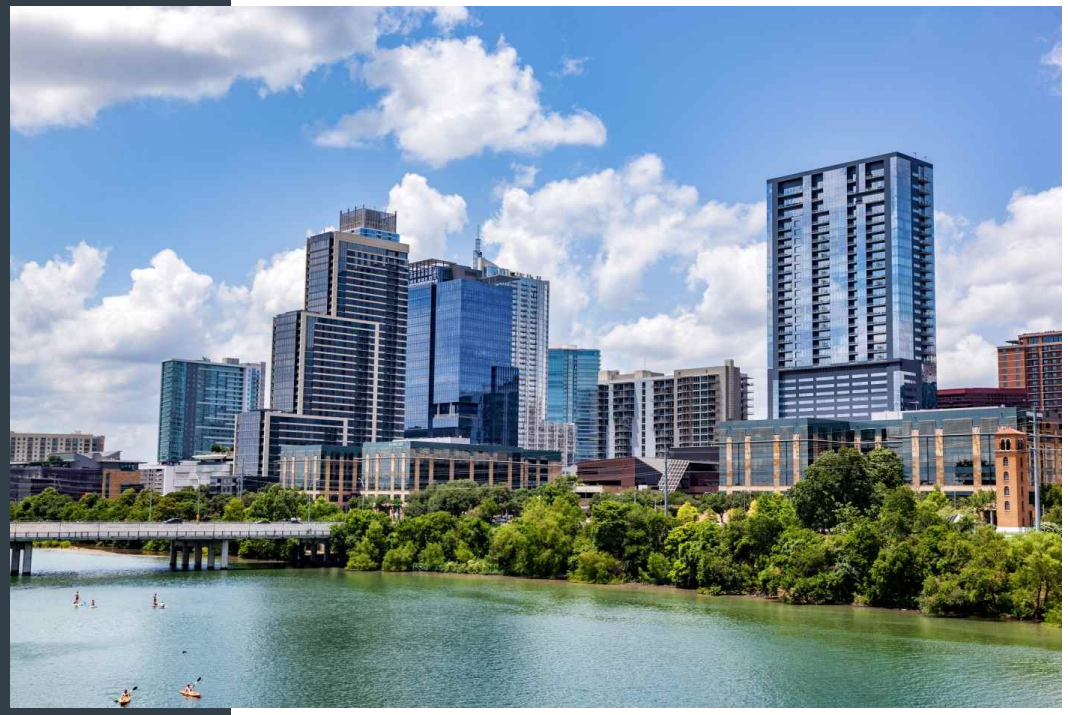
Geosyntec consultants

CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Enhancing 1,4-dioxane bioremediation at low concentrations by combining a metabolic degradation culture with adsorbents



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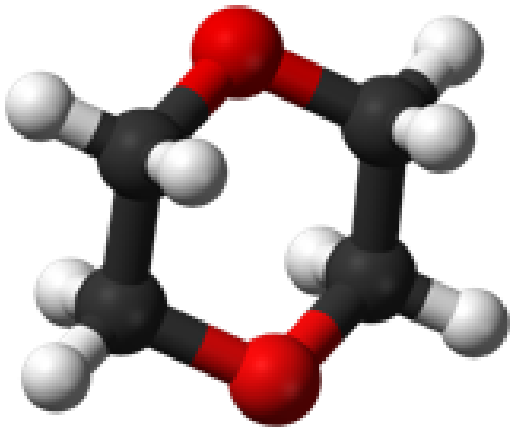
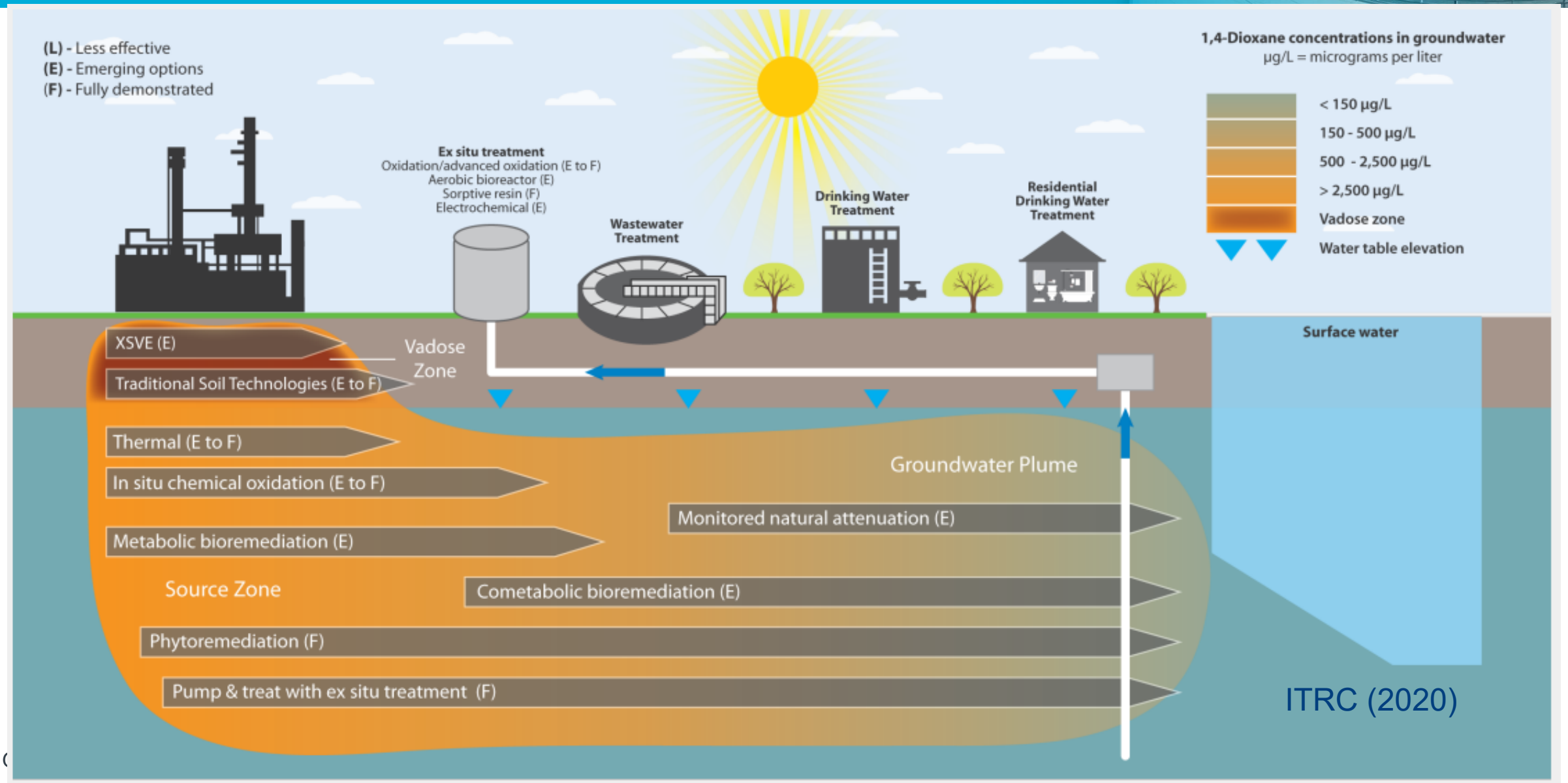
Introduction



- 1,4-Dioxane biodegradation
  - Metabolic vs. cometabolic
  - Kinetics considerations
- Combine biodegradation with adsorbents (biofilm carriers)
  - BioGAC for MTBE/TBA
    - K_{OW}: 1.24 (MTBE), 0.35 (TBA), -0.27 (1,4-dioxane)
  - Ambersorb, Biochar, Zeolite
- Proof of concept in short-term, high-concentration, batch or semi-continuous systems
  - Need studies for long-term, low concentration (<100 µg/L), continuous flow with practical contact time

