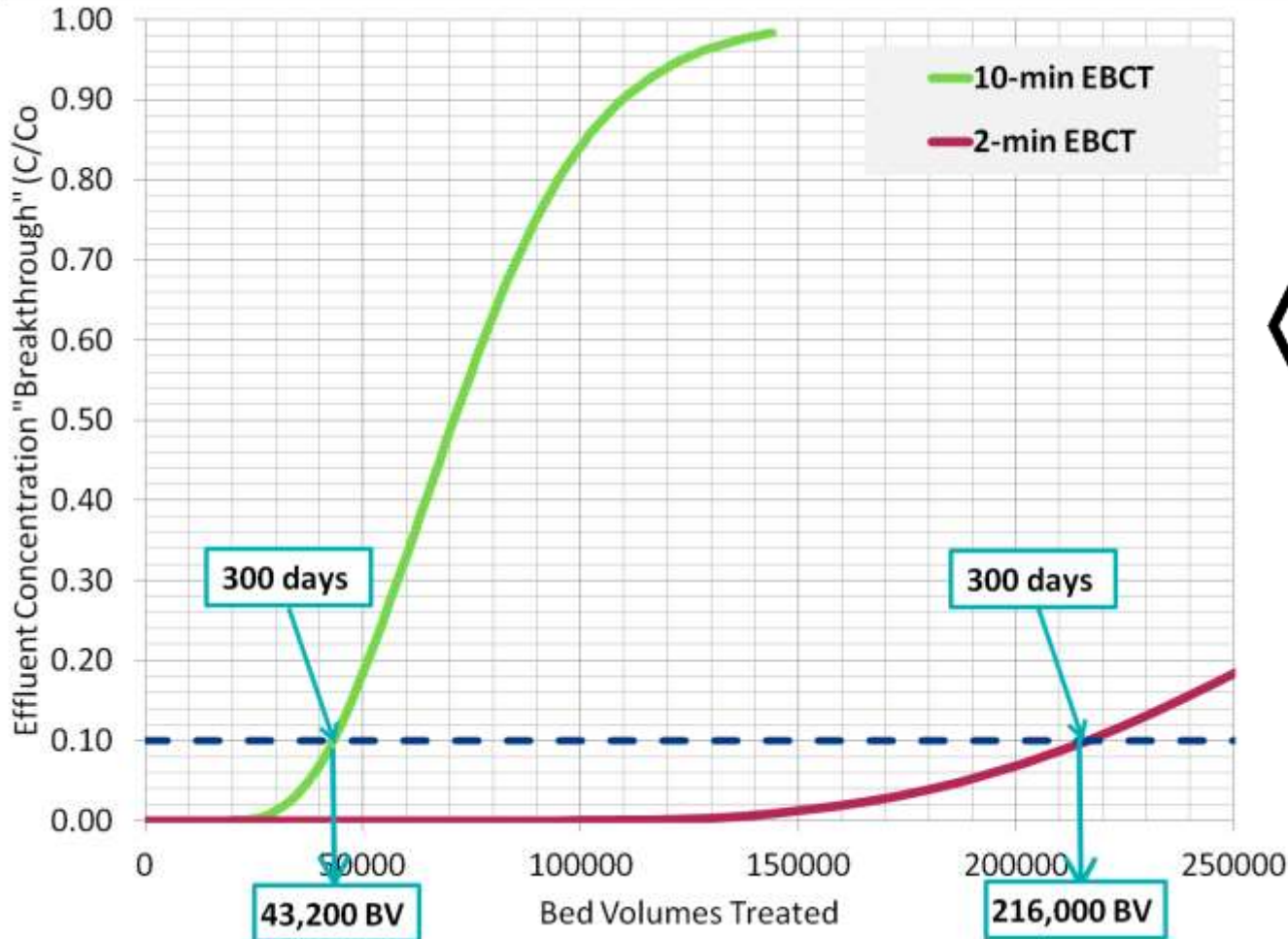
TEST CONDITIONS - 2



WATER QUALITY

Component	Value	Units
pH	8.1	-
Total Dissolved Solids	670	mg/L
Alkalinity	105	mg/L as CaCO ₃
Total Organic Carbon	0.3	mg/L

