

Biodegradation of MtBE Using an Innovative Biomass Concentrator Reactor

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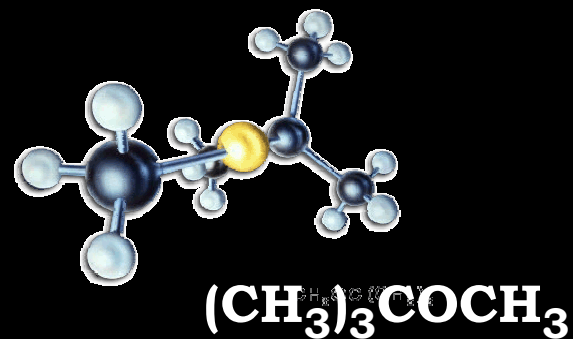
MtBE as Fuel Additive

- 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 O₃ 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



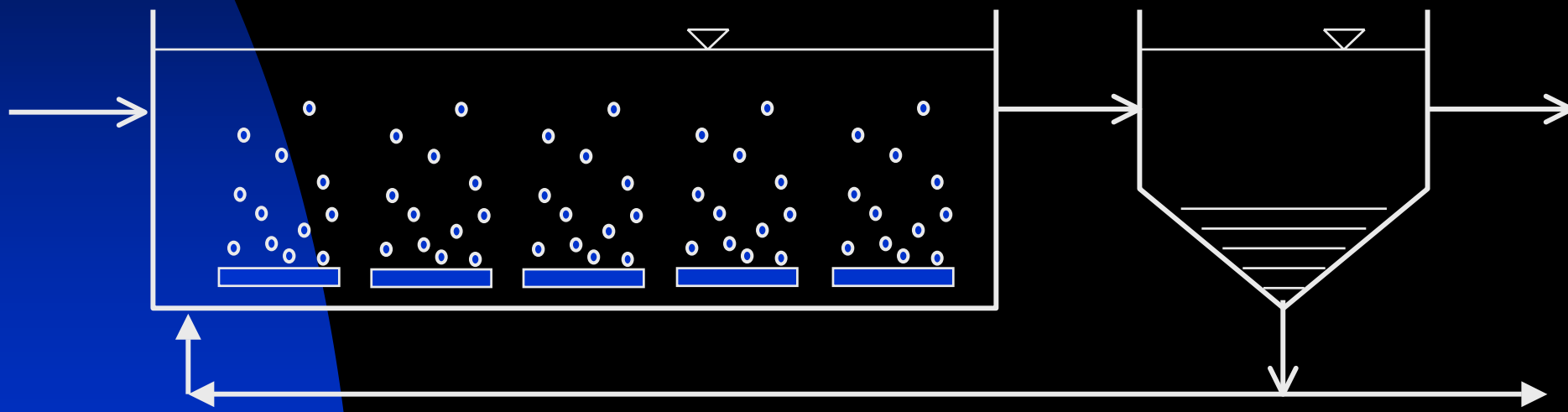
Methyl t-Butyl Ether (MtBE)

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



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)
- $1.0 \text{ mg MtBE/L} * 0.10 \text{ mg biomass/mg MtBE} = 0.10 \text{ mg biomass/L}$
- Thus, large fraction of biomass leaves system via effluent
- To get effective treatment to low MCLs, must retain ALL biomass