1,4-Dioxane Treatment Technologies



Full-Scale BioGAC System for MTBE and TBA

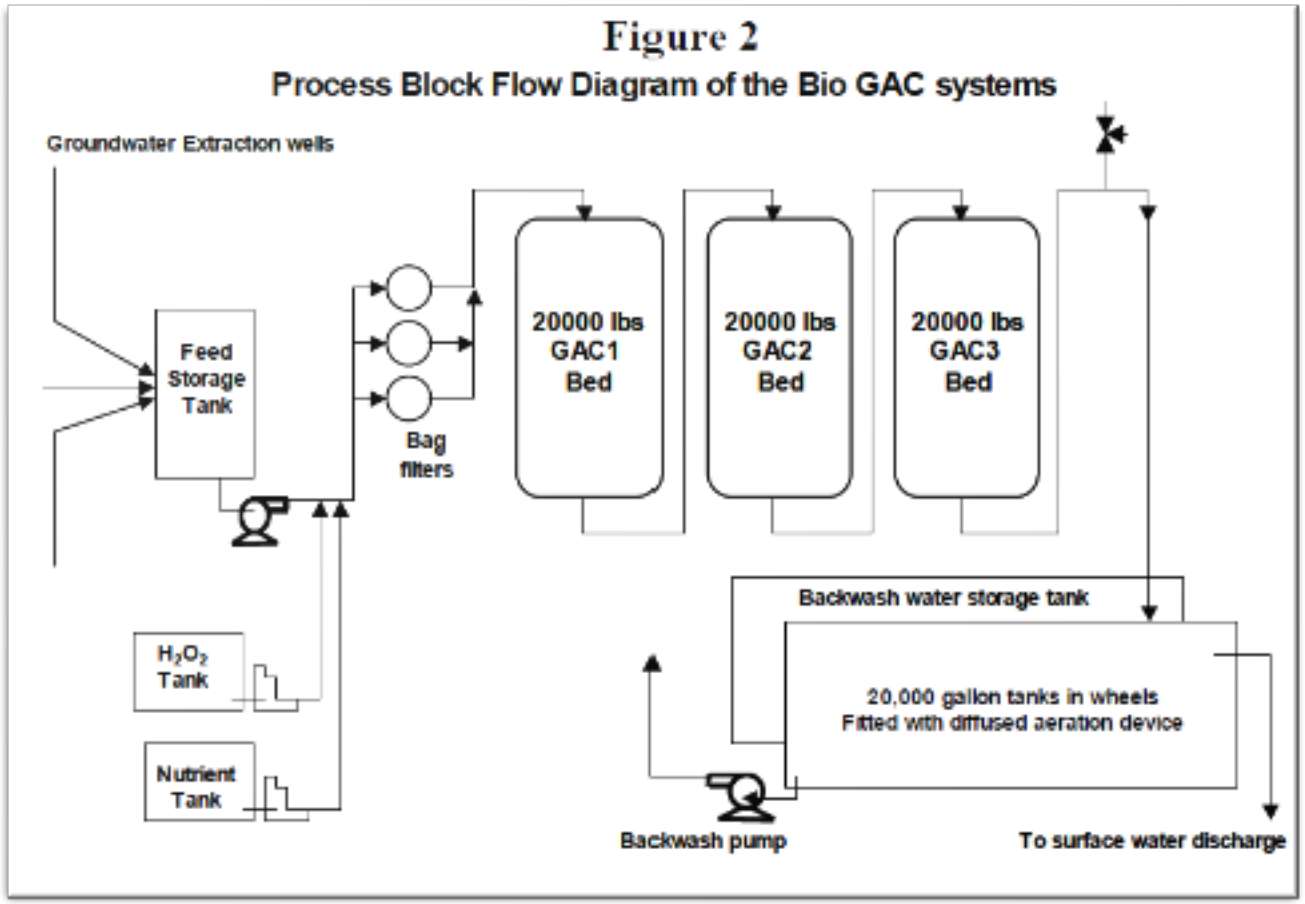


Table 3. Design and operating conditions of the BioGAC systems

Parameters	Values
Groundwater flow per system	Average 120 gpm
No. of carbon beds per system	3
Size of each bed	20000 Pounds
Activated carbon Type	Coconut shell based carbon
EBDT in each bed	Approximately 42 minutes

Table 4 Summary of BioGAC Performance

Parameters	IRM-1, average conc.		IRM-2, average conc.	
	Influent	Effluent	Influent	Effluent
MtBE, ppb	872	<1	1,192	<1
TBA, ppb	75	< 10	99	< 10
Petroleum Hydrocarbons, ppb	325	<100	495	<100
Total Aromatics, ppb	9	< 1	<1	< 1
Total Organic Carbon, mg/l	0.85	<0.5	1.2	0.65
Total Dissolved Solids, mg/l	200	190	280	270
Alkalinity, mg/l $CaCO_3$	82	80	140	140

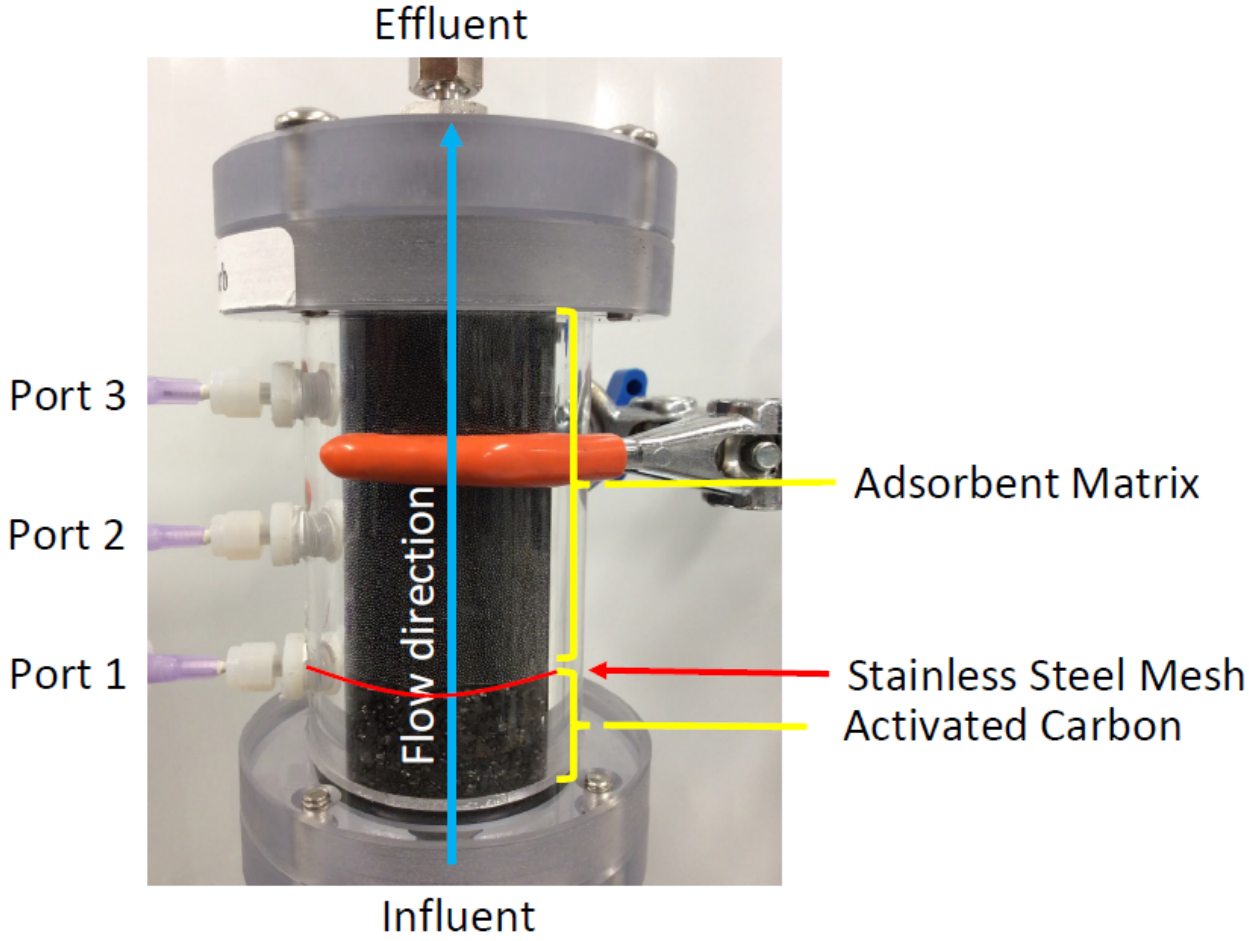
Paul Sun, et al., 2003

Site Background and Materials

- Actual groundwater from a confidential site
  - High perchlorate concentration (50 to 80 mg/L)
  - Relatively low 1,4-dioxane concentration (~75 µg/L on average)
  - Low CVOCs (mainly TCE, up to 15 µg/L)
  - Generally aerobic
- 90 gallons of groundwater in two shipments
  - 1100 lbs
- Bioaugmentation culture

