Biodegradation of MtBE Using an Innovative Biomass Concentrator Reactor

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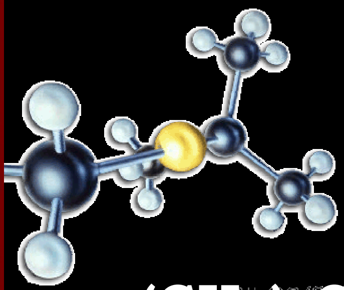
MtBE as Fuel Additive

- First used in U.S. as an octane enhancer in 1979
- In 1990, EPA initiated the oxyfuel and reformulated gasoline programs and implemented them in 1992 and 1994 to reduce CO and O_3 in high pollution areas
  - To meet oxyfuel requirements, producers add oxygenates to gasoline for more efficient combustion
  - 80% of all oxyfuels use MtBE as the oxygenate, 15% use ethanol
- Sources in the environment
  - Refineries where it is produced
  - LUSTs

Methyl t-Butyl Ether (MtBE)

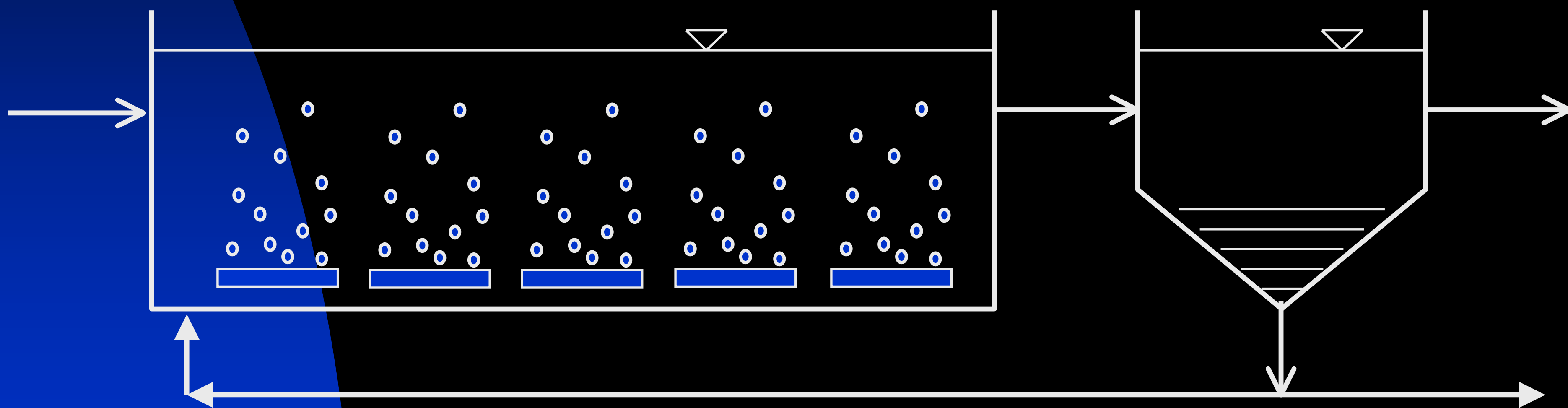
- Highly Water Soluble (>48 g/L)
- Low octanol-water partition coefficient (K_{ow})
  - Contaminates groundwater, migrates in aqueous plume
- Low taste and order thresholds
- Possible Health Effects
  - U.S. EPA DW Advisory: 20-40 μg/L
  - California DHS DW Advisory: 5 μg/L
  - 23 states have regulatory guidelines or standards ranging from 12 (WI) to 240 (MI) μg/L



$(CH_3)_3COCH_3$

MTBE Biodegradation

- Initially reported to resist biodegradation
- Yield coefficient very low (Y = 0.10)
  - 0.10 mg biomass produced per mg MTBE consumed
  - Explains why initial literature reported resistance to biodegradation
- Challenging for reactor design due to low yield



Challenges of Low Yield

- Groundwater typically 0.5 – 1.0 mg/L MtBE (at wellhead)
- 1.0 mg MtBE/L * 0.10 mg biomass/mg MtBE = 0.10 mg biomass/L
- Thus, large fraction of biomass leaves system via effluent
- To get effective treatment to low MCLs, must retain ALL biomass