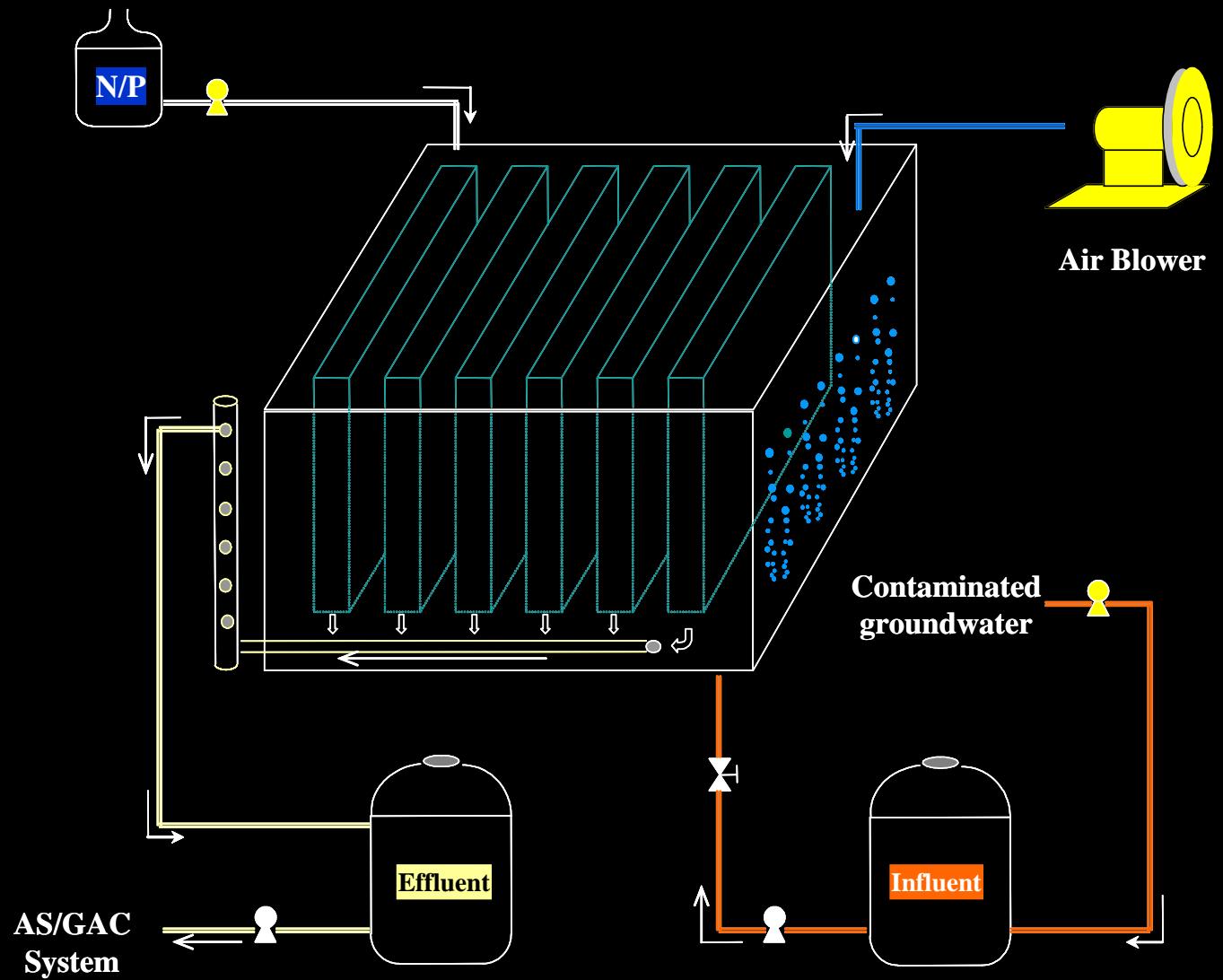
Applications of Biomembrane Technology

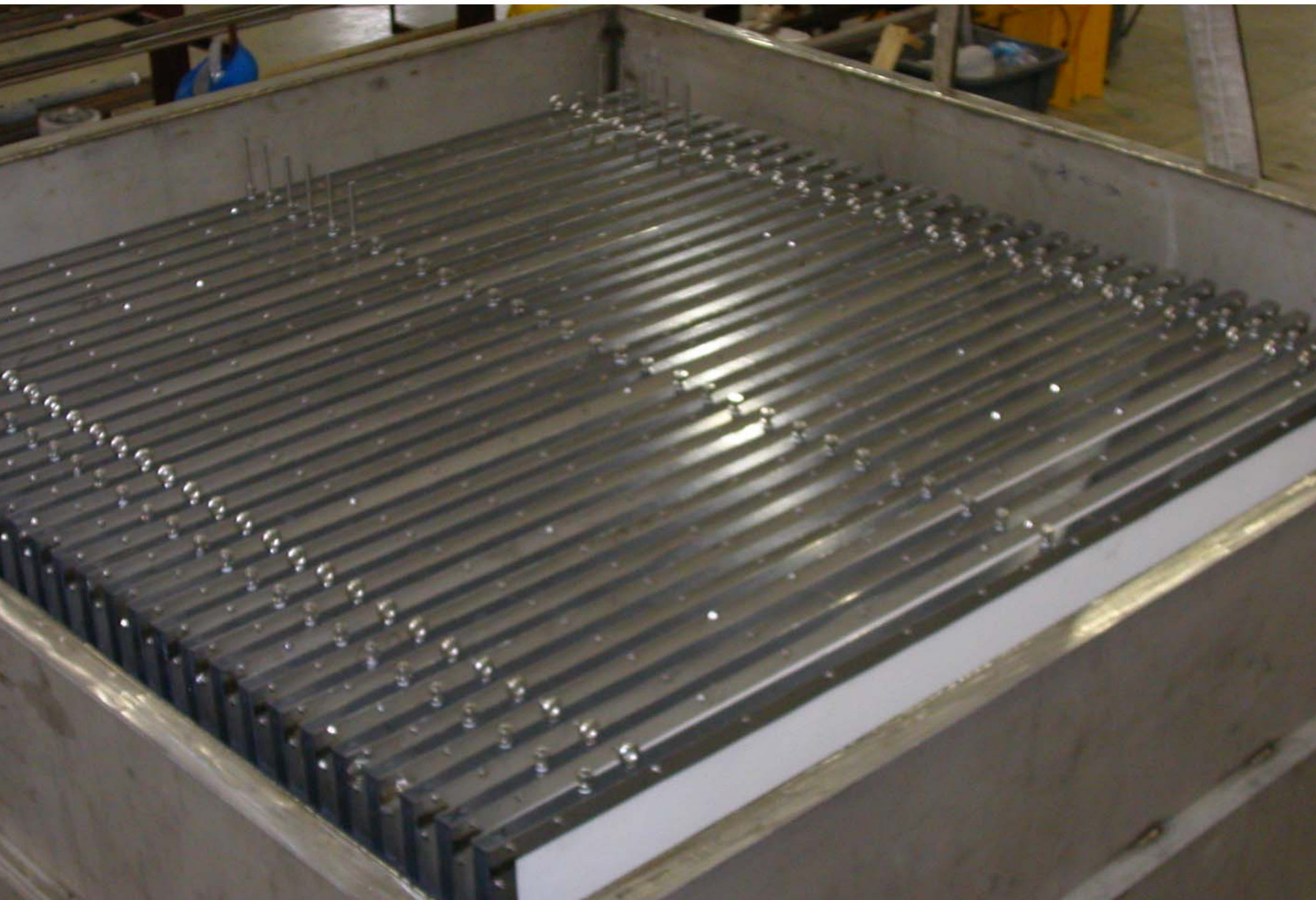
- **Municipal & Industrial Wastewater Treatment**
 - **Better solids separation to attain desired effluent quality**
 - **Solids wasting under complete control of operator**
- **Surface & Groundwater Treatment**
 - **Ideally suited for dilute streams**
 - **Ideally suited for soluble pollutants**
 - **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