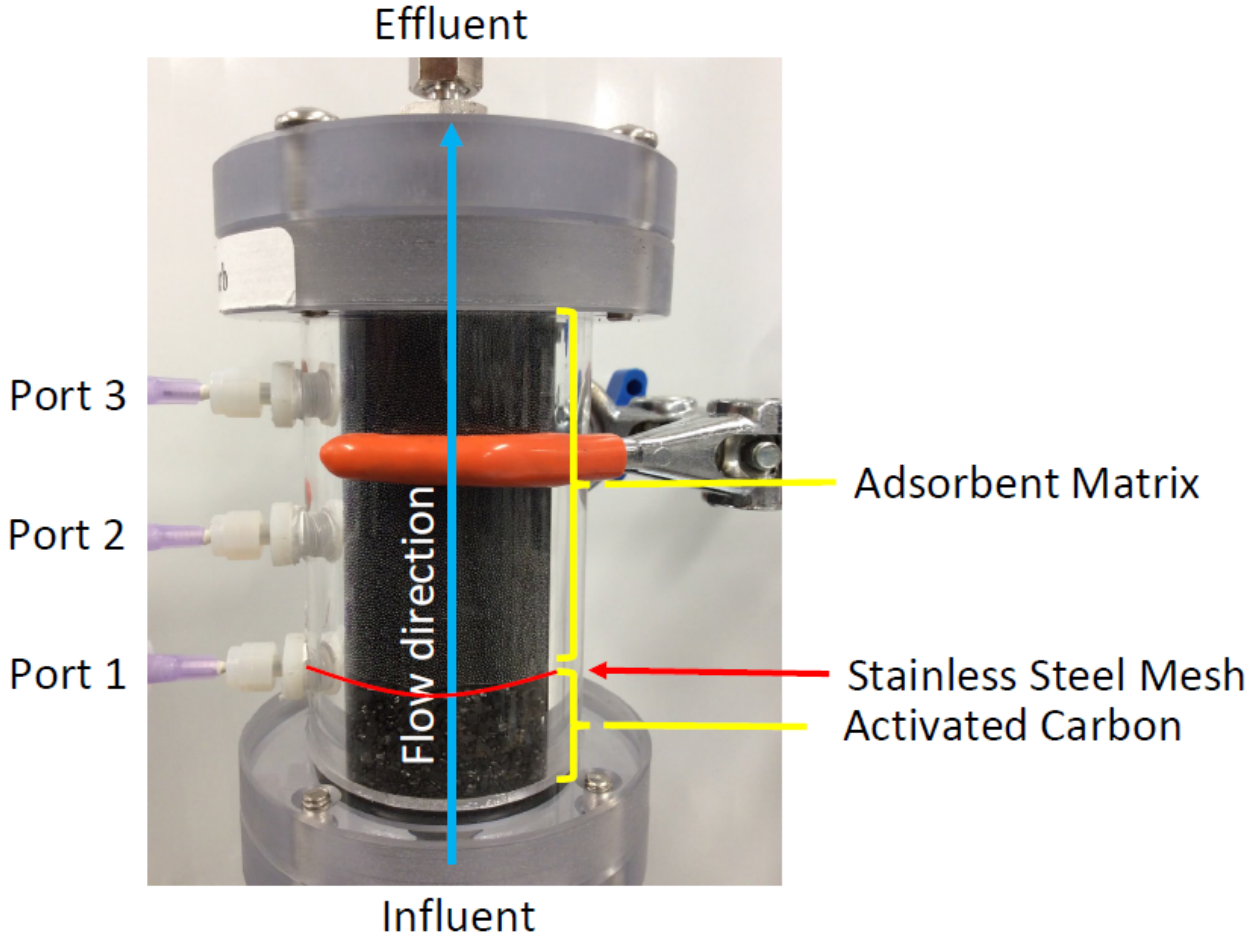
Column Construction

- Column packing:
  - Section 1: GAC
  - Sections 2 through 4:
    - Column A (Ambersorb) & Column B (Biochar) tested side by side
    - Column C: Zeolite (added later to evaluate an alternative to Ambersorb)
  - Stainless steel mesh as divider
- Flow Direction
- Empty bed contact time (EBCT) = 4 hours
- Each sampling port represents 1 hour EBCT



Bioaugmentation

- Mixed culture maintained at SiREM
- Recirculation of 200 mL culture for 3 days
- Timing
  - Columns A and B
    - GW recirculation Day 0 to 7
    - Bioaugmentation Day 7 to 10
  - Column C
    - Bioaugmentation Day -3 to 0
    - Flow-through GW feed on Day 0

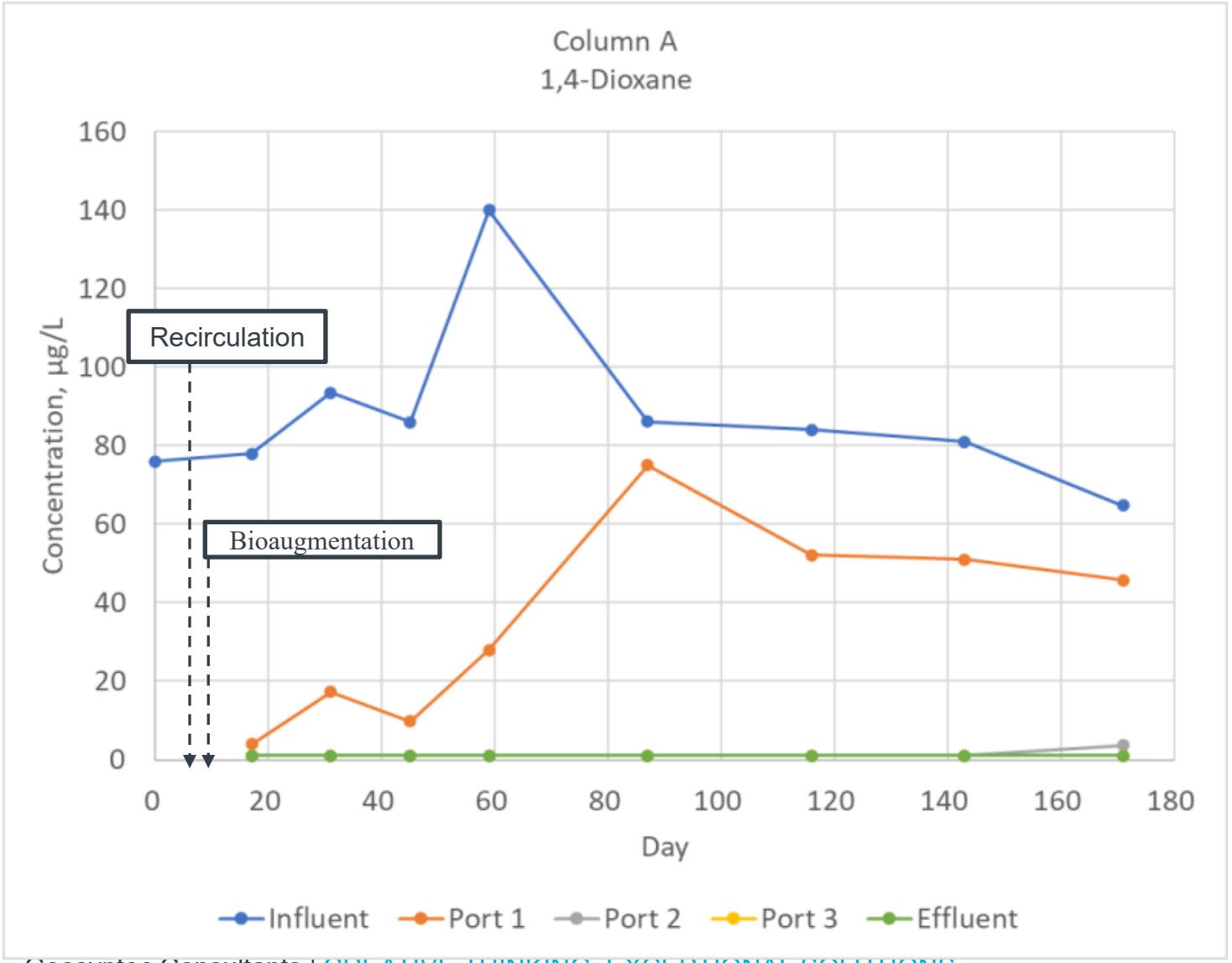


Sampling Plan (Typical)