Applications of Biomembrane Technology

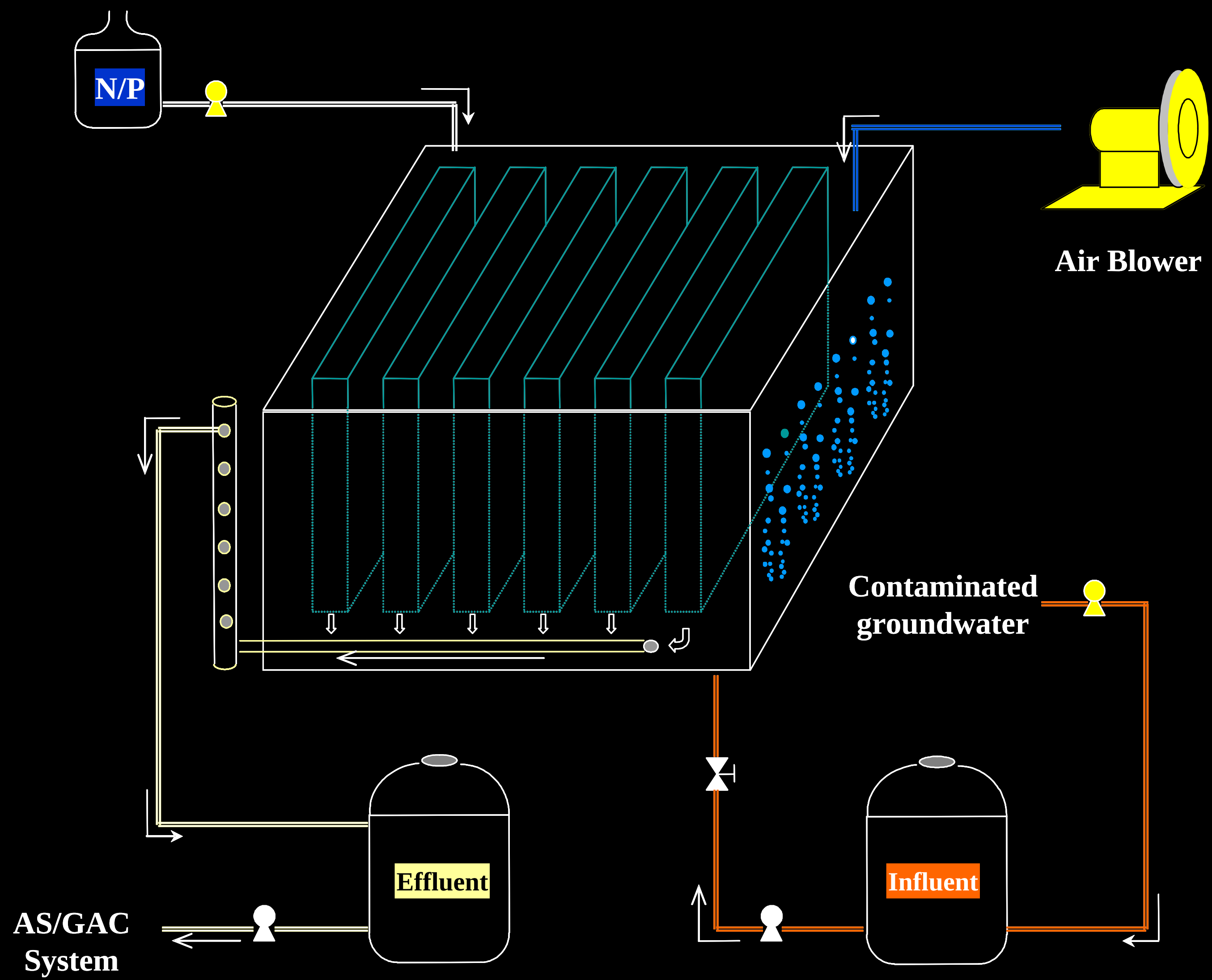
- Municipal & Industrial Wastewater Treatment
  - Better solids separation to attain desired effluent quality
  - Solids wasting under complete control of operator

- Surface & Groundwater Treatment
  - Ideally suited for dilute streams
  - Ideally suited for soluble pollutants
  - Biomass retention

Biomass Concentrator Reactor (BCR)

- MBR: very effective at retaining all biomass
  - Operational costs high due to requirements for pressure or vacuum to drive solid/liquid separation
- Design of BCR Based on Lab-Scale Porous-Pot
  - Designed to tolerate high flow due to higher surface area
- Cost Effective Alternative to MBR
  - Relies on gravity separation
  - Simple operating system
  - Low maintenance requirement

Schematic of the BCR



Flow Regime at Pascoag, RI

River

Membrane module being taken out for regeneration

Experimental Approach

- Culture preparation
  - Biomass grown in 55-gal drums for a year on MtBE and BTEX
  - Prior to traveling to Pascoag, biomass was settled and transferred to 1 drum, connected to an aerator, and transported by van
- BCR preparation
  - All plumbing and electrical connections completed prior to arrival
  - Plan was to start flow at 1 gpm, then gradually increase it to the final flow of 5 gpm within a month

Analytical

- Samples collected 3 times daily for 6.5 months (morning, noon, late afternoon)
  - Samples preserved at high pH, iced, and shipped to Cincinnati for analysis
  - Samples analyzed by GC/FID using heated purge and trap
  - Compounds measured included:
    - BTEX (benzene, toluene, ethylbenzene, xylenes)
    - MtBE (methyl-t-butyl ether)
    - tBA (t-butyl alcohol)
    - tBF (t-butyl formate)
    - tAA (t-amyl alcohol)
    - tAME (t-amyl methyl ether)
    - DIPE (diisopropyl ether)
    - Acetone
    - Methanol
    - Ethanol