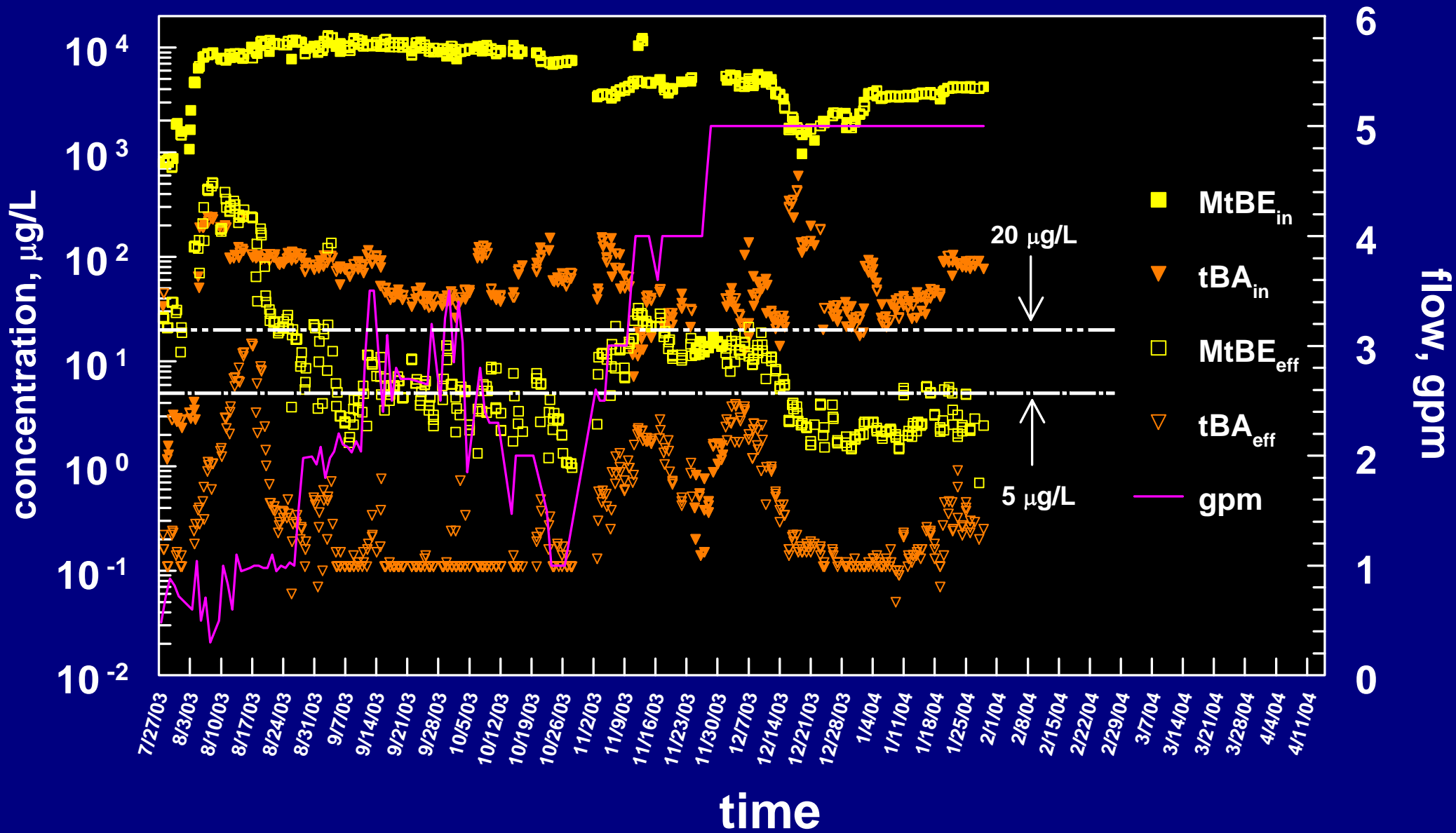
- Daily monitoring of temperature, pH, DO
- Samples of reactor contents collected weekly for:
 - TSS
 - VSS
 - NPOC