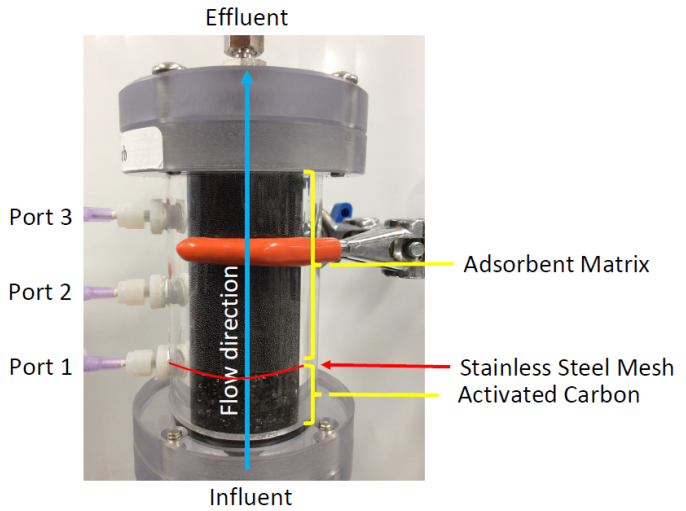
Sampling Location	Constituents	Week 0	Week 2	Week 4	Week 6	Week 8	Week 12	Week 16
Influent	VOCs	X	X	X	X	X	X	X
	Perchlorate	X	X	X	X	X	X	X
	1,4-Dioxane	X	X	X	X	X	X	X
	pH, DO, ORP	X	X	X	X	X	X	X
SP1	VOCs		X	X	X	X	X	X
	Perchlorate		X	X	X	X	X	X
	1,4-Dioxane		X	X	X	X	X	X
	pH, DO, ORP		X	X	X	X	X	X
SP2	VOCs							
	Perchlorate							
	1,4-Dioxane		X	X	X	X	X	X
	pH, DO, ORP		X	X	X	X	X	X
SP3	VOCs							
	Perchlorate							
	1,4-Dioxane		X	X	X	X	X	X
	pH, DO, ORP		X	X	X	X	X	X
Effluent	VOCs							
	Perchlorate		X	X	X	X	X	X
	1,4-Dioxane		X	X	X	X	X	X
	pH, DO, ORP		X	X	X	X	X	X

- Modified as needed
- Column C post-analysis of adsorbed 1,4-dioxane

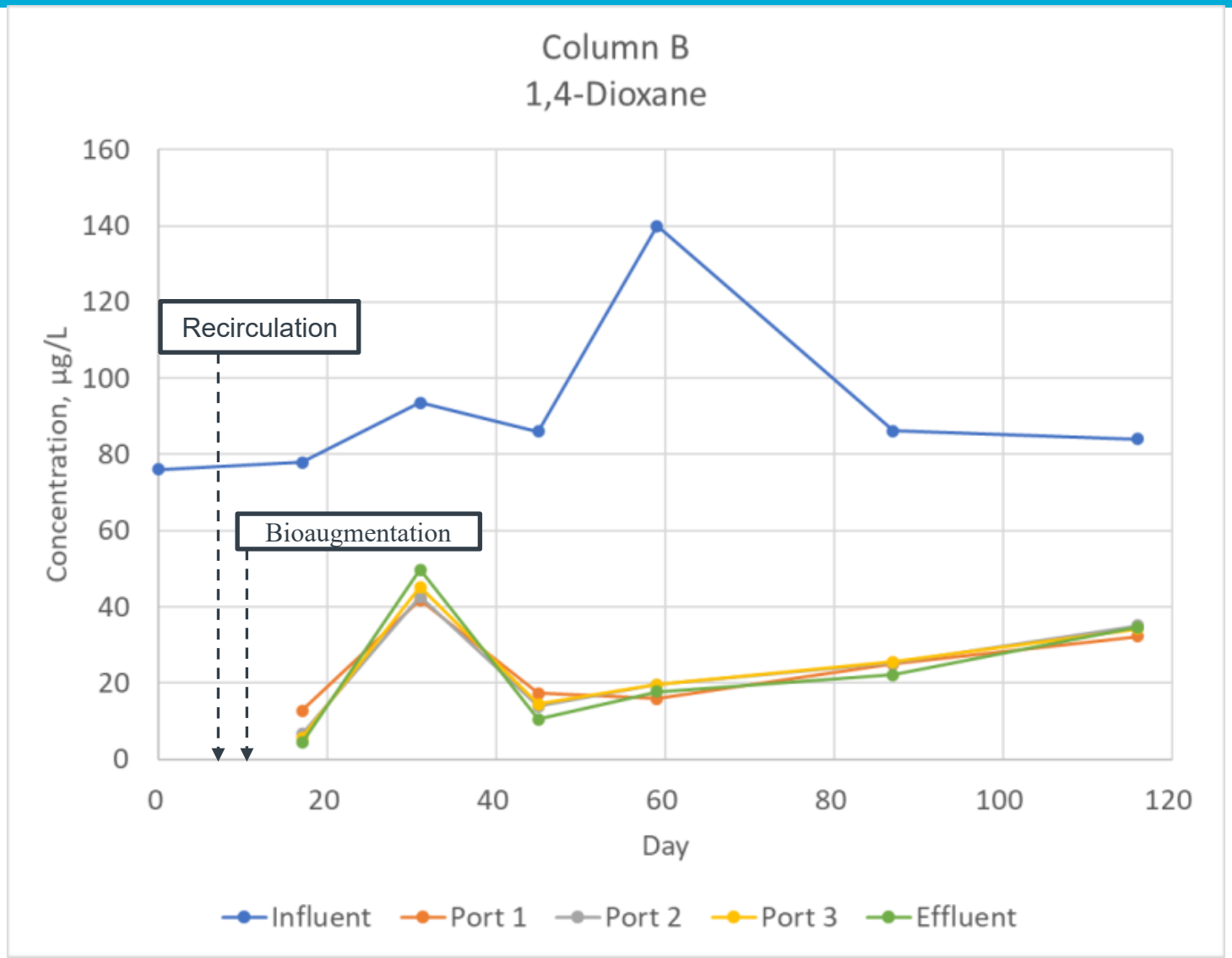
Results: Column A 1,4-Dioxane



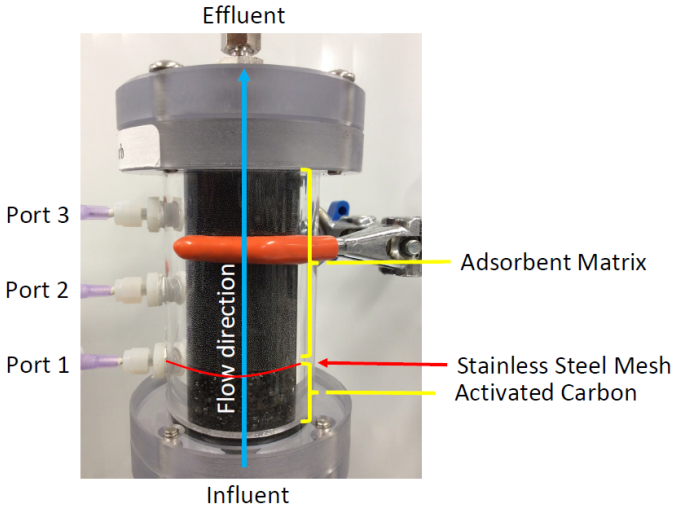
- Port 1:
  - Very high initial removal through Day 45
  - Rapid concentration increase through Day 87
  - "Steady state" removal after Day 87 (~35%)
- Port 2:
  - Non-detect until Day 171
  - 3.7 µg/L on Day 171
  - 3,800 BV after bioaugmentation
- Port 3 and Effluent
  - Non-detect throughout