REFRESHER: READING BREAKTHROUGH CURVES

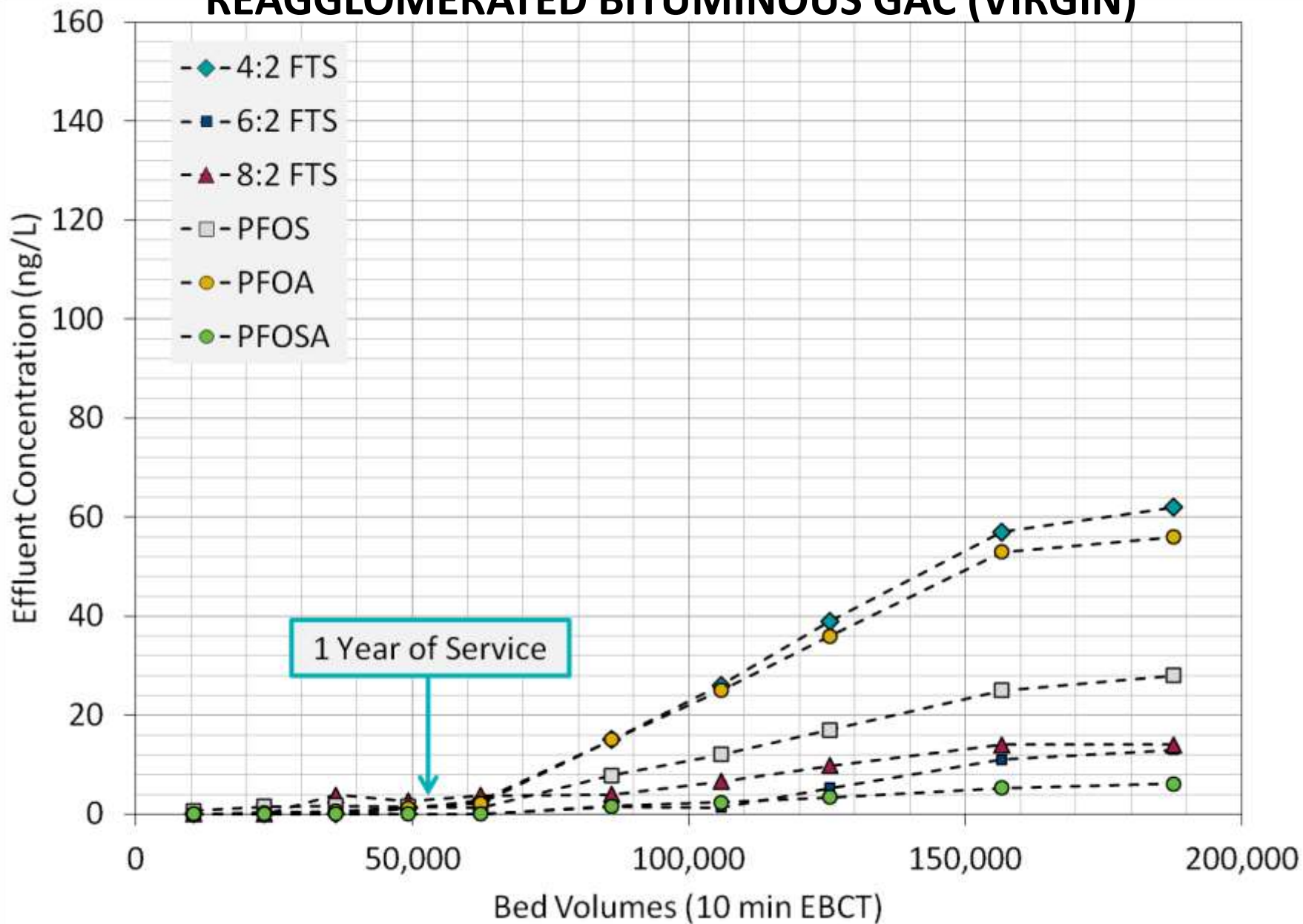


REMEMBER

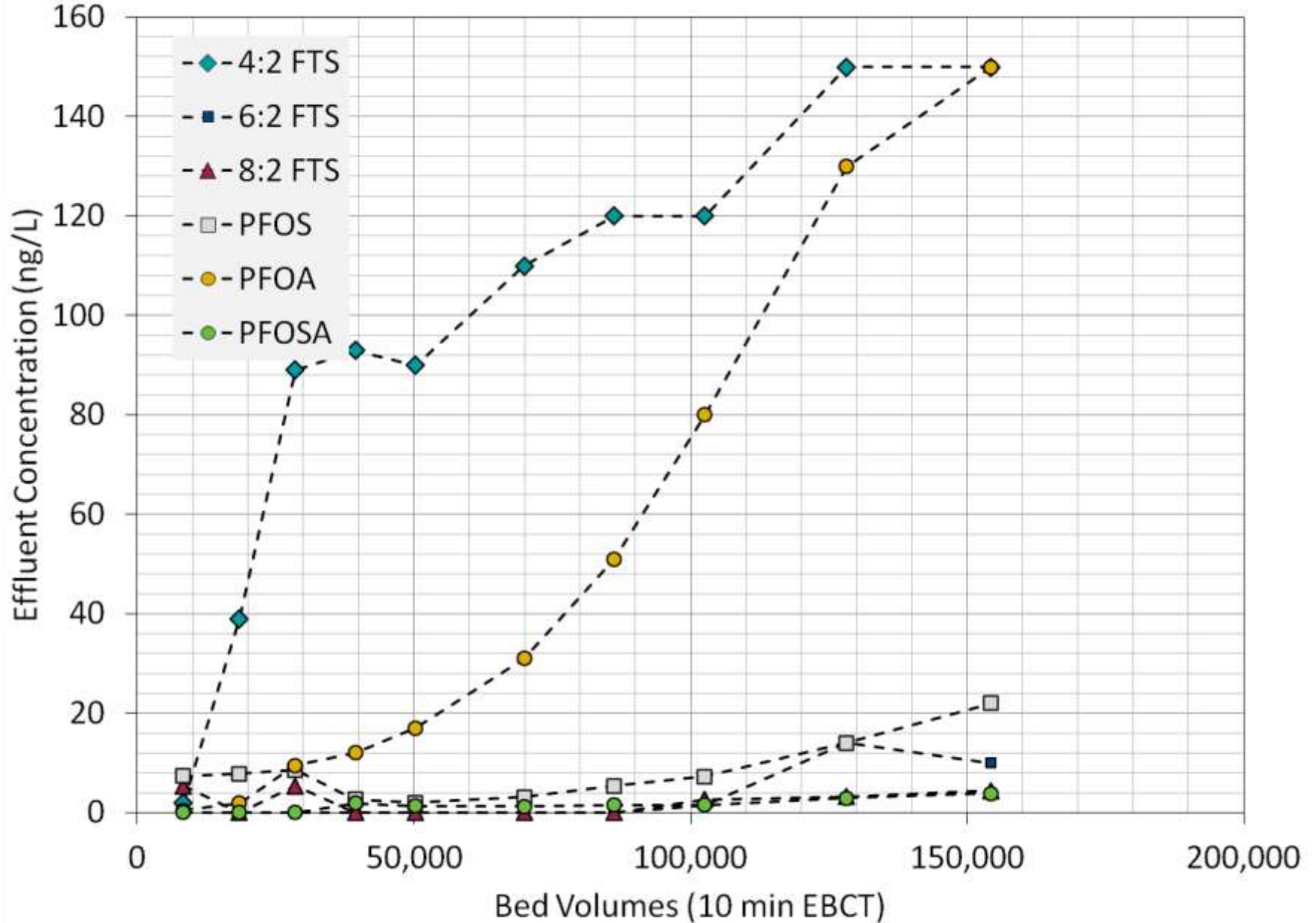
- Usually shown as normalized values.
- C/Co - What is influent concentration?
- "Bed Volumes" does not equal actual run time.

PFAS BREAKTHROUGH CURVES

REAGGLOMERATED BITUMINOUS GAC (VIRGIN)