Other Measurements

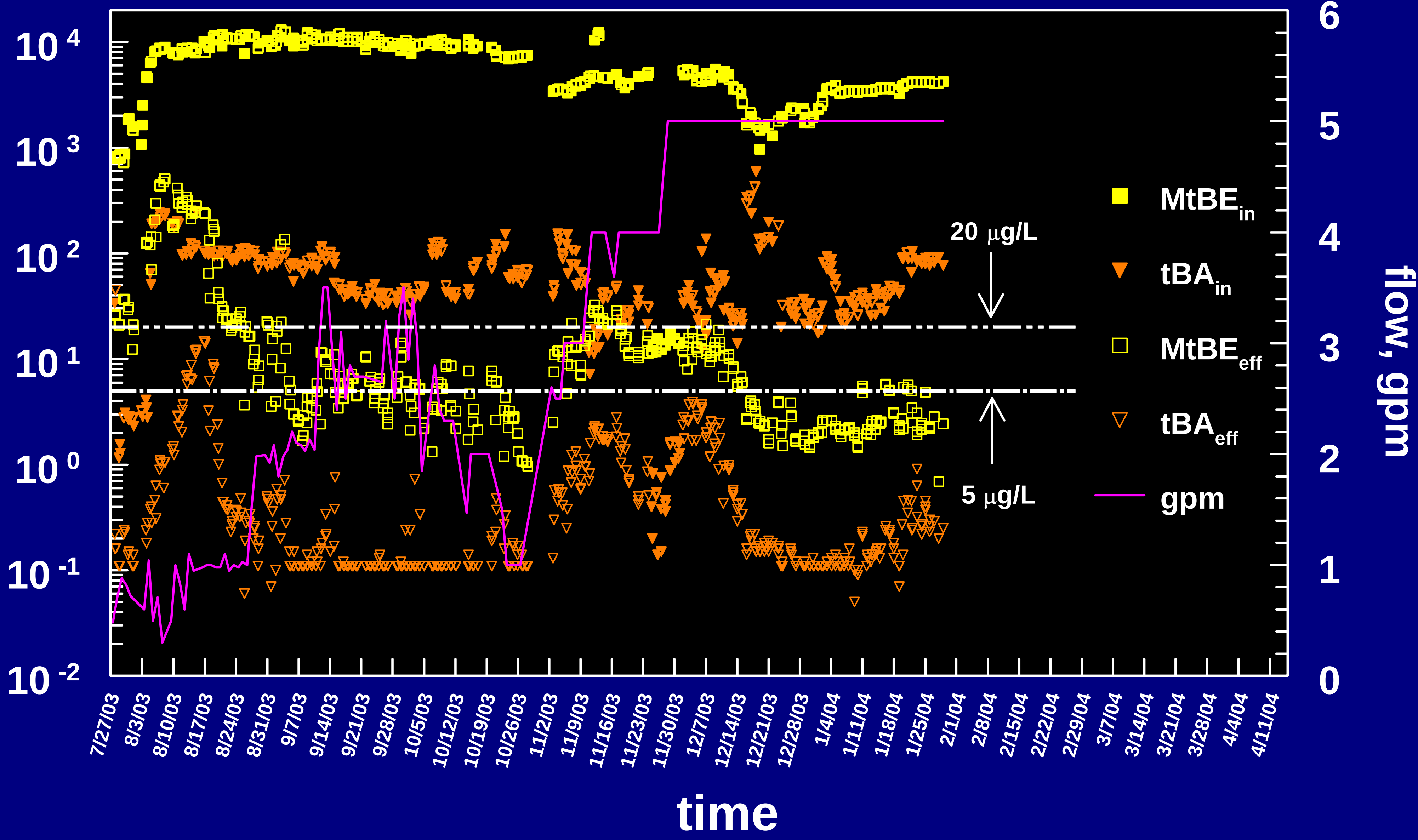
- Daily monitoring of temperature, pH, DO
- Samples of reactor contents collected weekly for:
  - TSS
  - VSS
  - NPOC

Membrane Regeneration

- Membranes were regenerated as part of a planned schedule whether they needed it or not
  - Removed one at a time, soaked in a stainless steel dip tank containing chlorine bleach for 4 hours, then soaked in dilute nitric acid for another 4 hours, rinsed, and placed back into reactor
  - Membranes were cleaned once in the 6-month period