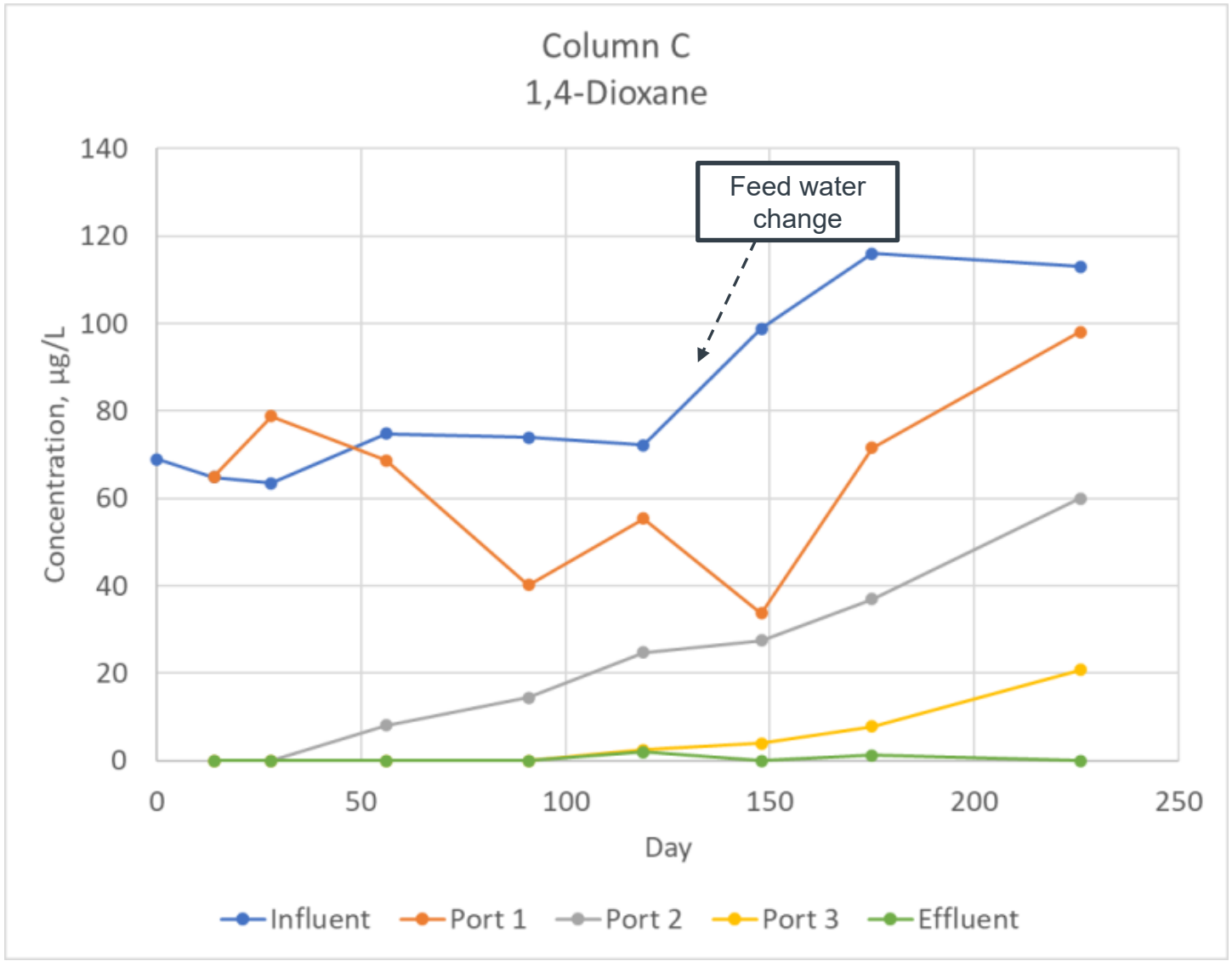
Results: Column B 1,4-Dioxane



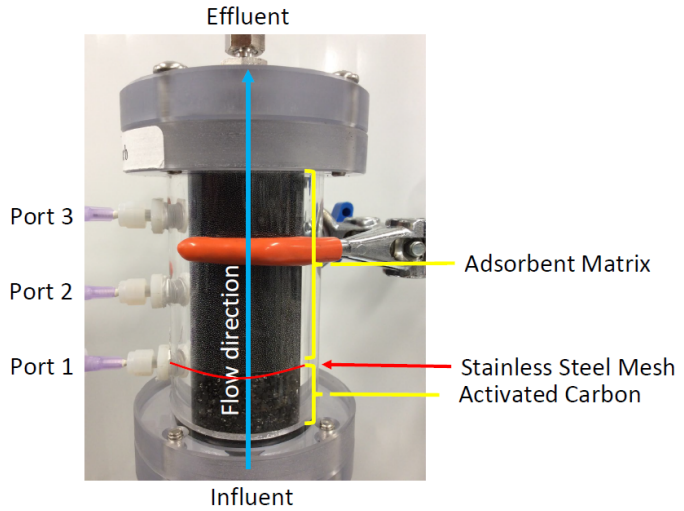
- Port 1:
  - Very high initial removal on Day 17
  - Gradual concentration increase from Day 45 to Day 116
  - ~60% removal on Day 116
- Port 2, 3, effluent:
  - Closely tracking Port 1
  - Biochar was not providing additional treatment



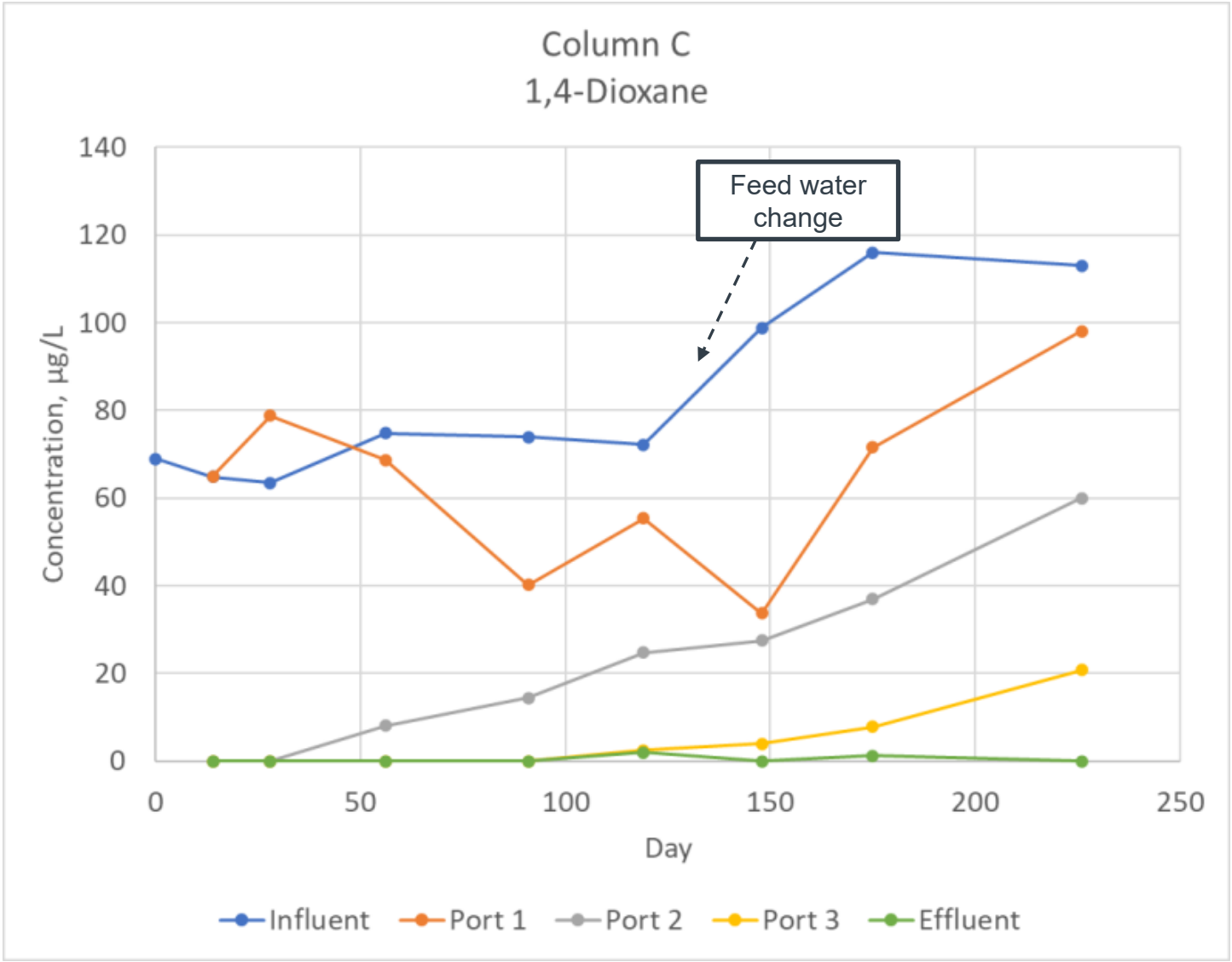
Results: Column C 1,4-Dioxane



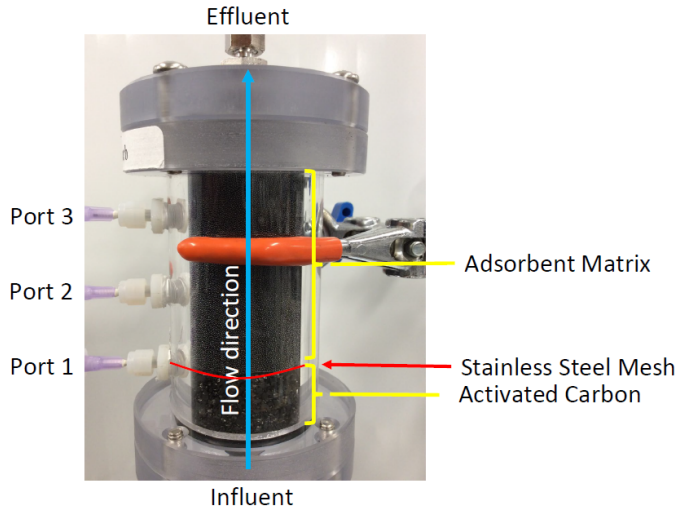
- Port 1:
  - Possible breakthrough on Day 14 (no or very little biodegradation)
  - Gradual concentration decrease from Day 28 to Day 119
  - Average ~35% removal on Day 91 & 119
    - Steady state?
  - Concentration increase after feed water change