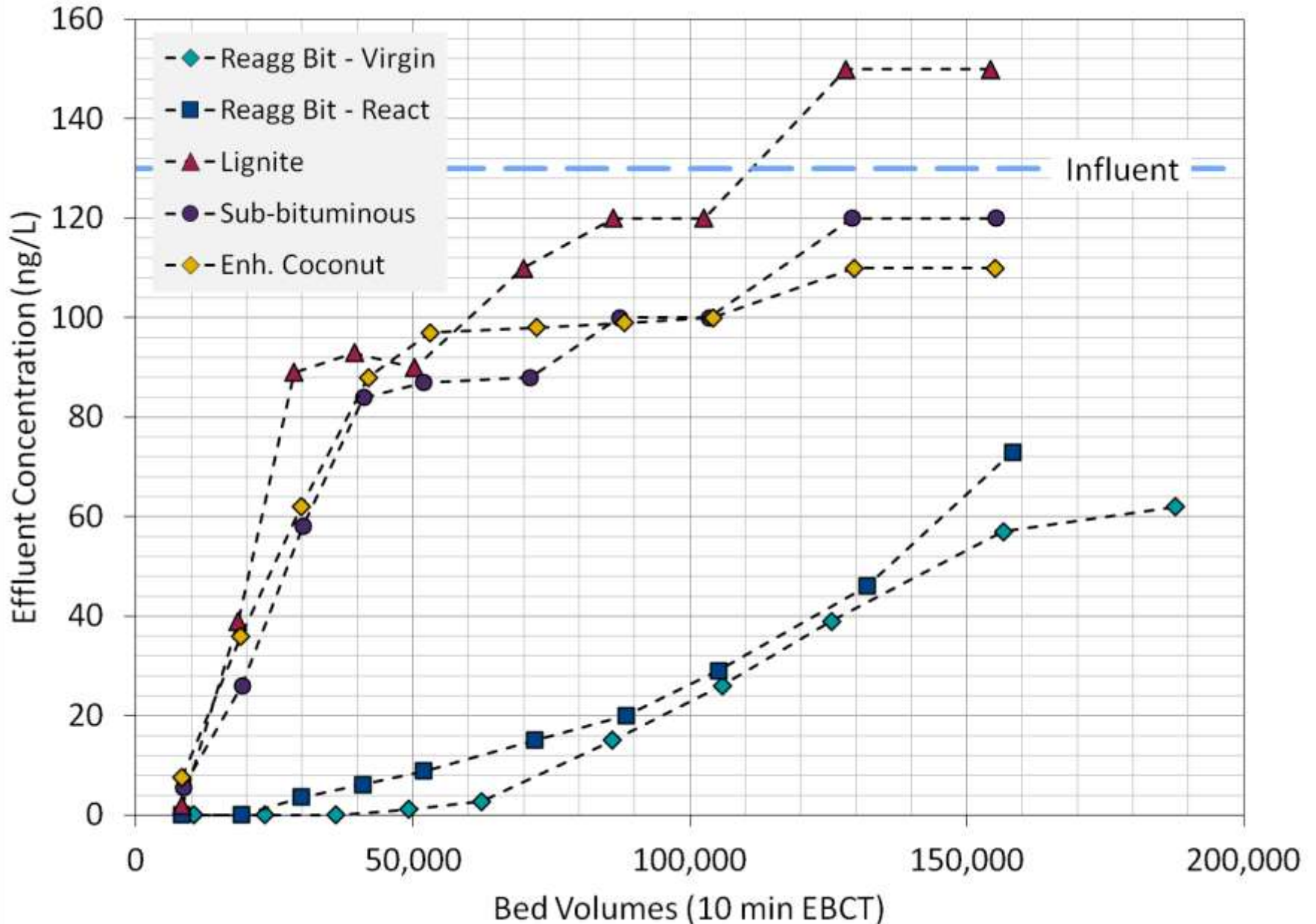


PFAS BREAKTHROUGH CURVES LIGNITE-BASED GAC



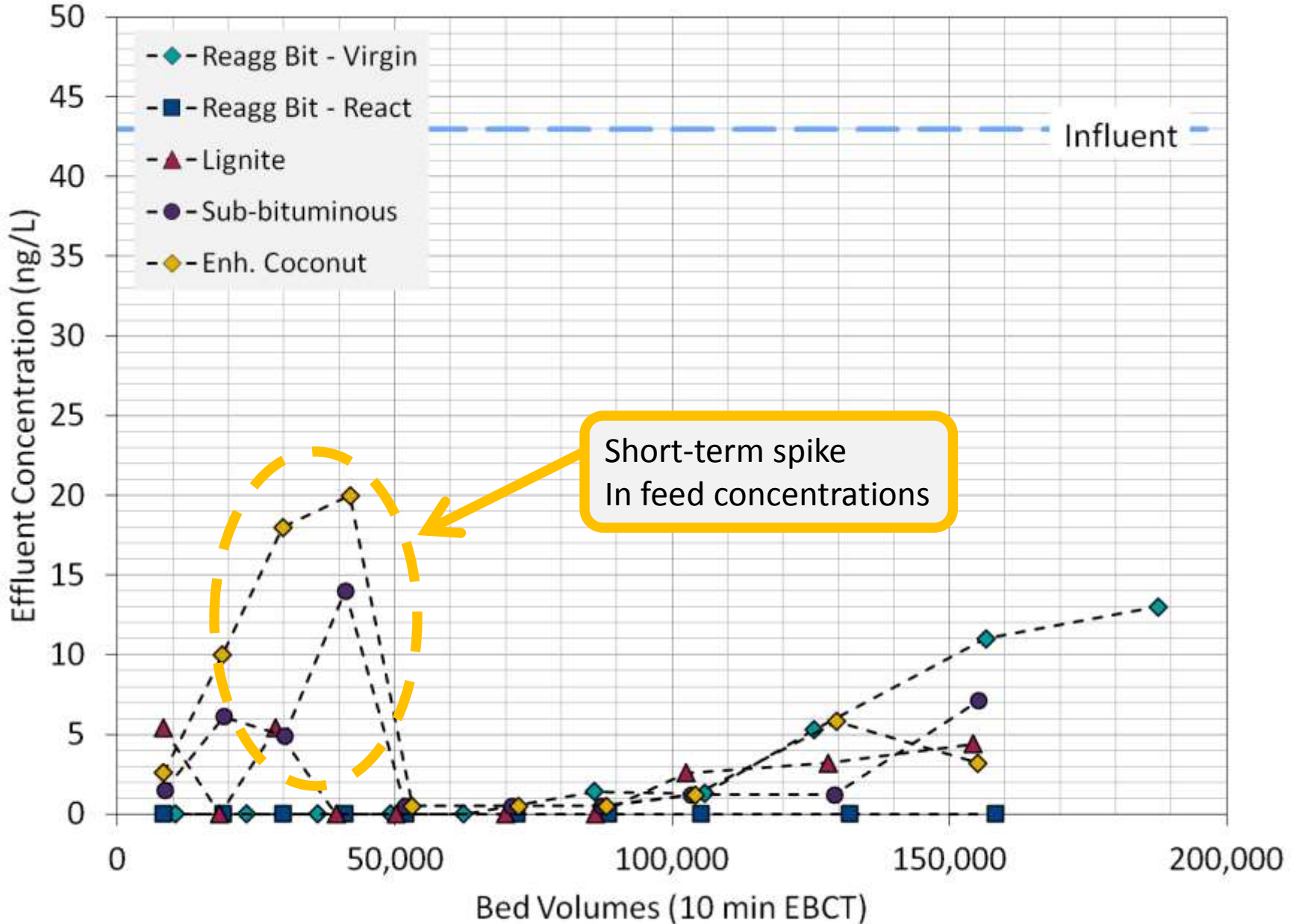
PFAS BREAKTHROUGH CURVES

4:2 FTS



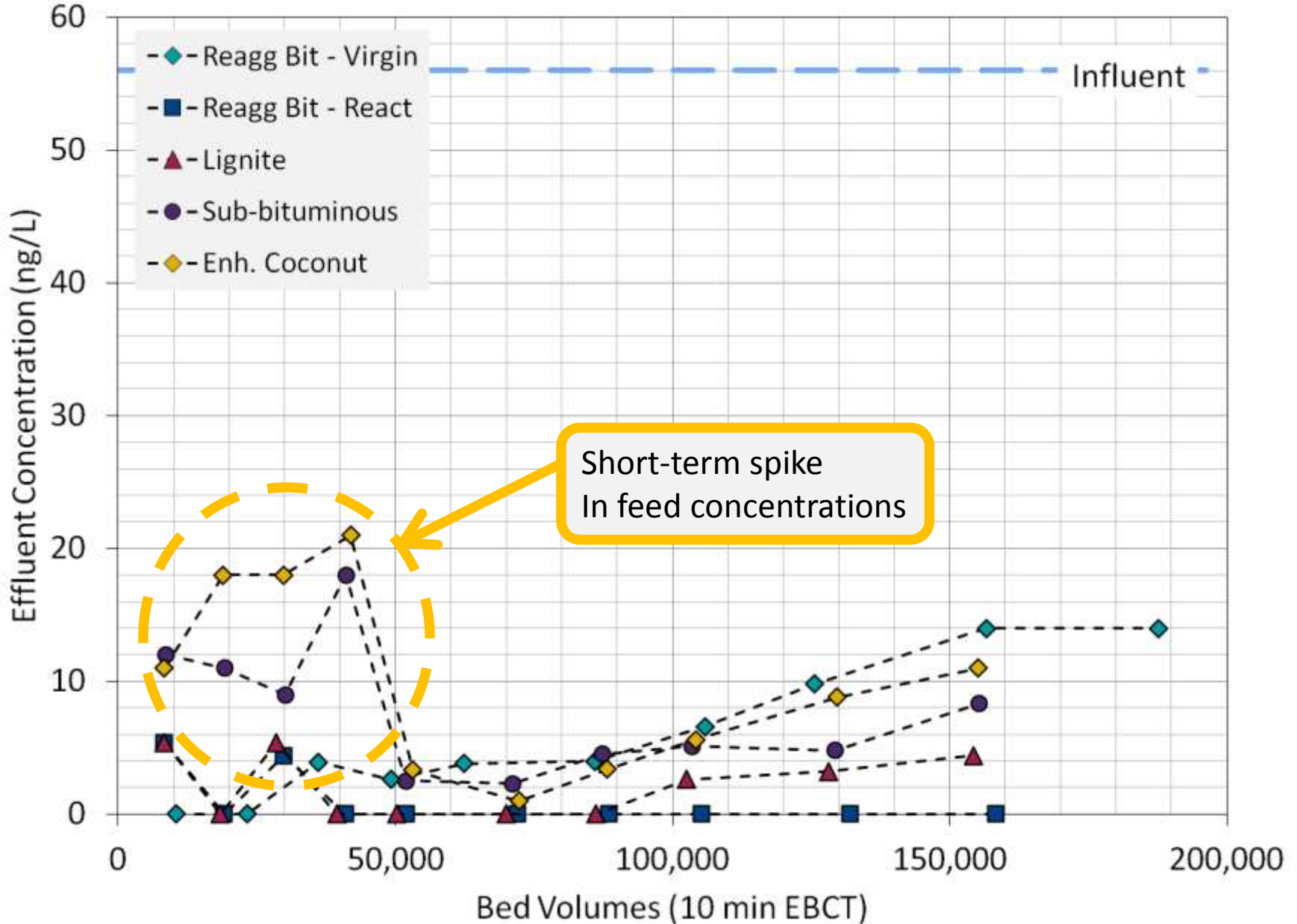
PFAS BREAKTHROUGH CURVES

6:2 FTS



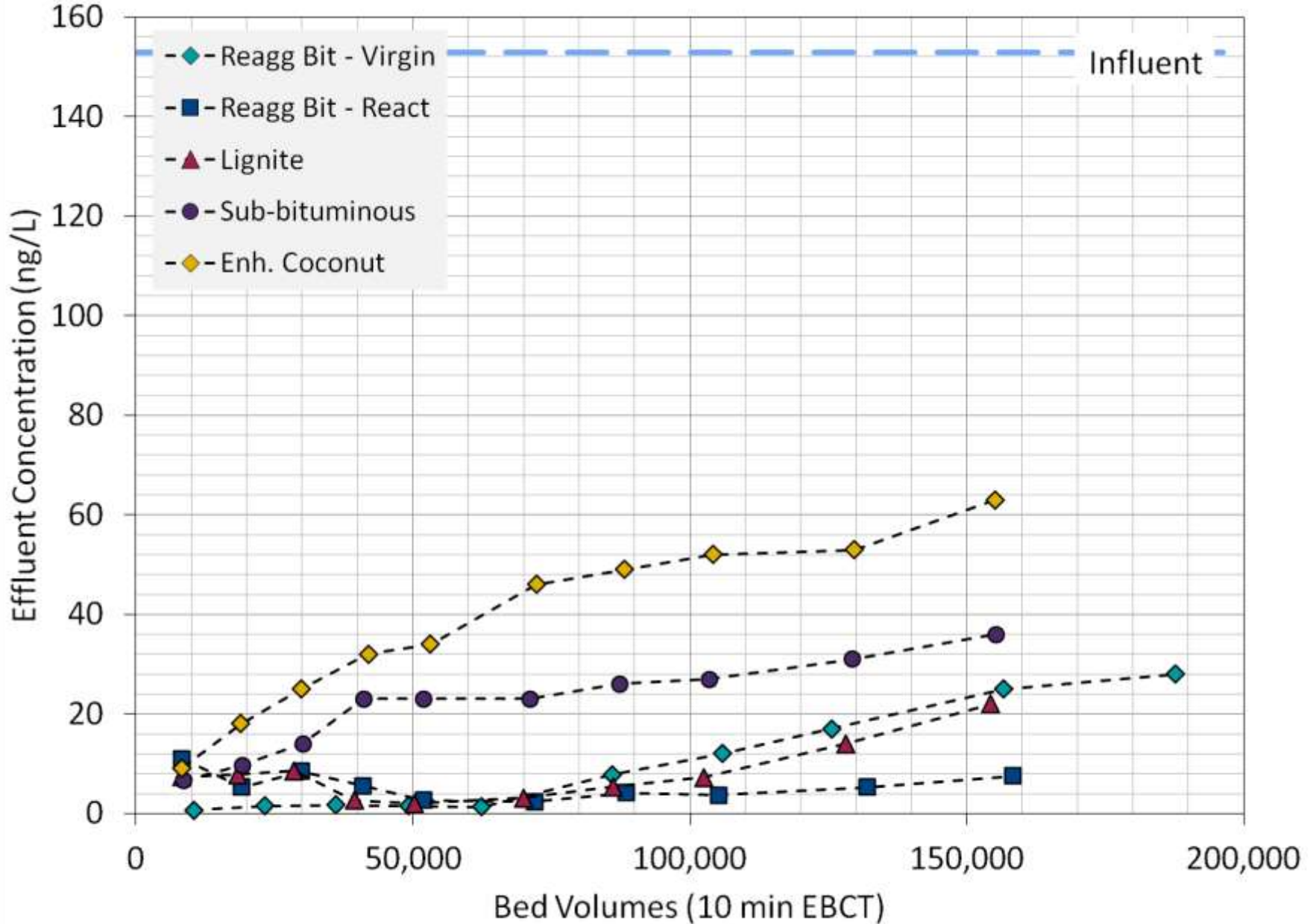
PFAS BREAKTHROUGH CURVES

8:2 FTS



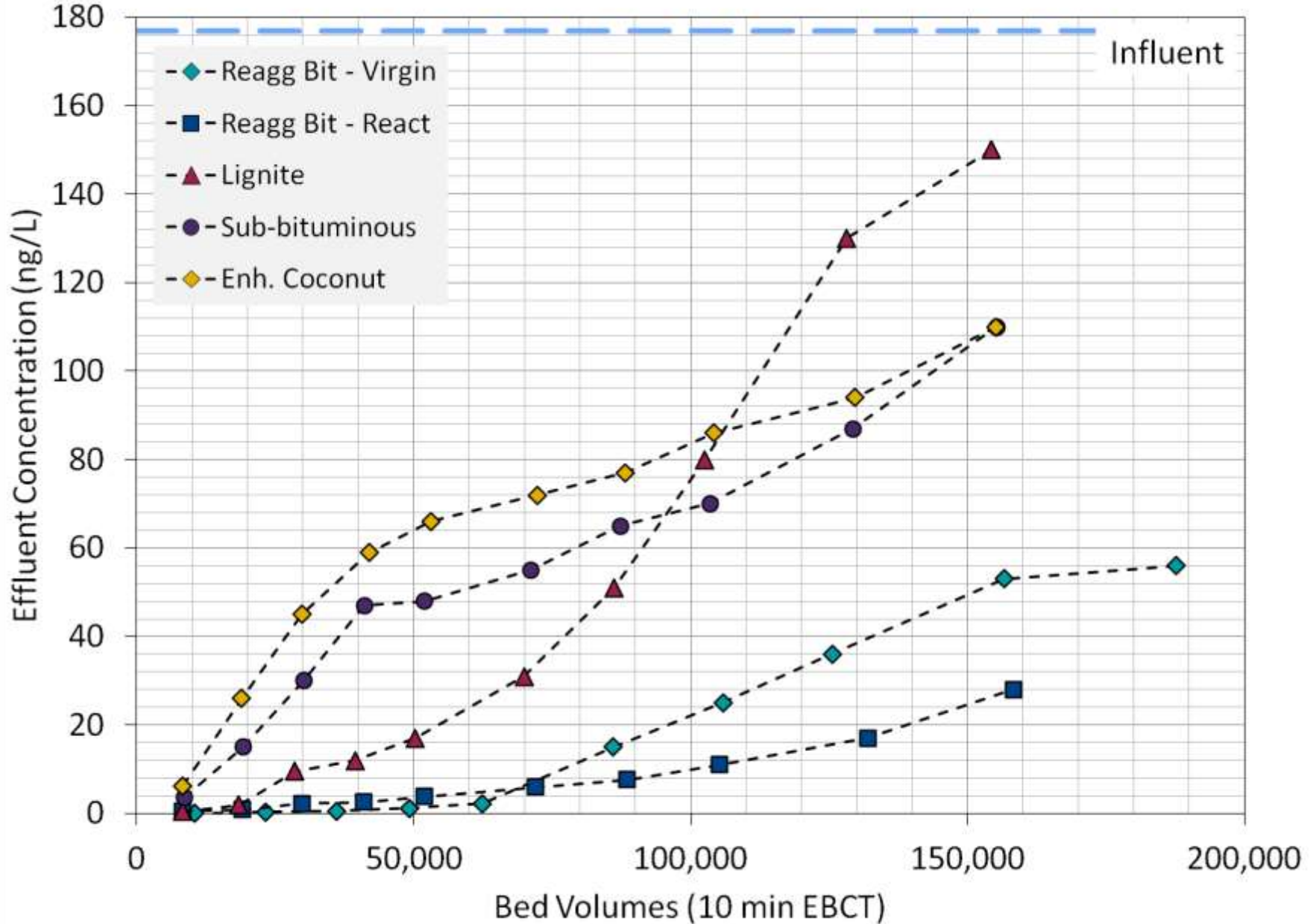
PFAS BREAKTHROUGH CURVES

PFOS