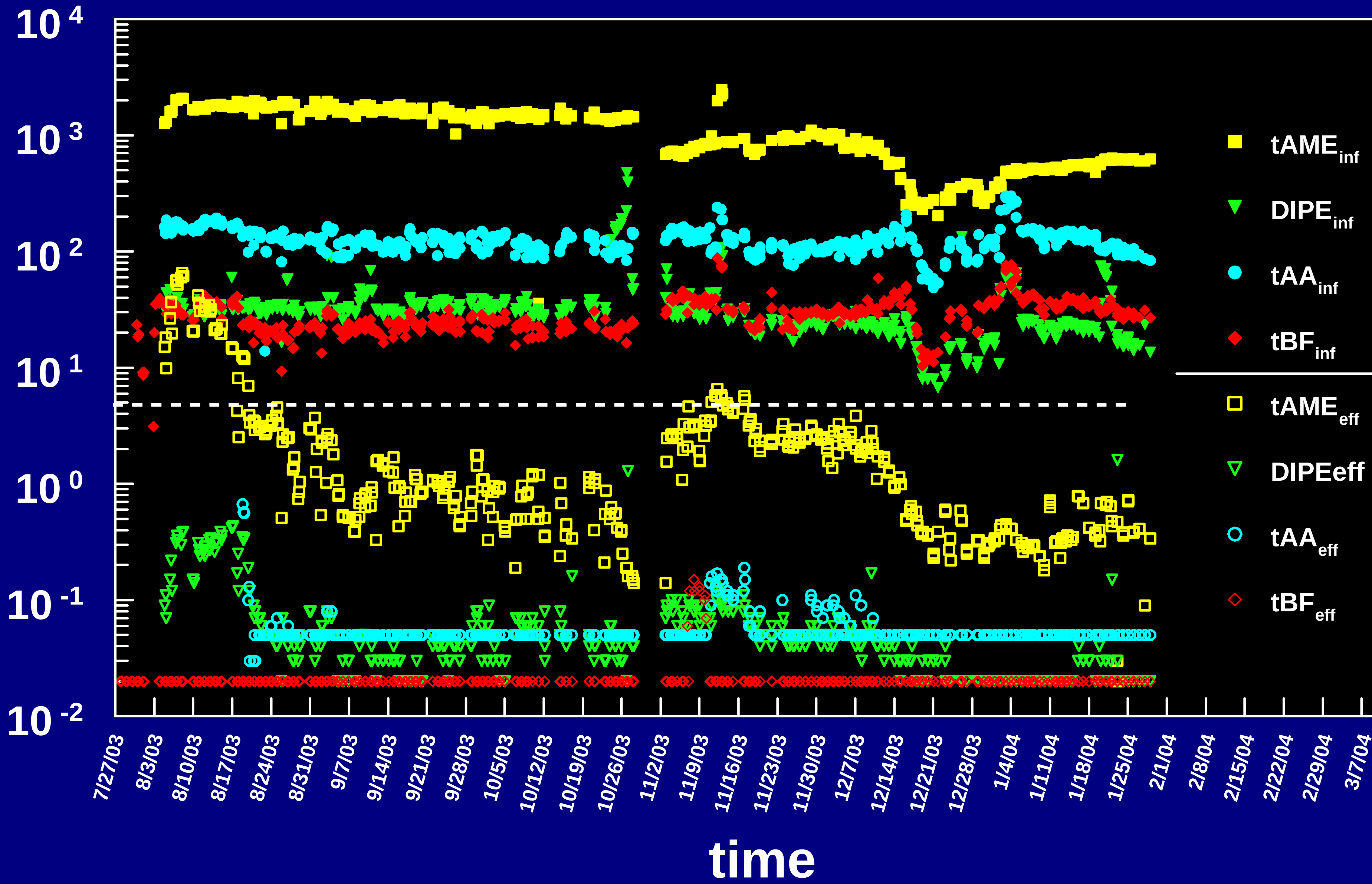
Experimental Results

MtBE and tBA

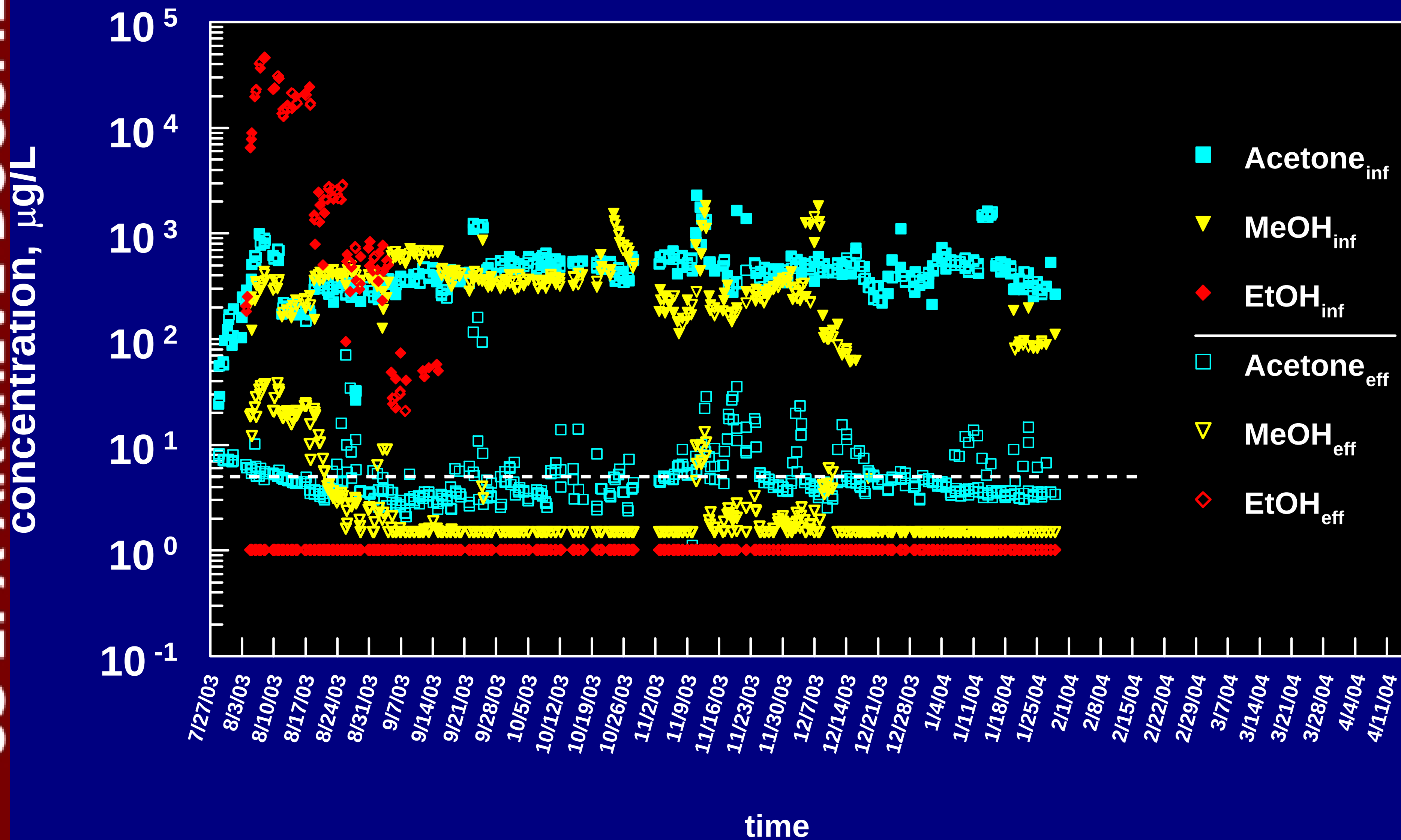


10 4
10 3
10 2
10 1
10 0
10 -1
10 -2
6
5
4
3
2
1
0
flow, gpm
20 µg/L
5 µg/L
MtBEin
tBAin
MtBEeff
tBAeff
gpm
7/27/03
8/3/03
8/10/03
8/17/03
8/24/03
8/31/03
9/7/03
9/14/03
9/21/03
9/28/03
10/5/03
10/12/03
10/19/03
10/26/03
11/2/03
11/9/03
11/16/03
11/23/03
11/30/03
12/7/03
12/14/03
12/21/03
12/28/03
1/4/04
1/11/04
1/18/04
1/25/04
2/1/04
2/8/04
2/15/04
2/22/04
2/29/04
3/7/04
3/14/04
3/21/04
3/28/04
4/4/04
4/11/04
time