Membrane Regeneration

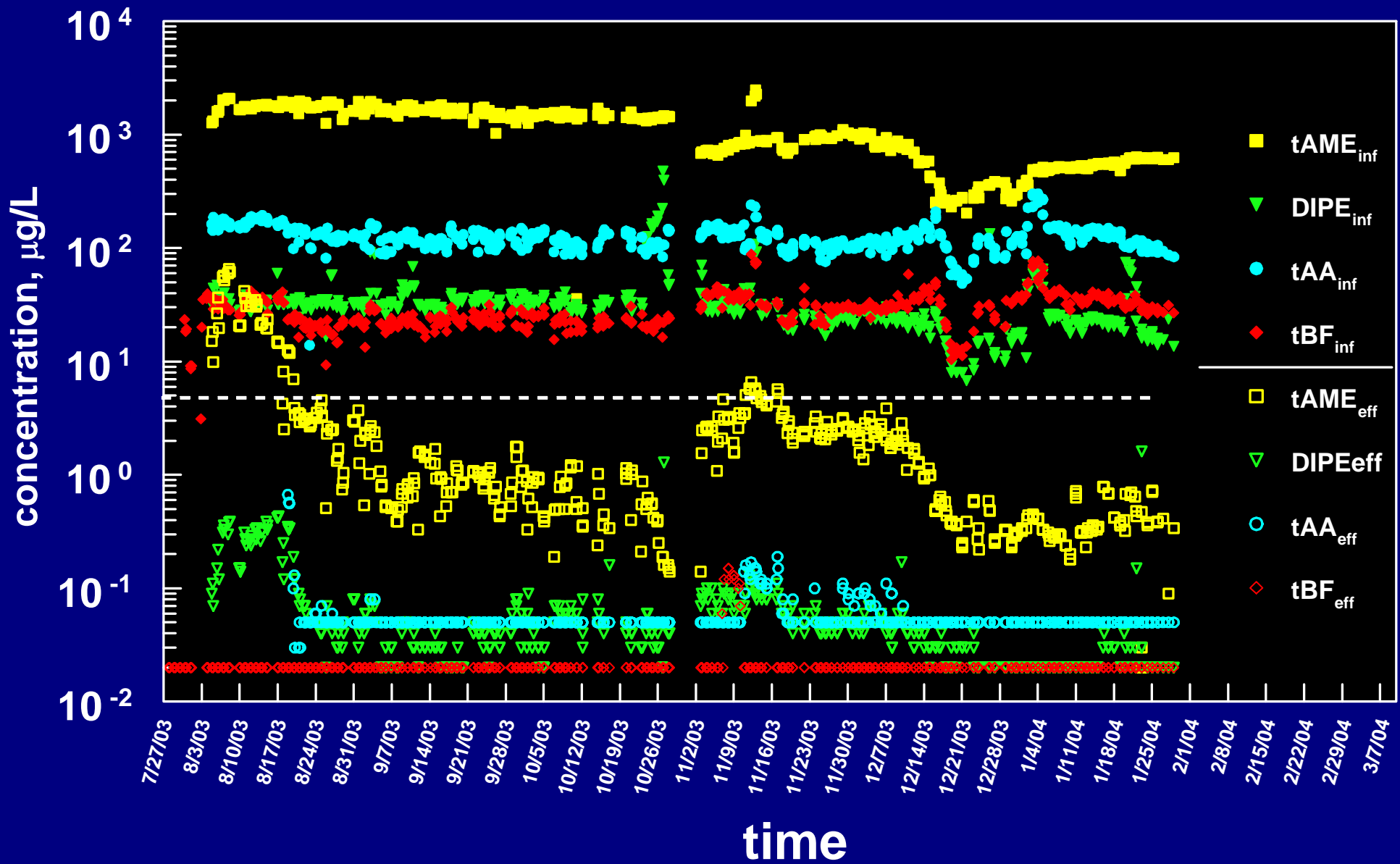
- Membranes were regenerated as part of a planned schedule whether they needed it or not
 - Removed one at a time, soaked in a stainless steel dip tank containing chlorine bleach for 4 hours, then soaked in dilute nitric acid for another 4 hours, rinsed, and placed back into reactor
 - Membranes were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