Results: Column C 1,4-Dioxane



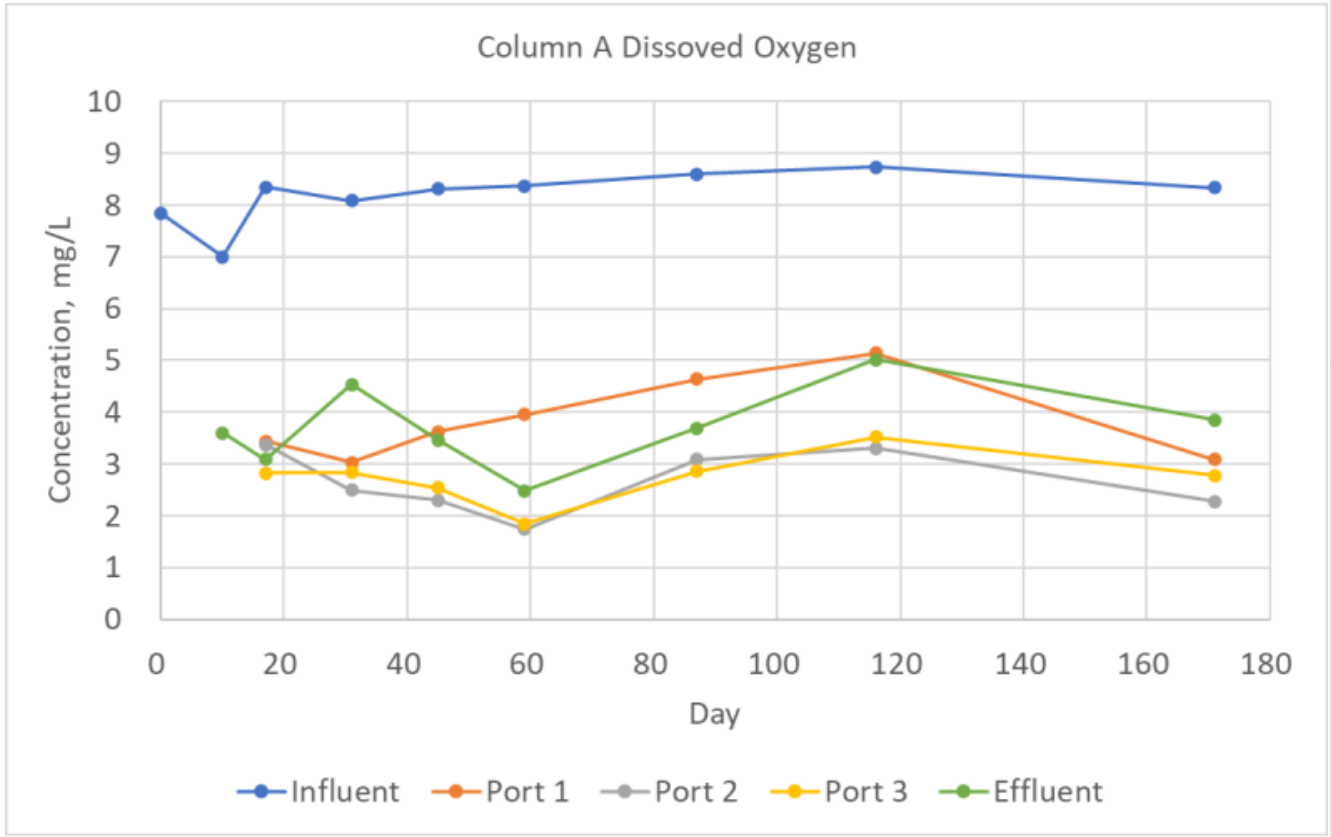
- Port 2:
  - Gradual concentration increase
  - Breakthrough on Day 56
- Port 3
  - Gradual concentration increase
  - Breakthrough on Day 119
- Effluent
  - Generally non-detect or very low detection
  - 2 µg/L on Day 119, 1.2 µg/L on Day 175
  - ND<4.4 µg/L on Day 226

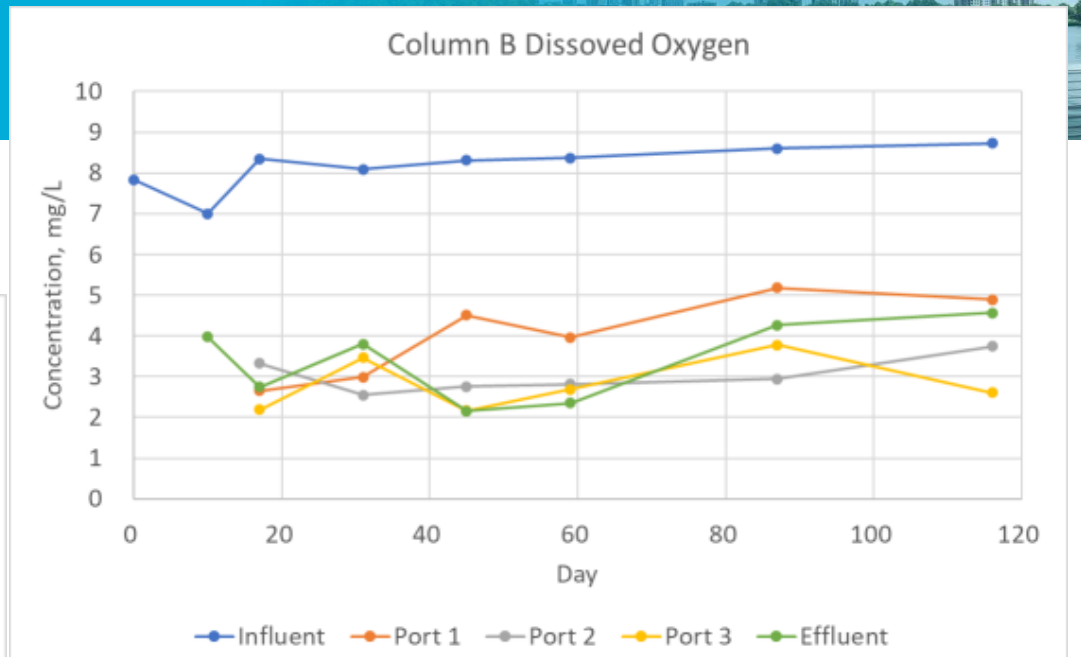


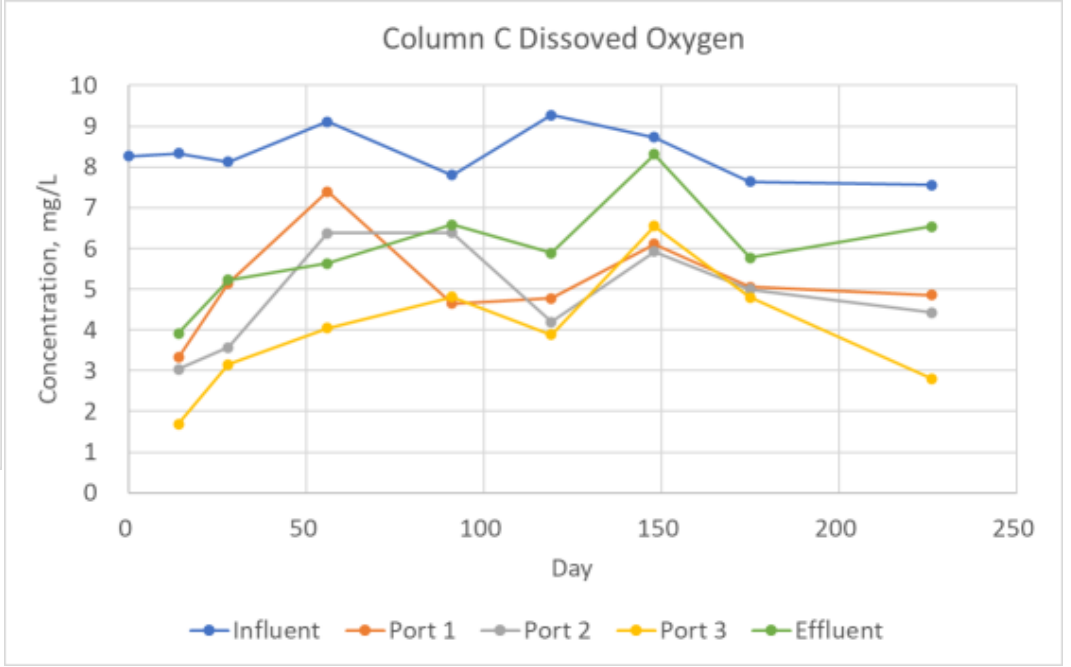
Summary

	Column A	Column B	Column C
Startup	GW recirculation followed by bioaugmentation	GW recirculation followed by bioaugmentation	Bioaugmentation without pre-loading
Runtime after bioaugmentation	161 days ~1,000 BVs	106 days, ~600 BVs	226 days ~1,300 BVs
1,4-Dioxane biodegradation in GAC?	Yes	Yes	Yes
1,4-Dioxane breakthrough	Port 2 or Port 3	Effluent	Port 3
TCE breakthrough	Not observed	Not observed	Not observed
Perchlorate	Not treated	Not treated	Not treated
Notes	Long time to reach steady state conditions		Long time to establish biodegradation