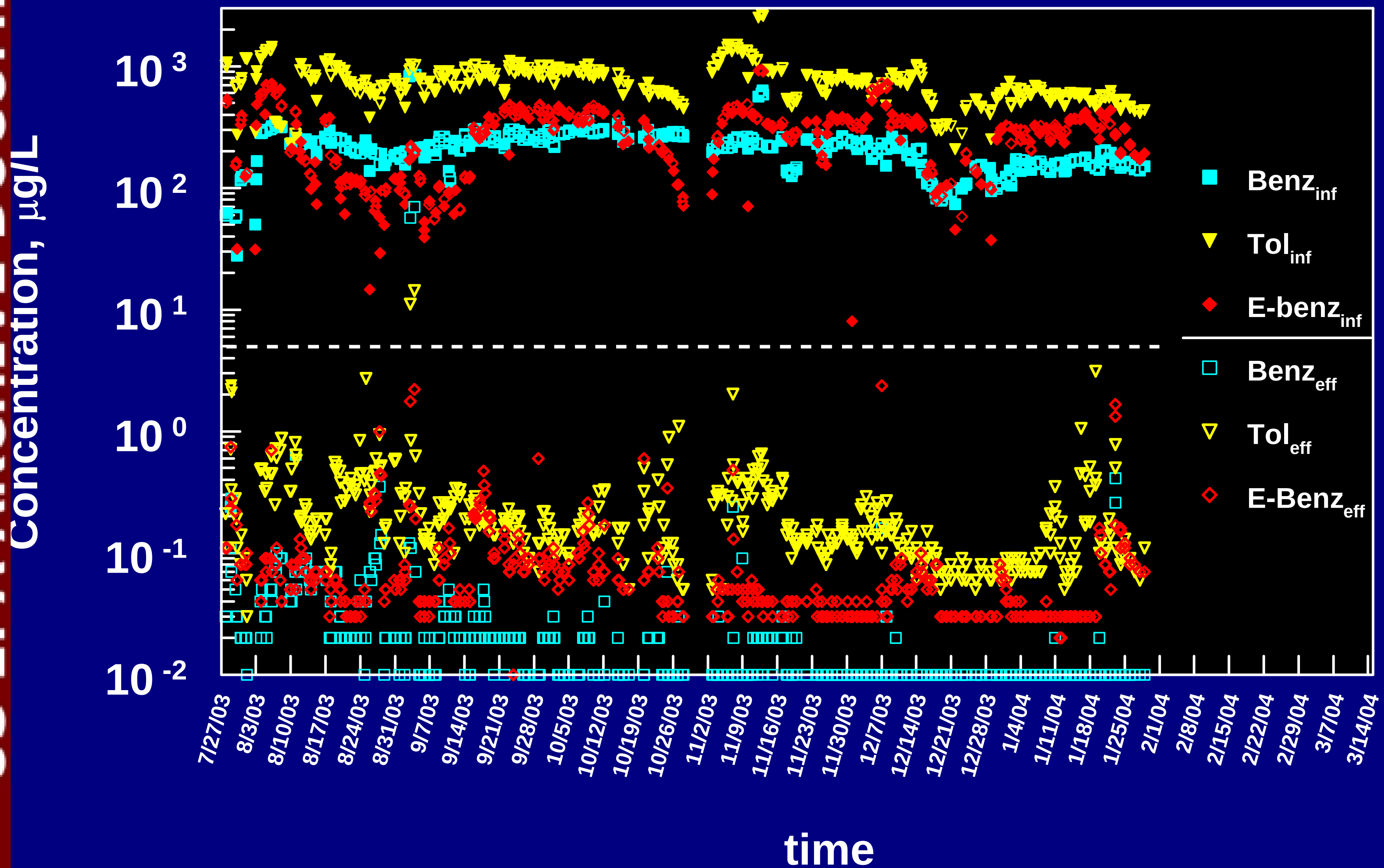
Other Oxygenates



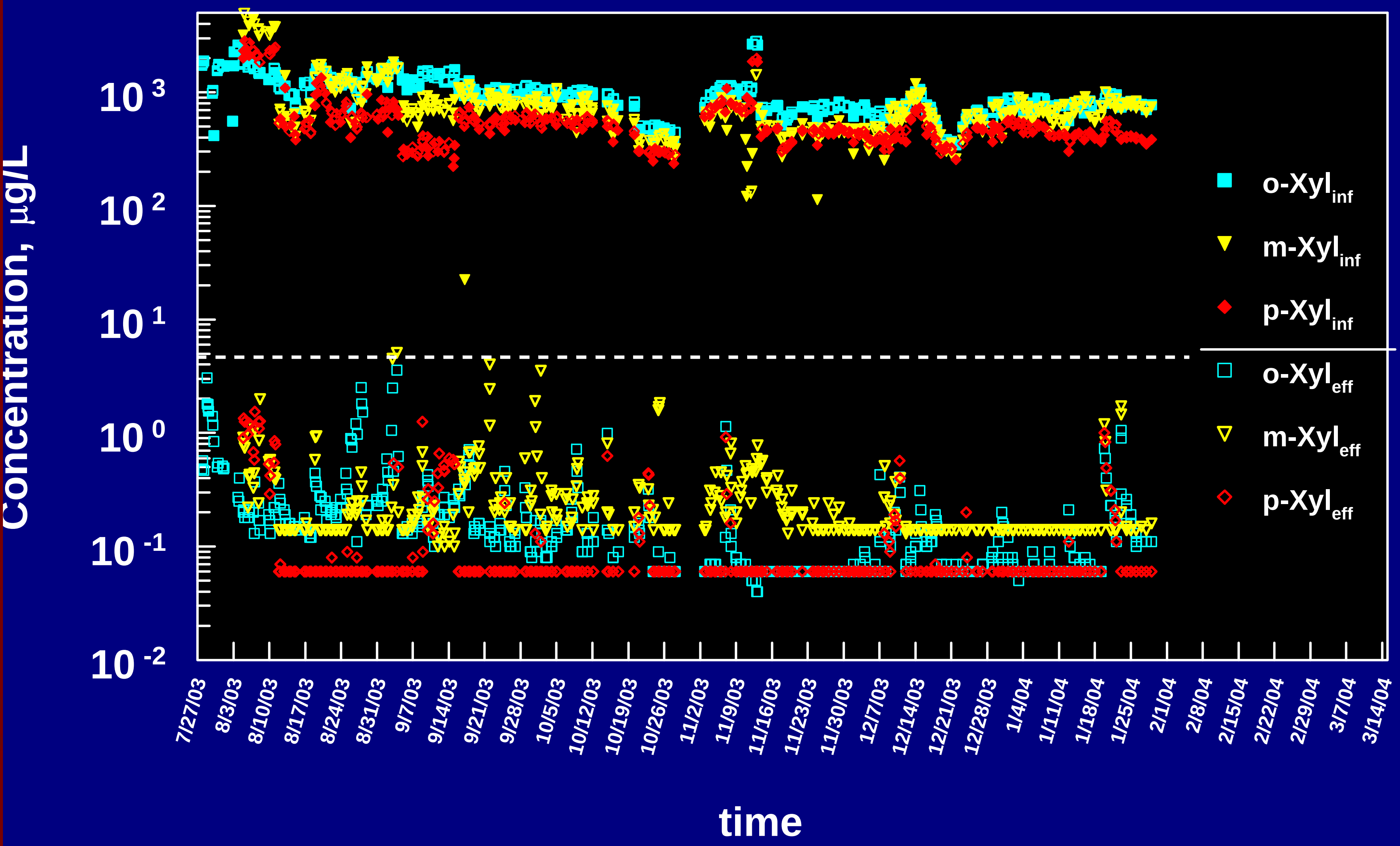
Alcohols and Acetone



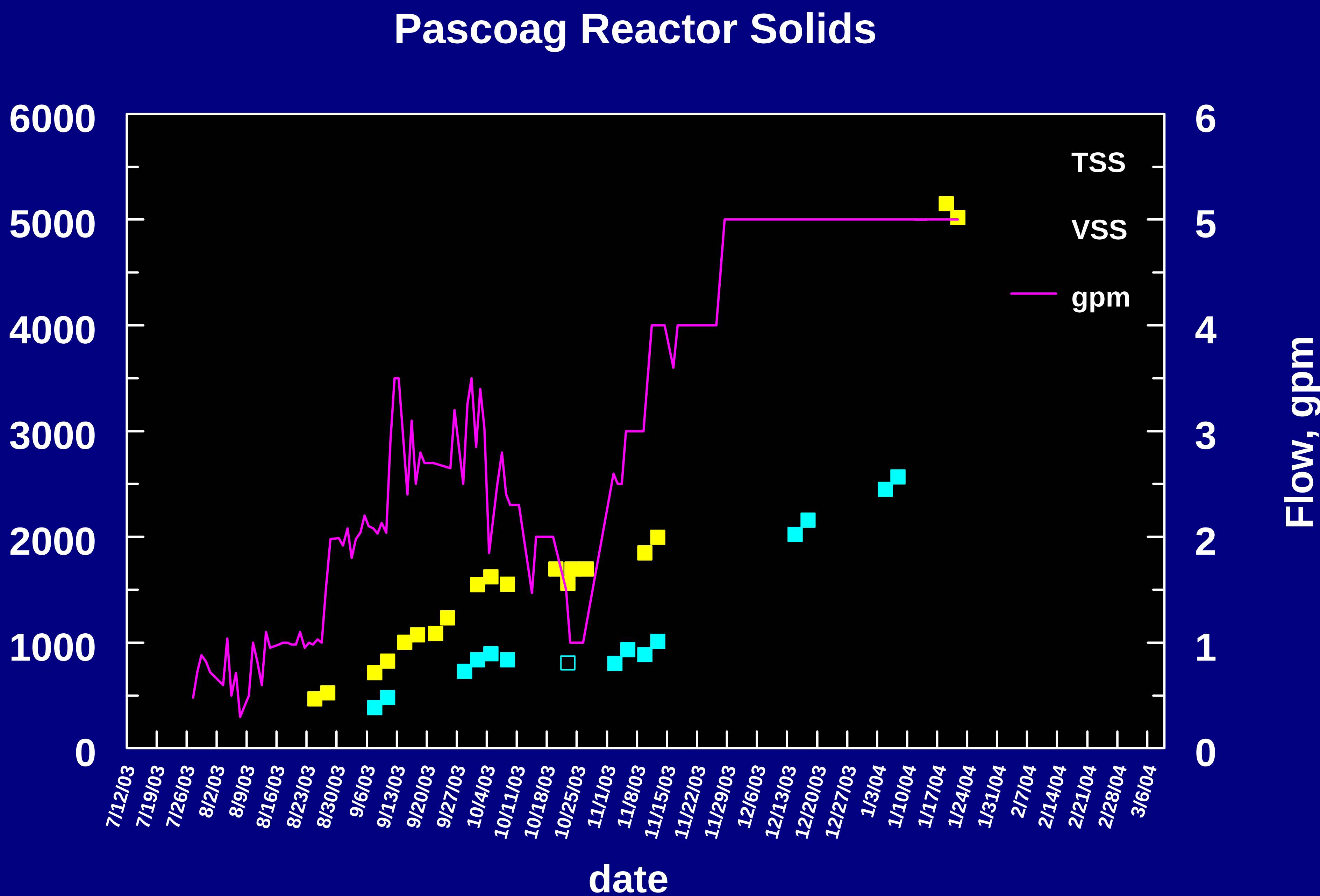
Benzene, Toluene, Ethylbenzene



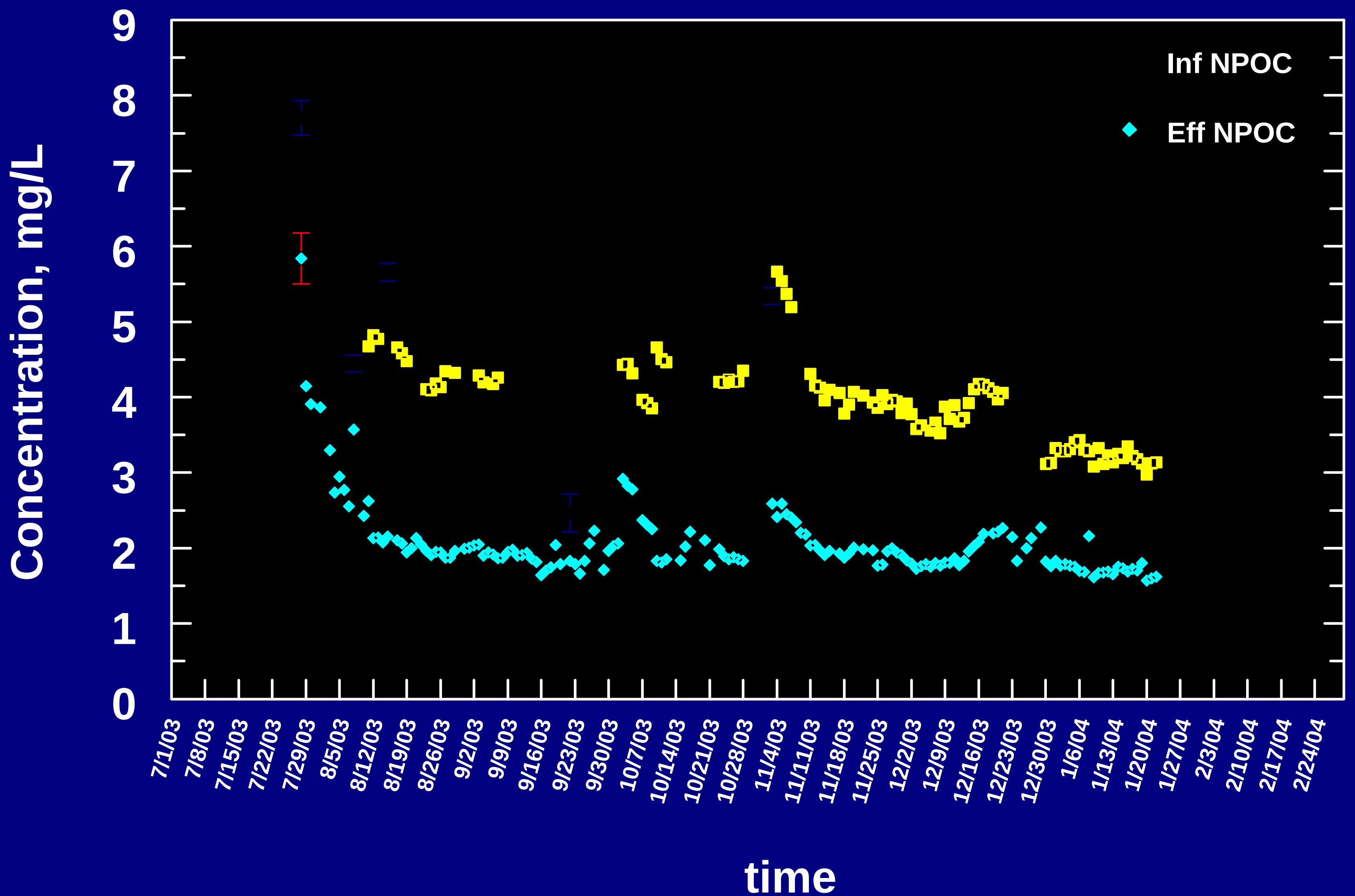
o-, m-, p-Xylenes



Concentration, μg/L
10 3
10 2
10 1
10 0
10 -1
10 -2
7/27/03
8/3/03
8/10/03
8/17/03
8/24/03
8/31/03
9/7/03
9/14/03
9/21/03
9/28/03
10/5/03
10/12/03
10/19/03
10/26/03
11/2/03
11/9/03
11/16/03
11/23/03
11/30/03
12/7/03
12/14/03
12/21/03
12/28/03
1/4/04
1/11/04
1/18/04
1/25/04
2/1/04
2/8/04
2/15/04
2/22/04
2/29/04
3/7/04
3/14/04
time
o-Xyl inf
m-Xyl inf
p-Xyl inf
o-Xyl eff
m-Xyl eff
p-Xyl eff


Pascoag Reactor Solids
6000
5000
4000
3000
2000
1000
0
6
5
4
3
2
1
0
TSS
VSS
gpm
Flow, gpm
7/12/03
7/19/03
7/26/03
8/2/03
8/9/03
8/16/03
8/23/03
8/30/03
9/6/03
9/13/03
9/20/03
9/27/03
10/4/03
10/11/03