Experimental Results

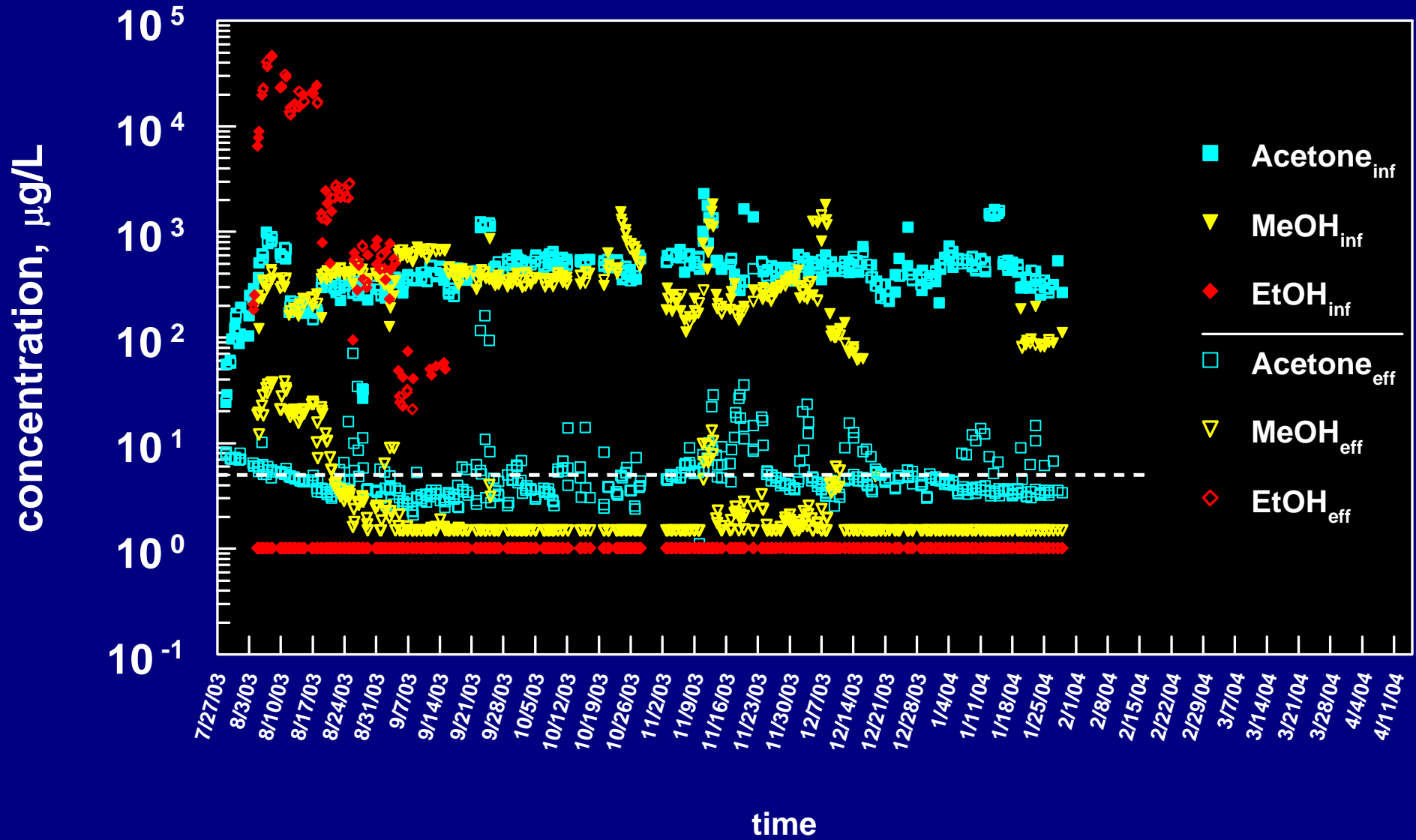