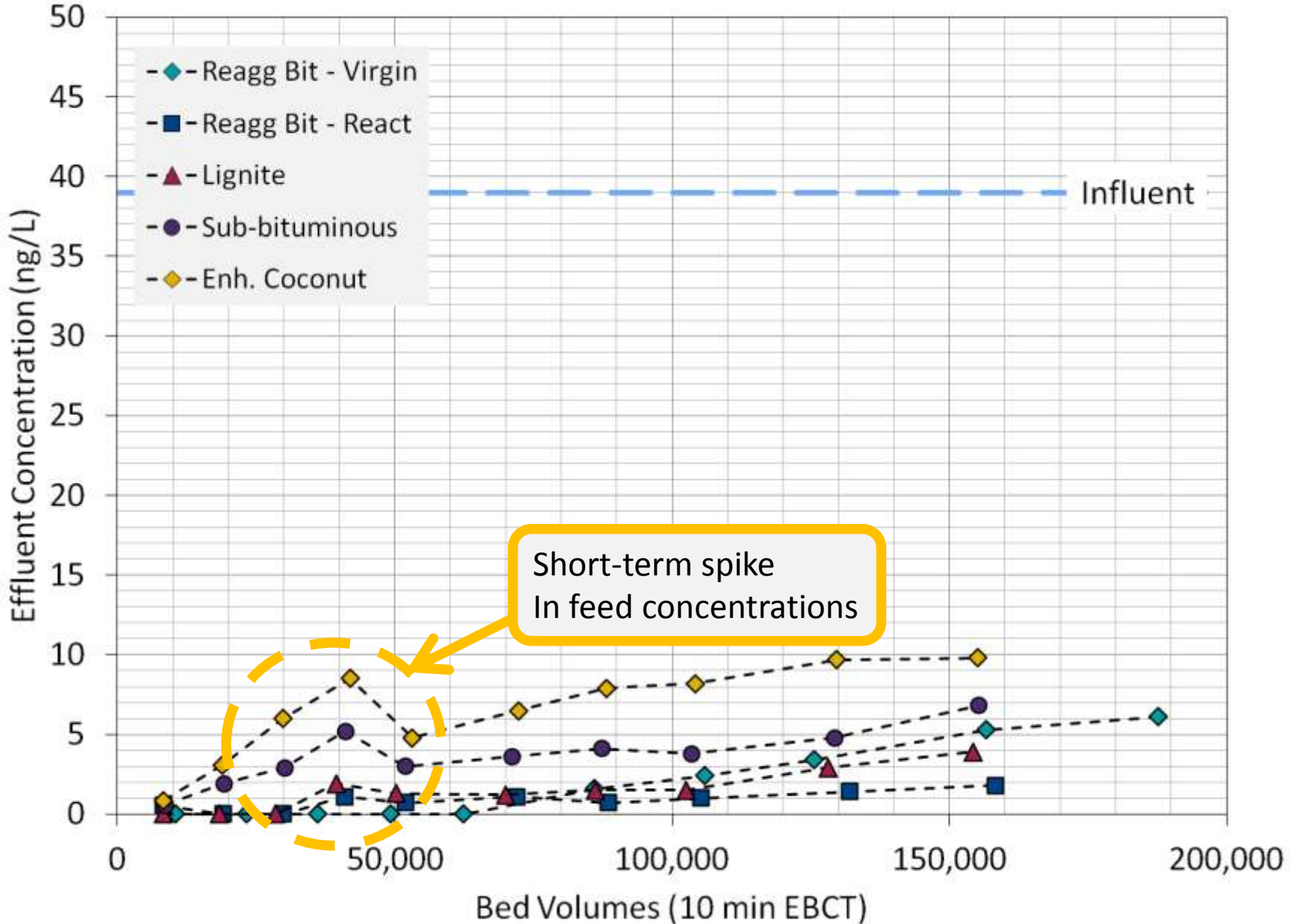
PFAS BREAKTHROUGH CURVES

PFOA



PFAS BREAKTHROUGH CURVES

PFOSA



INITIAL CONCLUSIONS



ALL 4 PRECURSORS REMOVABLE WITH GAC

- 4:2 FTS most difficult
 - Lower molecular weight (shorter chain).
 - Large variation in removal.
 - Most-favorable performance with reaggl. bituminous GACs.



SENSITIVITY TO VARYING INFLUENT CONCENTRATIONS

- Reaggl. bituminous GAC minimally affected.