10/18/03
10/25/03
11/1/03
11/8/03
11/15/03
11/22/03
11/29/03
12/6/03
12/13/03
12/20/03
12/27/03
1/3/04
1/10/04
1/17/04
1/24/04
1/31/04
2/7/04
2/14/04
2/21/04
2/28/04
3/6/04
date

Non-Purgeable Organic Carbon



Economic Comparison of BCR, MBR, and Air Stripping

- Assumptions:
  - 2 mg/L MtBE influent
  - 5 mg/L MtBE effluent
  - 3 groundwater flow rates (0.1, 0.3, and 1.0 mgd)
  - Air stripping equipped with GAC off-gas treatment

Economic Evaluation of E*x-Situ* Reactors

Cost of *ex-situ* treatments, $/1000 gal*

Flow	Stripping	MBR	BCR
0.1 mgd	2.11	1.76	1.05
0.3 mgd	0.88	0.93	0.82
1.0 mgd	0.41	0.54	0.55

*Estimates by Richard Scharp, EPA-NRMRL

Summary and Conclusions

Summary

- Despite substantial flow control problems during the first 3.5 months of operation, all contaminants were reduced to less than the desired 5 µg/L
  - UCL_{95} for final 4 months = 6.1 µg/L
  - UCL_{95} for final 2 months = 2.6 µg/L
- All VOCs were substantially degraded to near detection limits, including all oxygenates and hydrocarbons
- Final effluent was nearly drinking water quality as determined by NPOC levels attained

Conclusions

- *Ex-situ* pump-and-treat using BCR technology is a technologically and economically viable treatment strategy for contaminated groundwater
- MtBE is fully biodegradable to CO_2 and H_2O under aerobic conditions
  - Due to its high water solubility, MtBE especially amenable to ex-situ pump-and-treat
- License agreement with environmental remediation firm in Cincinnati (Tipton Environmental)
  - Will be able to manufacture reactors very inexpensively, thereby reducing estimated costs substantially
- O&M costs still uncertain
- Maximum flow potential still unknown

EPA