MtBE and tBA



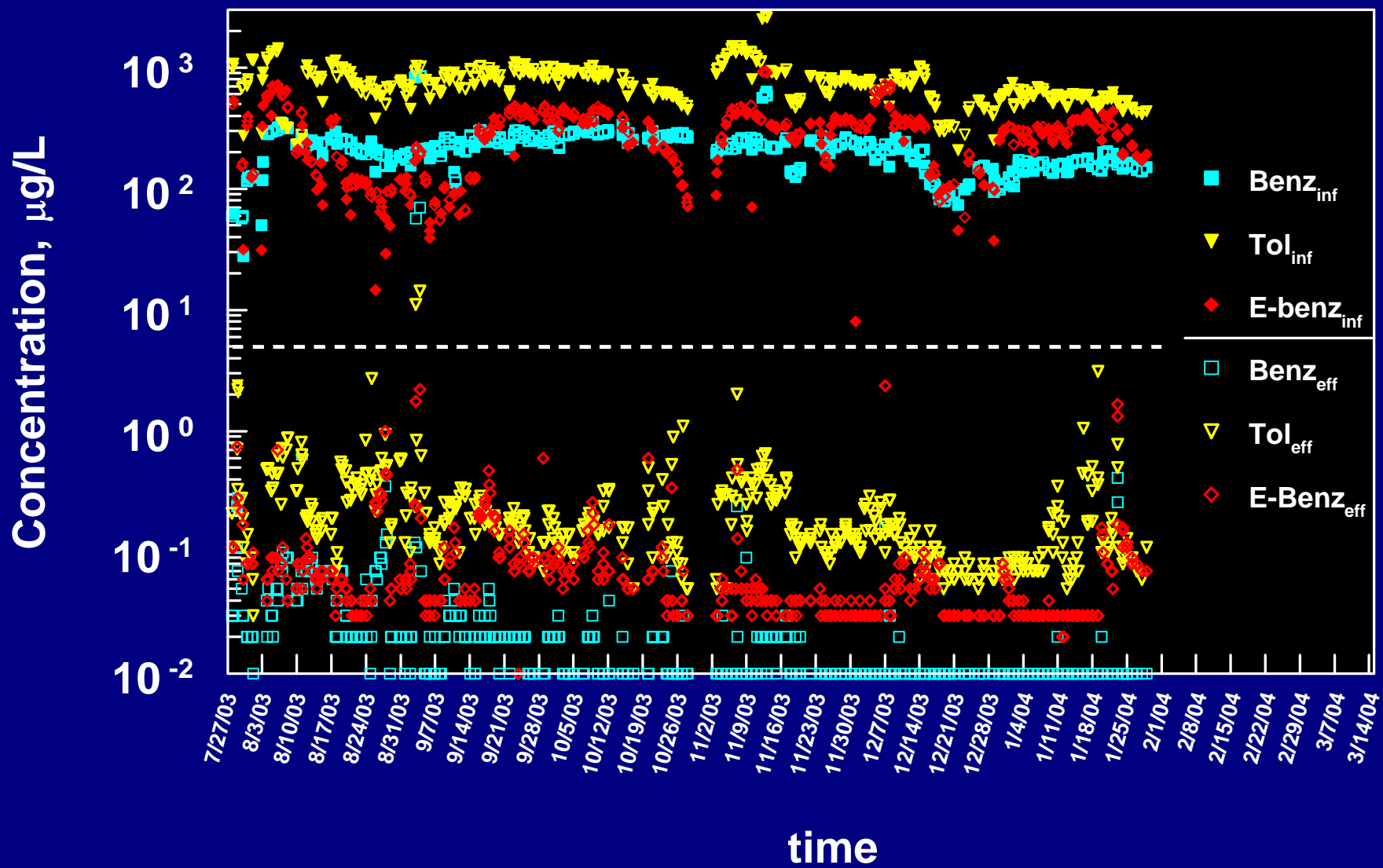
Other Oxygenates