- Sub-bituminous & enhanced coconut showed rapid increase in breakthrough during spike.
- Some sensitivity evident in lignite breakthrough curve.

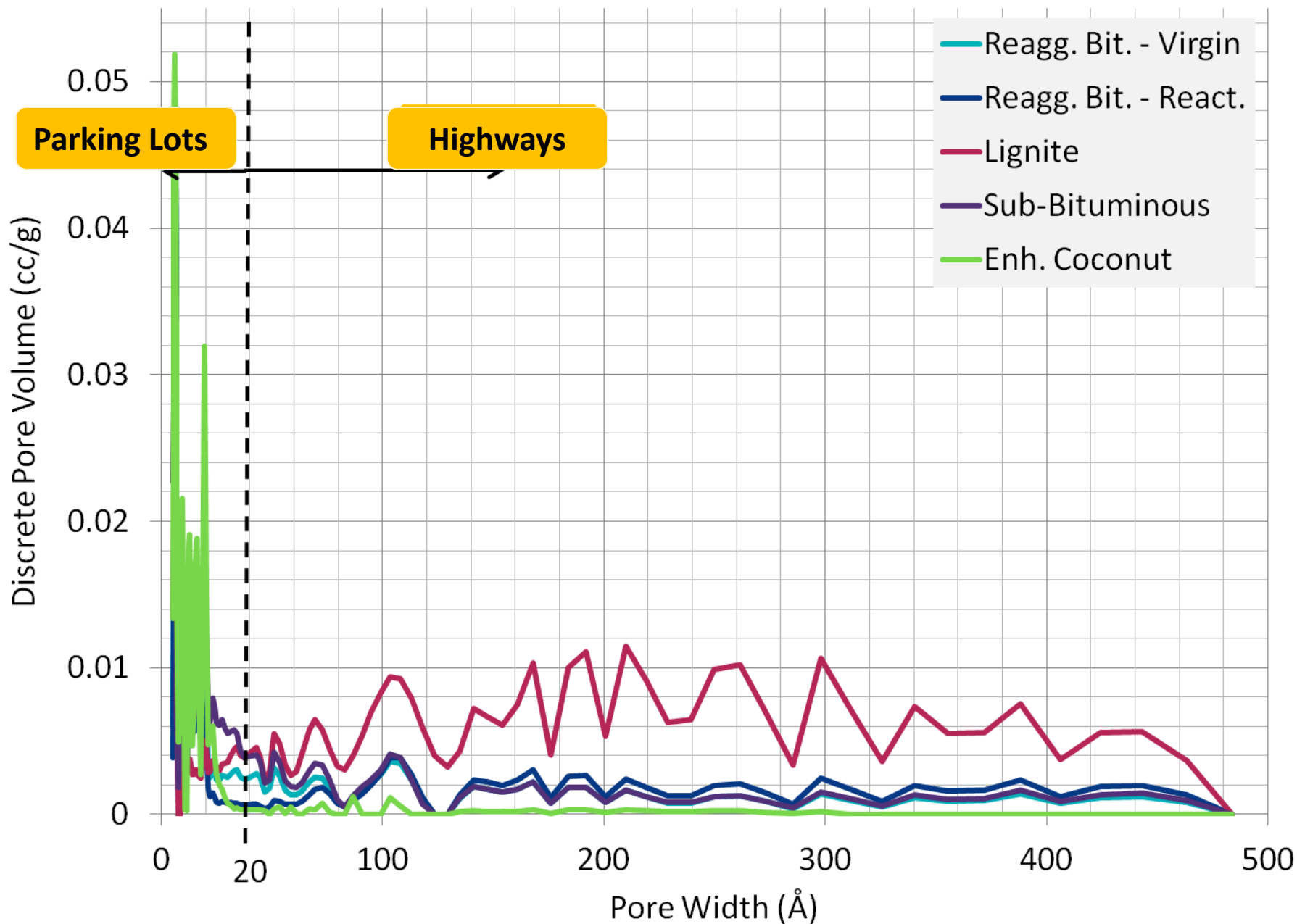
PROPERTIES vs. PERFORMANCE

4:2 FTS
REMOVAL

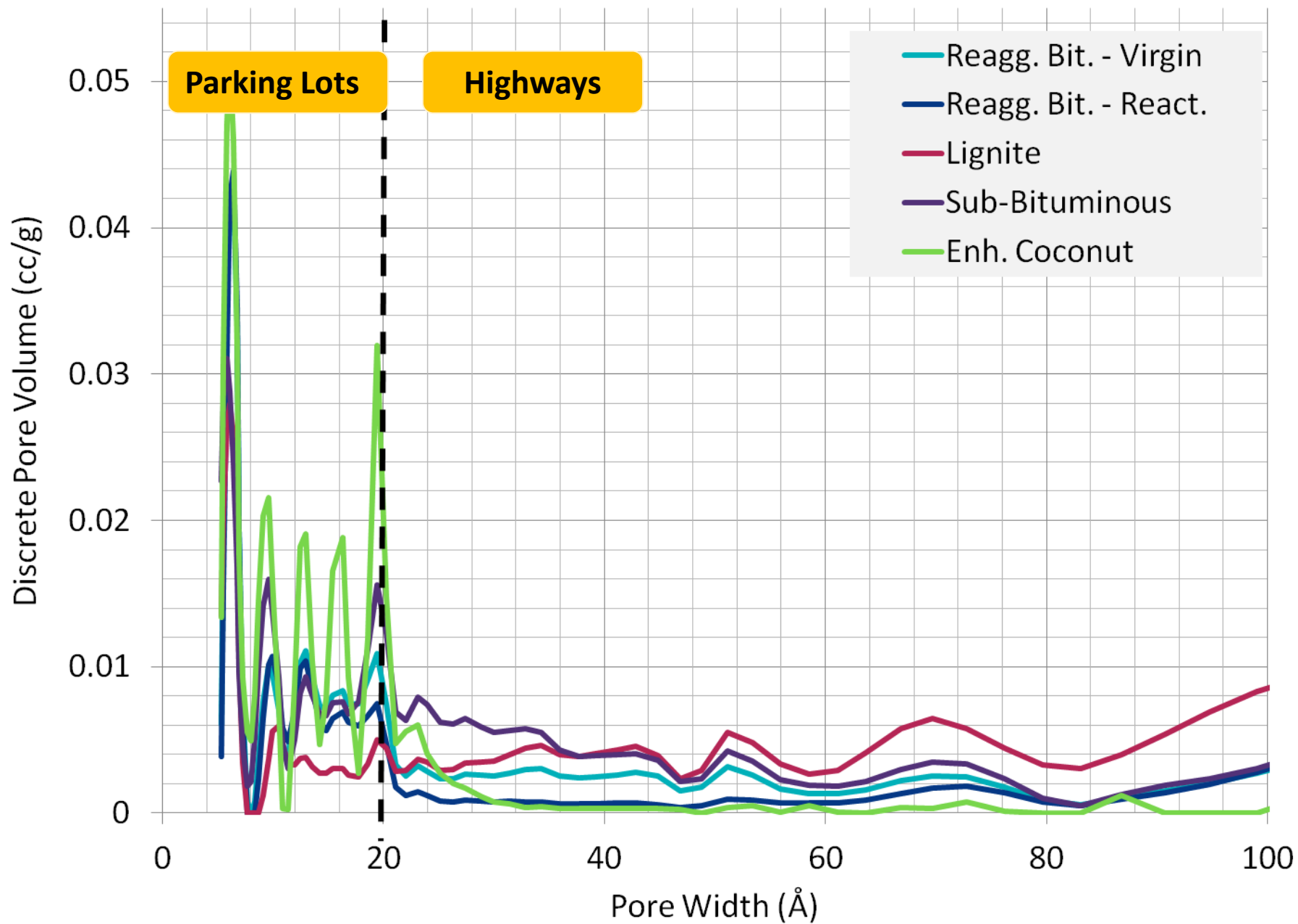
In addition to surrogate adsorbate tests, porosity of test GACs was evaluated using nitrogen adsorption isotherms and compared to performance.