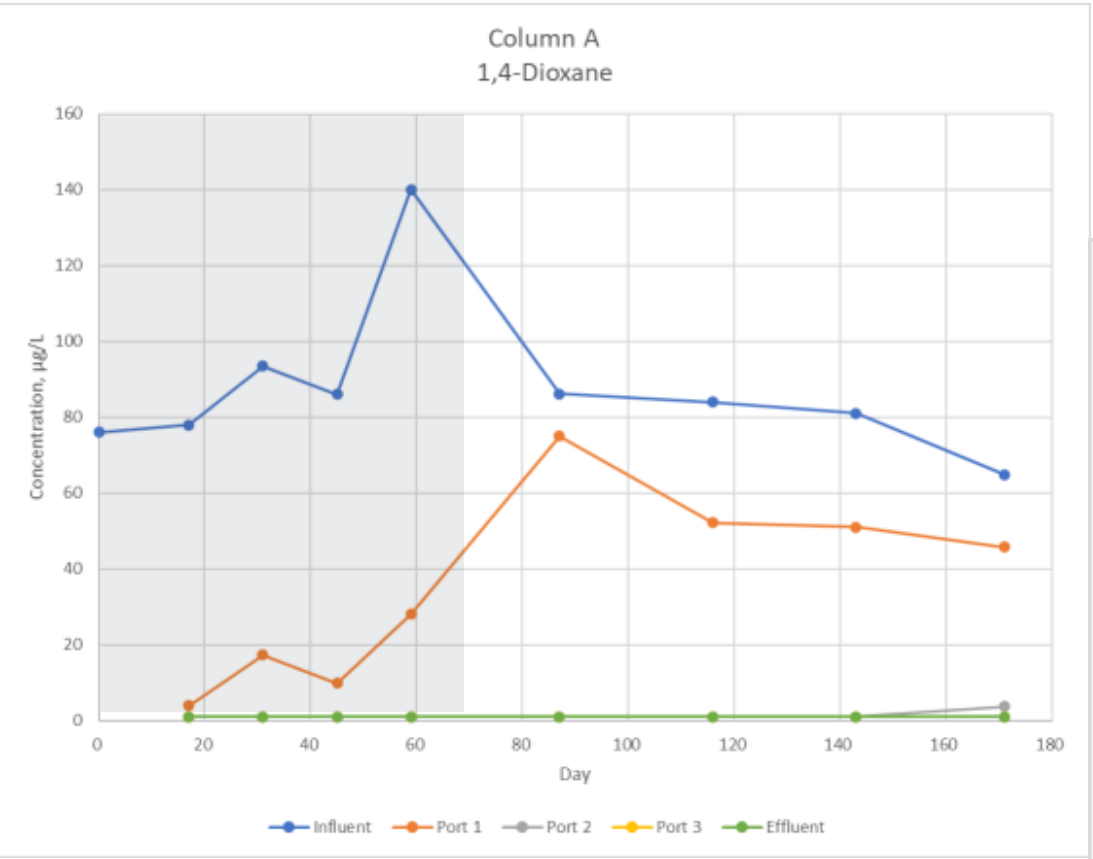
Results: Dissolved Oxygen

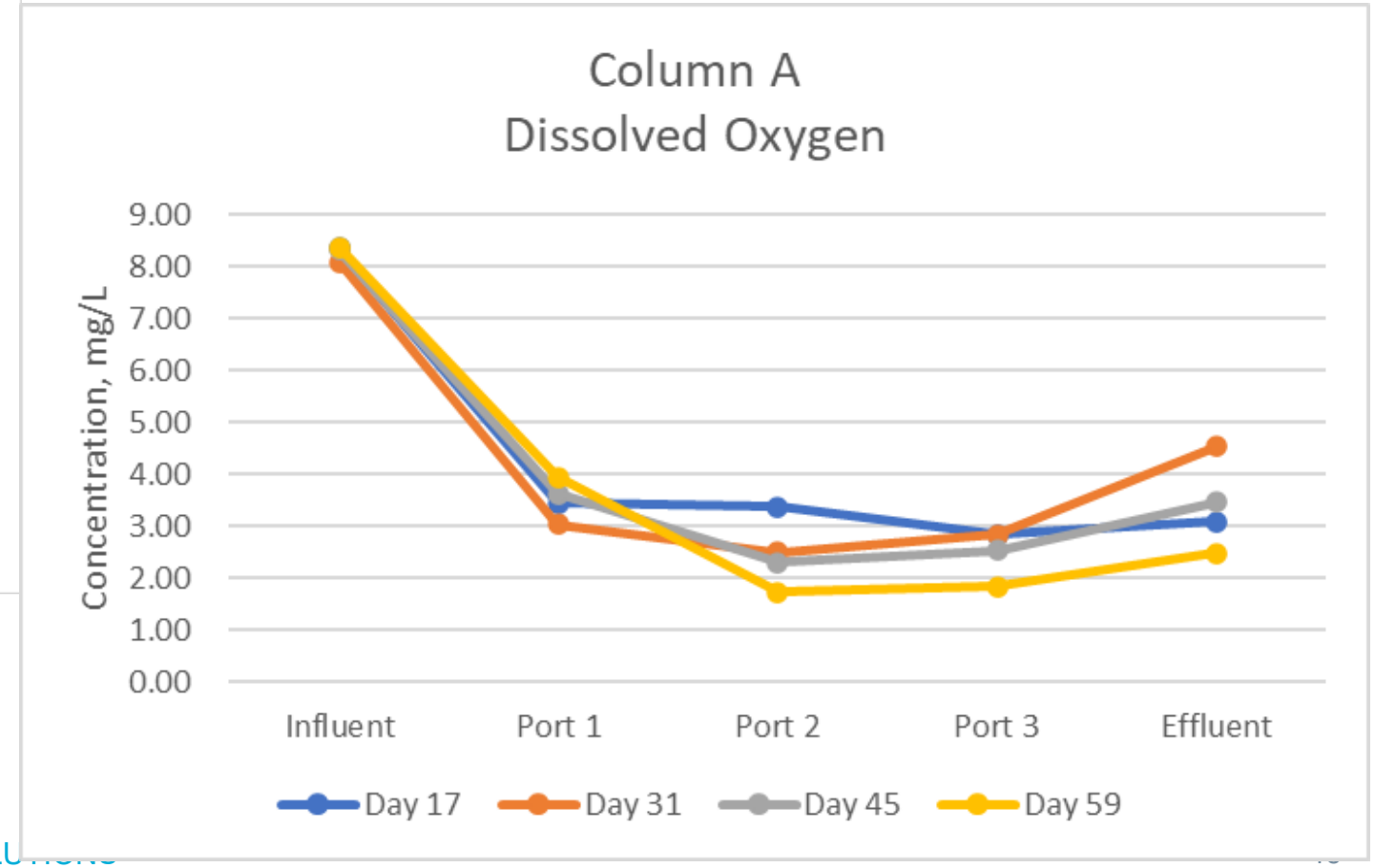




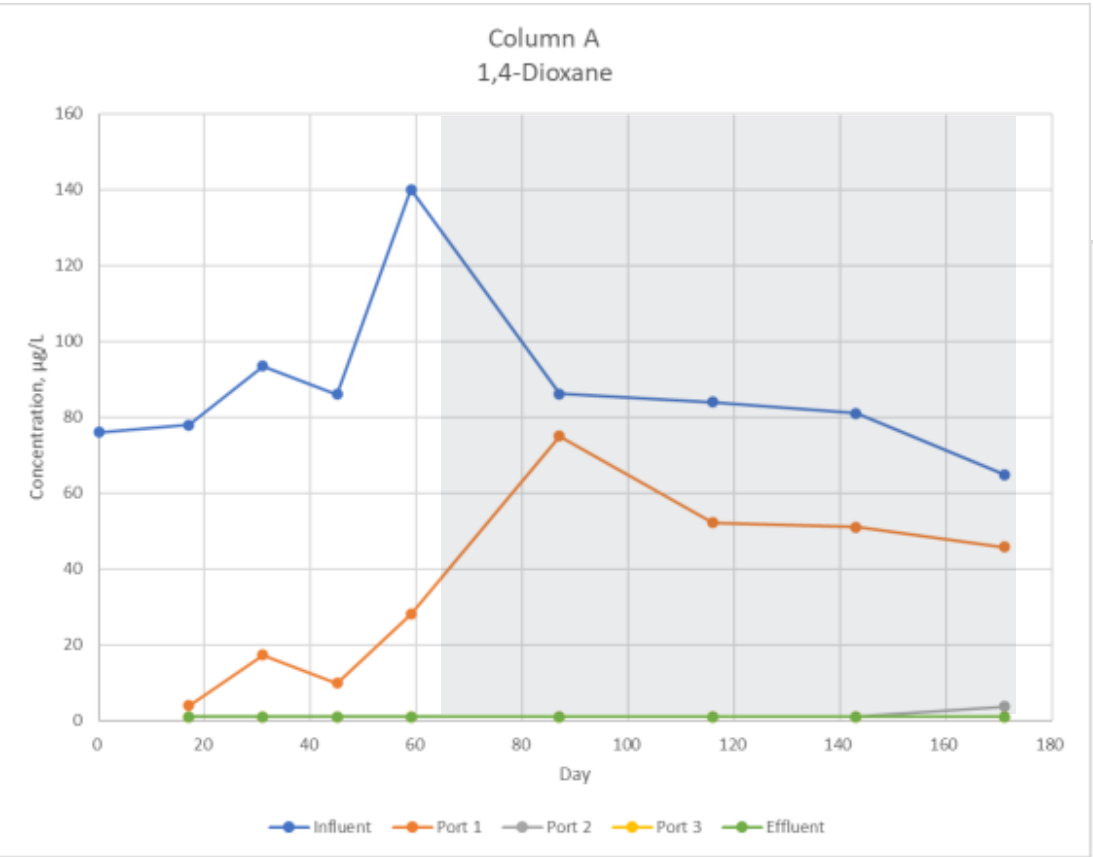


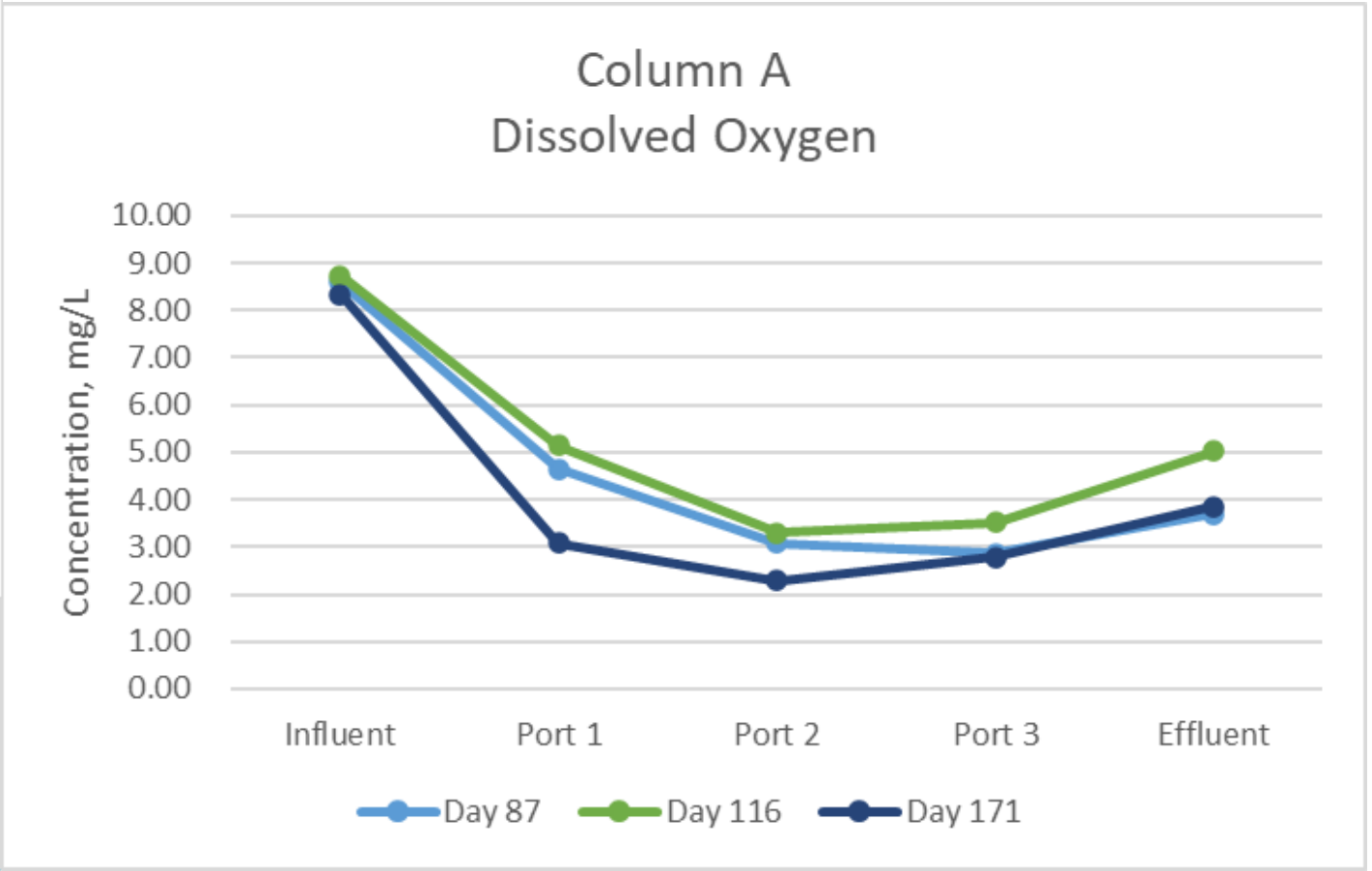
Results: Dissolved Oxygen in Column A





Results: Dissolved Oxygen in Column A





Adsorption vs. Biodegradation

Column C - GAC (Influent to Port 1)		
Average 1,4-Dioxane concentration in Influent (µg/L)	82.9	C1
Average 1,4-Dioxane concentration to Port 1 (µg/L)	63.9	C2
Flow rate (ml/min)	0.48	681 mL/day
Time elapsed (day)	226	2020/11/25 - 2020/04/13 (date of beginning of continuous flow)
1,4-dioxane loading to adsorbent (µg)	2968	= (C1-C2) x flow rate x time elapsed
Adsorbed 1,4-Dioxane on GAC (µg/g)	19	Measured
Volume of adsorbent (mL)	28.4	
Density of adsorbent (g/mL)	0.5	Estimated GAC density
Mass of adsorbent (g)	14	= Volume x density
Mass of 1,4-dioxane adsorption (µg)	270	= Adsorbed 1,4-Dioxane on adsorbent (µg/g) x mass of adsorbent (g)
Biodegradation of 1,4-dioxane (µg)	2698	= Loading - adsorption

Column C - Zeolite (Port 1 to 4)		
Average 1,4-Dioxane concentration to Port 1 (µg/L)	63.9	C1
Average 1,4-Dioxane concentration to Port 4 (µg/L)	0.7	C2
Flow rate (ml/min)	0.48	681 mL/day