GAC Source Material	BV to 50% Breakthrough	Apparent Density	Iodine Number (mg/g)	Xylenol Orange Dye Number (mg/g/hr)	Molasses Number
Reagglomerated Bituminous Coal - Virgin	206,300	0.543	1030	13.5	189
Reagglomerated Bituminous Coal – React.	150,500	0.546	905	13.4	236
Lignite Coal	36,200	0.377	605	17.4	416
Sub-Bituminous Coal	38,600	0.350	1015	21.7	154
Coconut Shell	38,800	0.414	1290	13.5	288

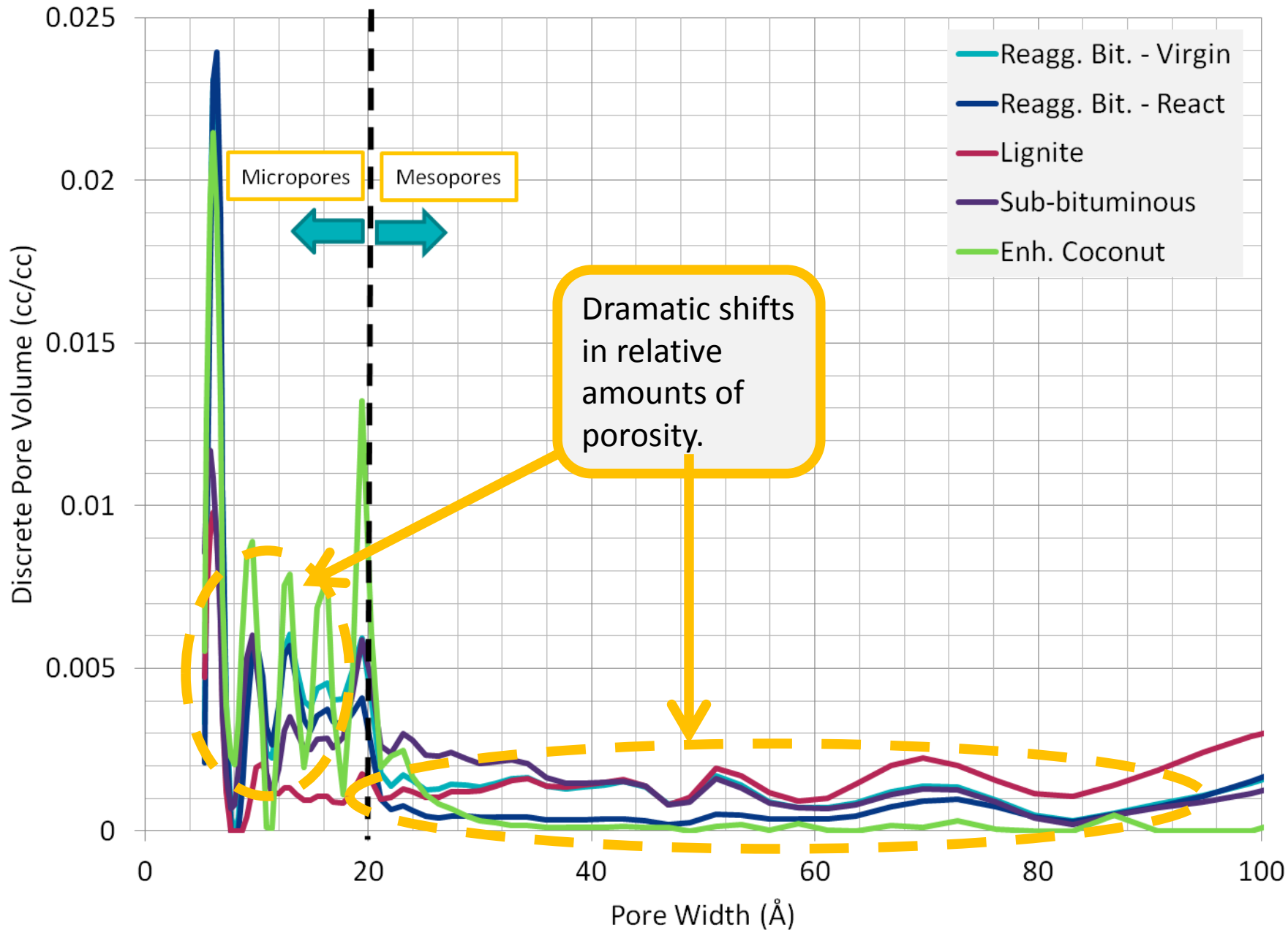
GAC POROSITY: ~5 - 500 Å



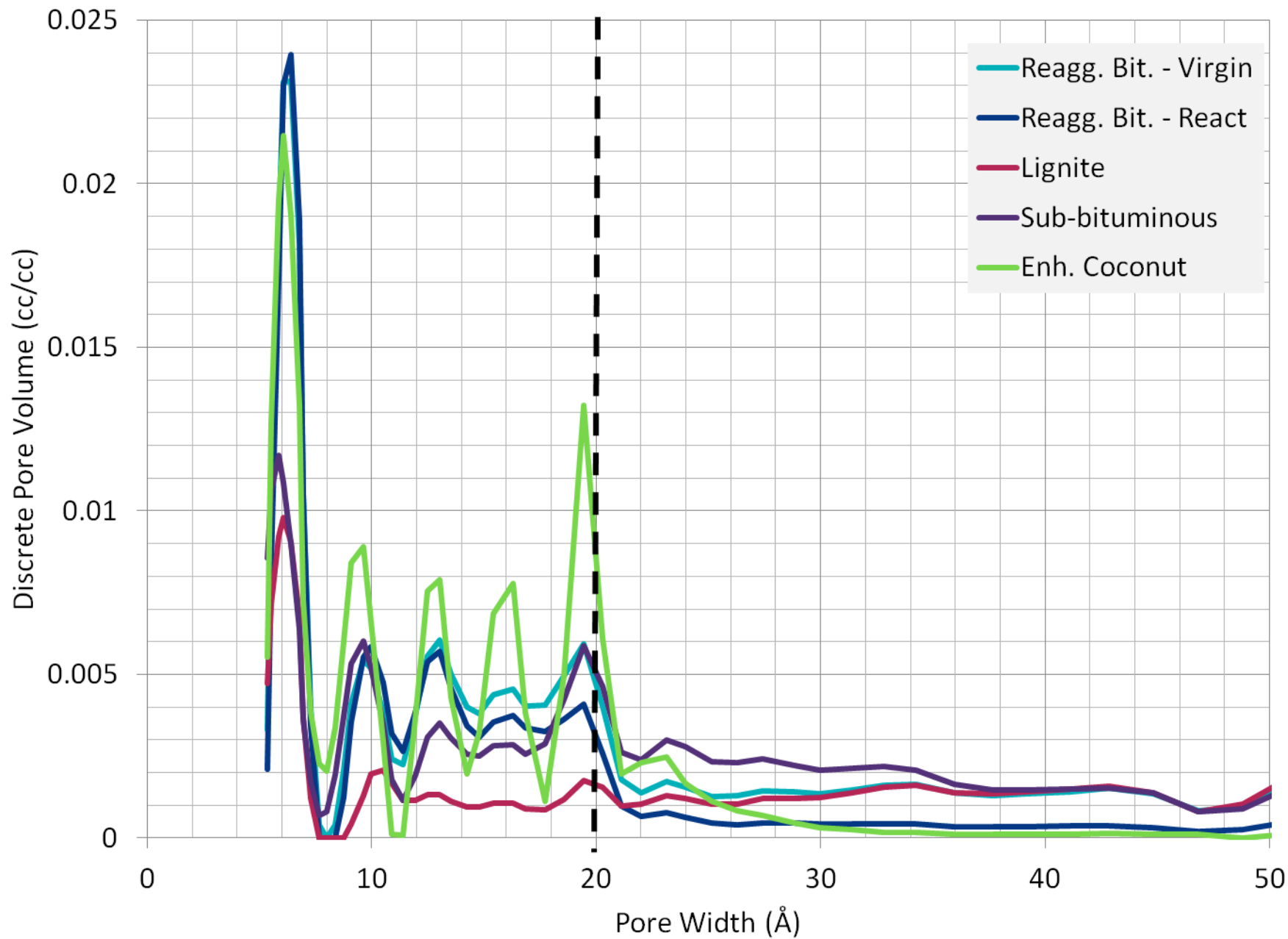
GAC POROSITY: ~5 - 100 Å



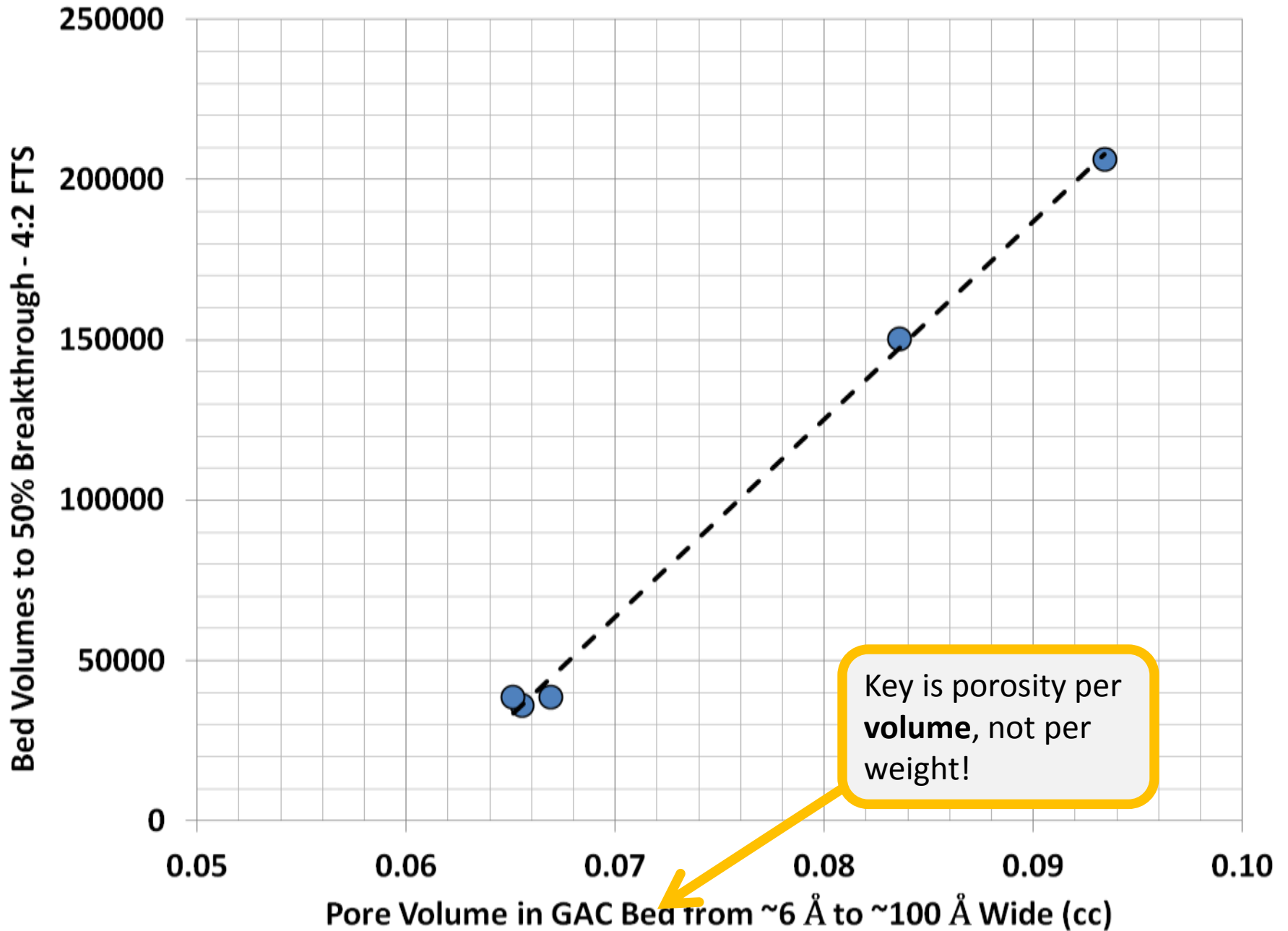
GAC POROSITY: NORMALIZED TO VOLUME IN BED



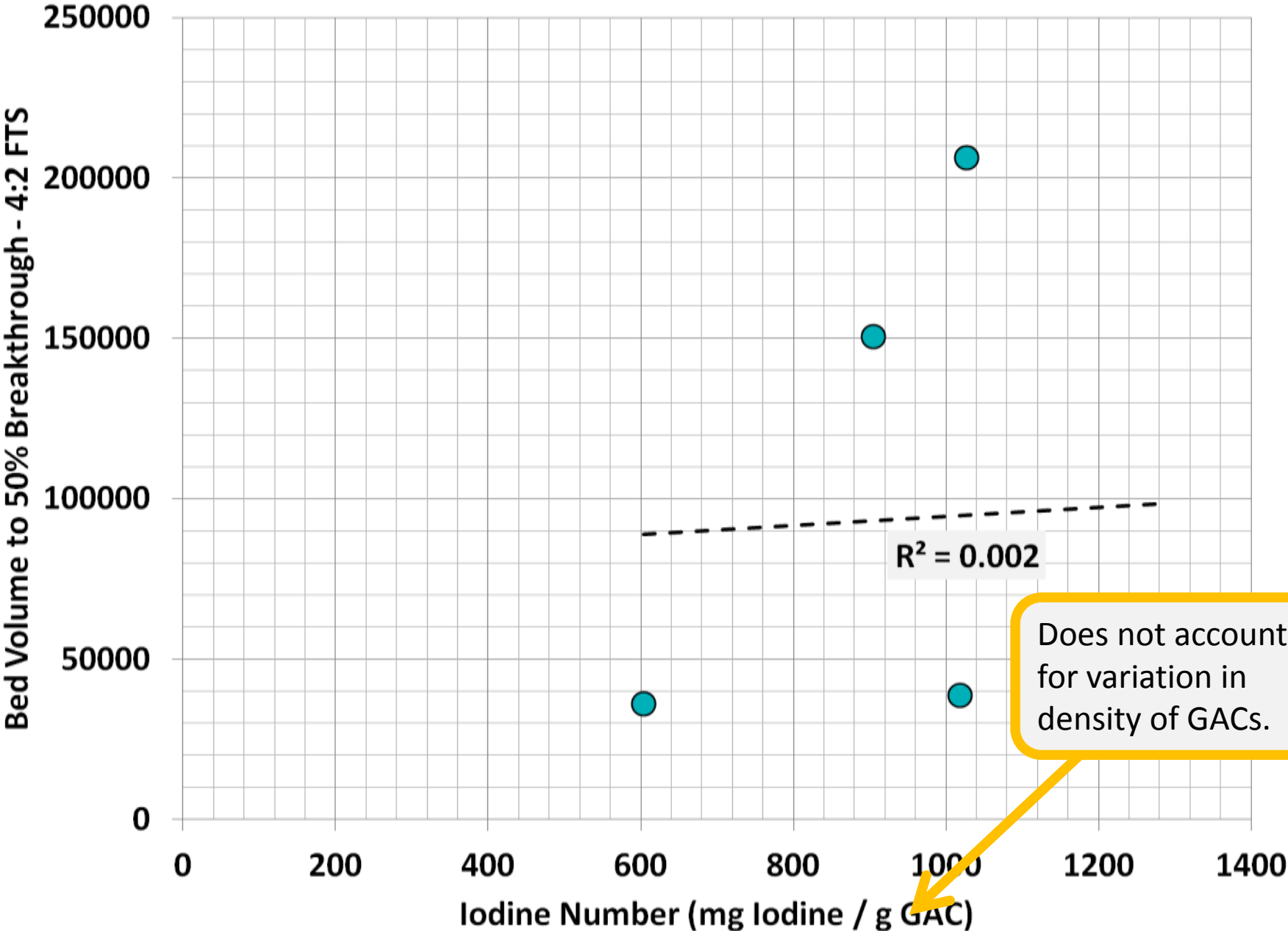
GAC POROSITY: HOW MUCH IS IN THE BED?



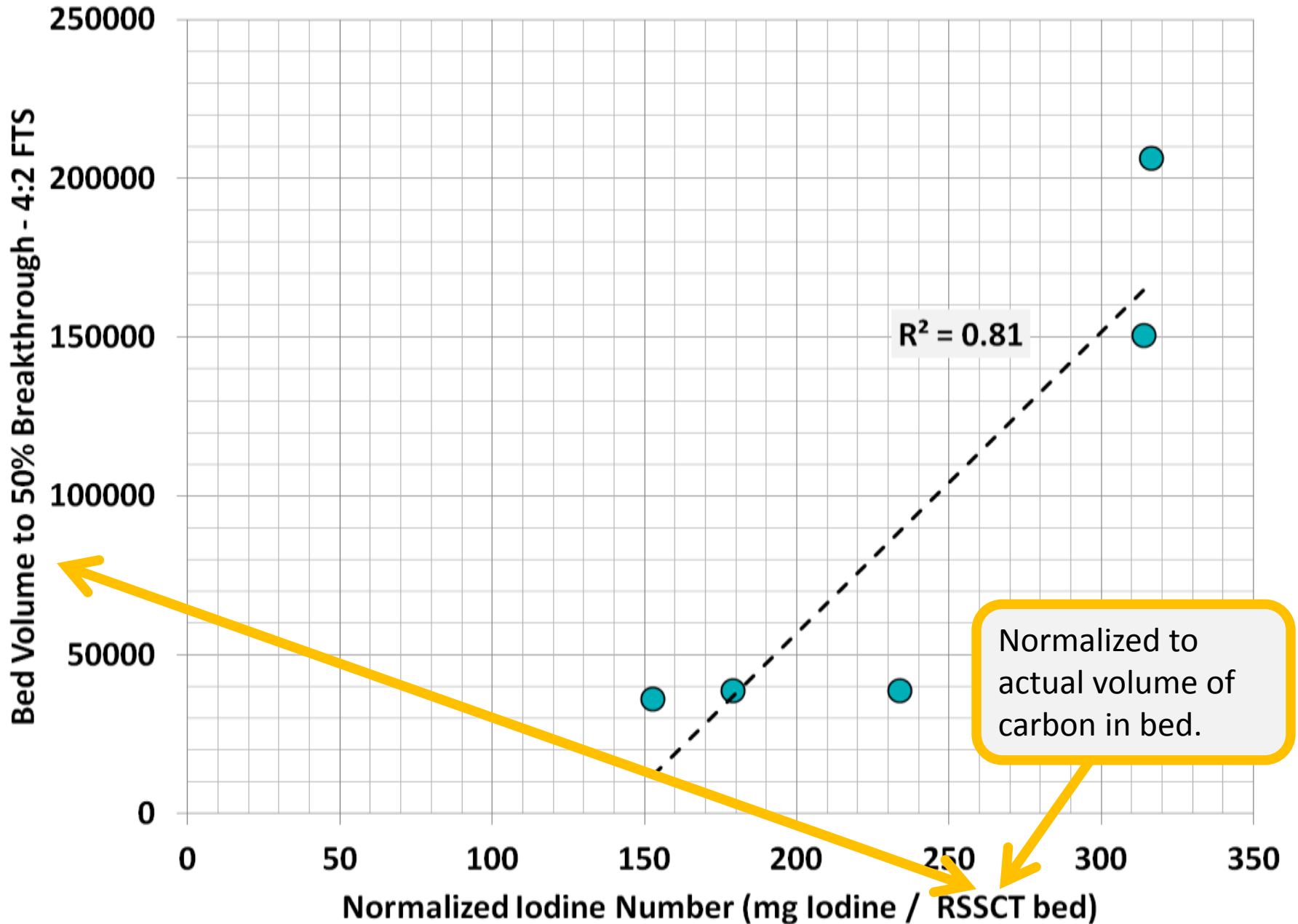
GAC POROSITY: RELATED TO PERFORMANCE?



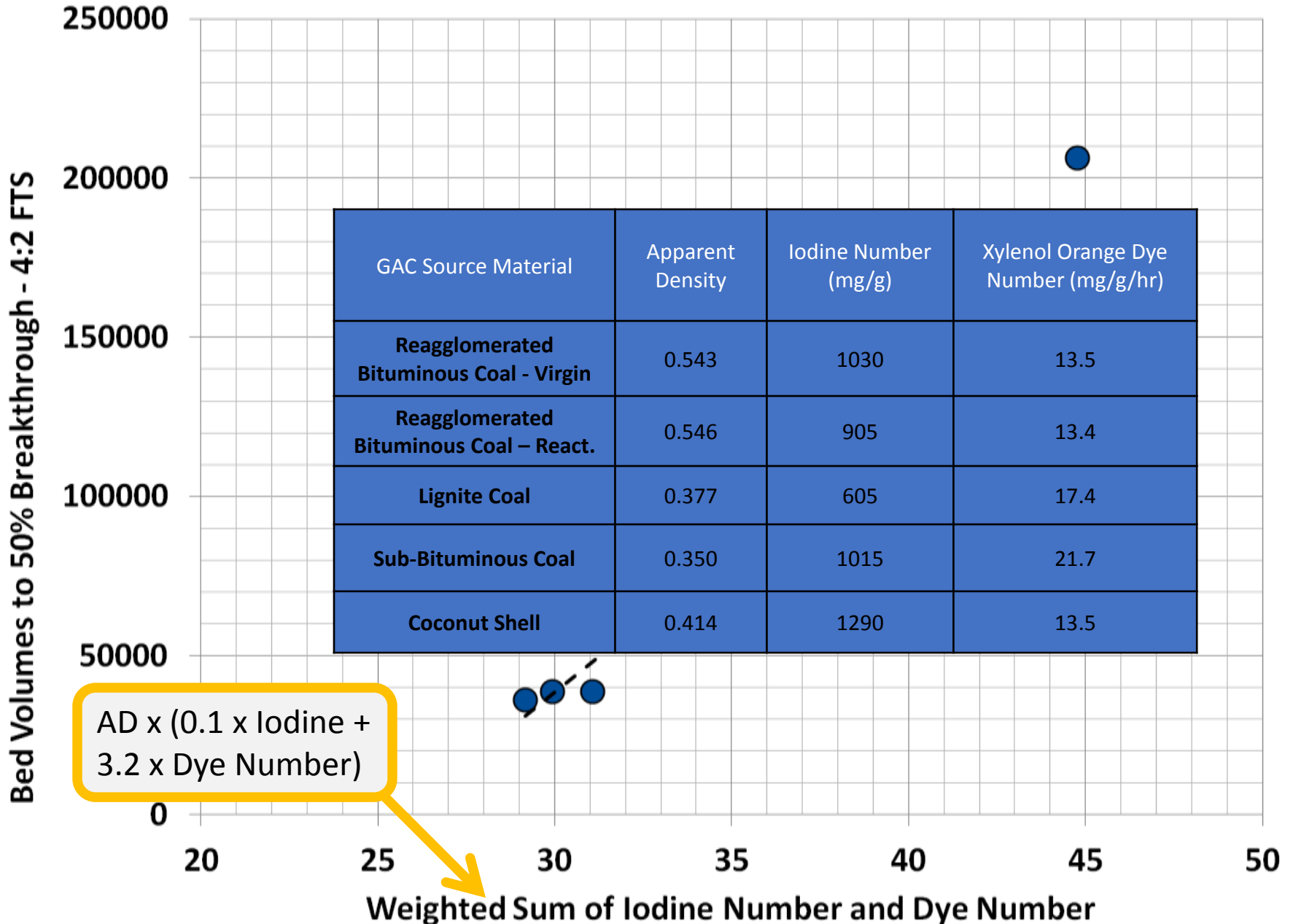
IODINE NUMBER: RELATED TO PERFORMANCE?



NORMALIZED IODINE NUMBER: RELATED TO PERFORMANCE?



IODINE & DYE NUMBER COMBINED: RELATED TO PERFORMANCE?



CONCLUSIONS



PRECURSORS ARE REMOVABLE ALONG WITH PFOA & PFOS

- Compound structure impacts removal as expected
- GAC performance varies widely among source materials
- Reactivated GAC can offer performance on-par, or nearly on-par, with its virgin counterpart, depending on the target contaminant

GAC SELECTION MUST CONSIDER INTERPLAY BETWEEN PROPERTIES

- No single specification can adequately guide carbon selection
- Porosity is key, but only when considered alongside bed density
- “Old” methods such as Iodine Number are still valuable, especially when combined with some measure of adsorption rate, such as Dye Number

**Thank you for your time.
Questions?**

**Eric Forrester
fforrester@calgoncarbon.com
412-787-6821**