Time elapsed (day)	226	2020/11/25 - 2020/04/13 (date of beginning of continuous flow)
1,4-dioxane loading to adsorbent (µg)	9873	= (C1-C2) x flow rate x time elapsed
Adsorbed 1,4-Dioxane on adsorbent (µg/g)	26.6	Measured
Volume of adsorbent (mL)	85.2	
Density of adsorbent (g/mL)	0.72	Provided by manufacturer
Mass of adsorbent (g)	61.34	= Volume x density
Mass of 1,4-dioxane adsorption (µg)	1632	= Adsorbed 1,4-Dioxane on adsorbent (µg/g) x mass of adsorbent (g)
Biodegradation of 1,4-dioxane (µg)	8241	= Loading - adsorption

Conclusions

- Combining adsorbents with a metabolizing culture shows promise in treating 1,4-dioxane at environmentally relevant conditions.
- GAC, Ambersorb, zeolite were effective adsorbents to promote 1,4-dioxane degradation, but not biochar.
- Site co-contaminants (perchlorate and TCE) did not interfere with 1,4-dioxane removal.
- A long time was needed to establish the equilibrium between adsorption and biodegradation, regardless the startup sequence.
- No primary substrates, aeration, or nutrients were needed.
- Post-test adsorbent analysis indicates the main 1,4-dioxane removal mechanism was biodegradation.

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