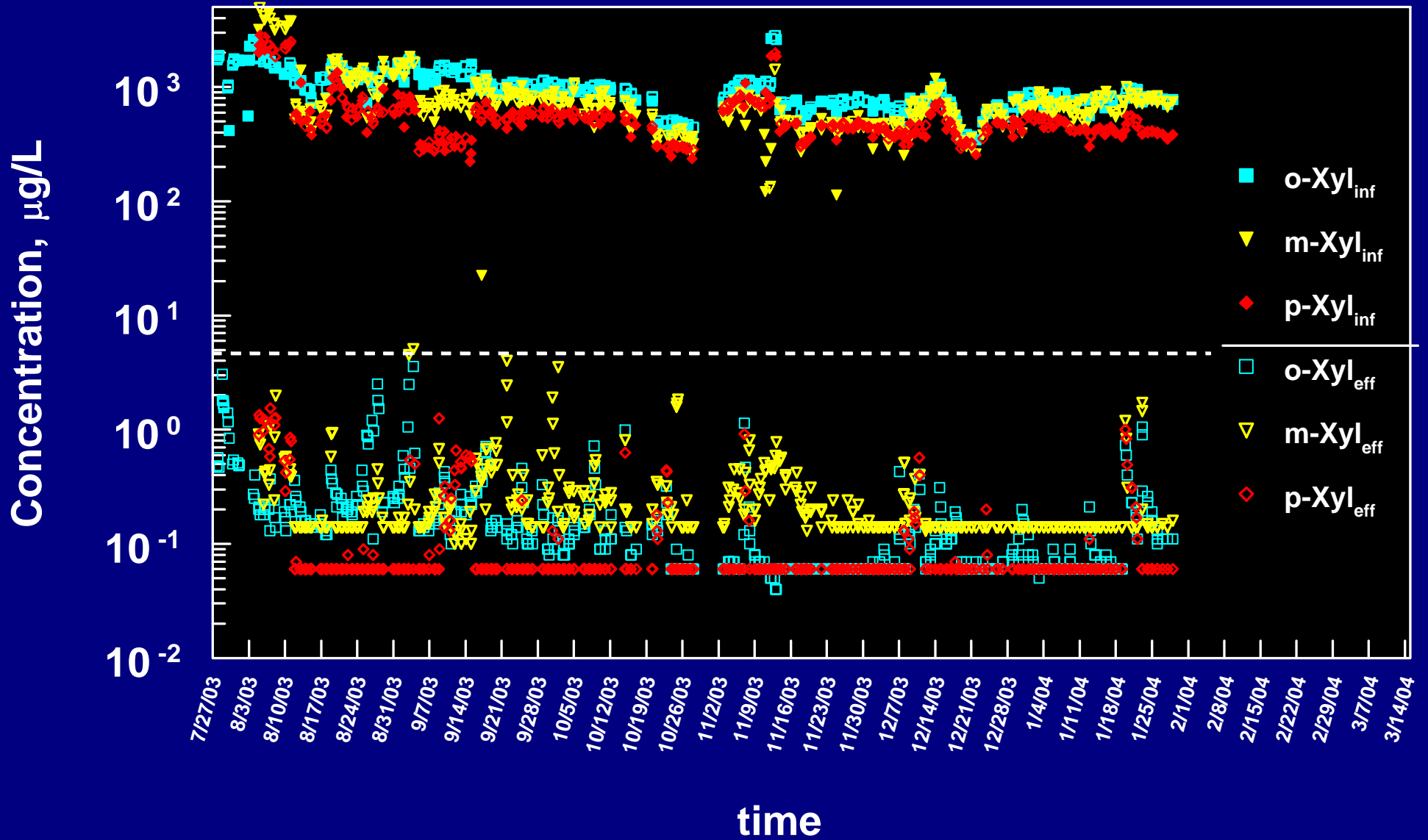
Alcohols and Acetone



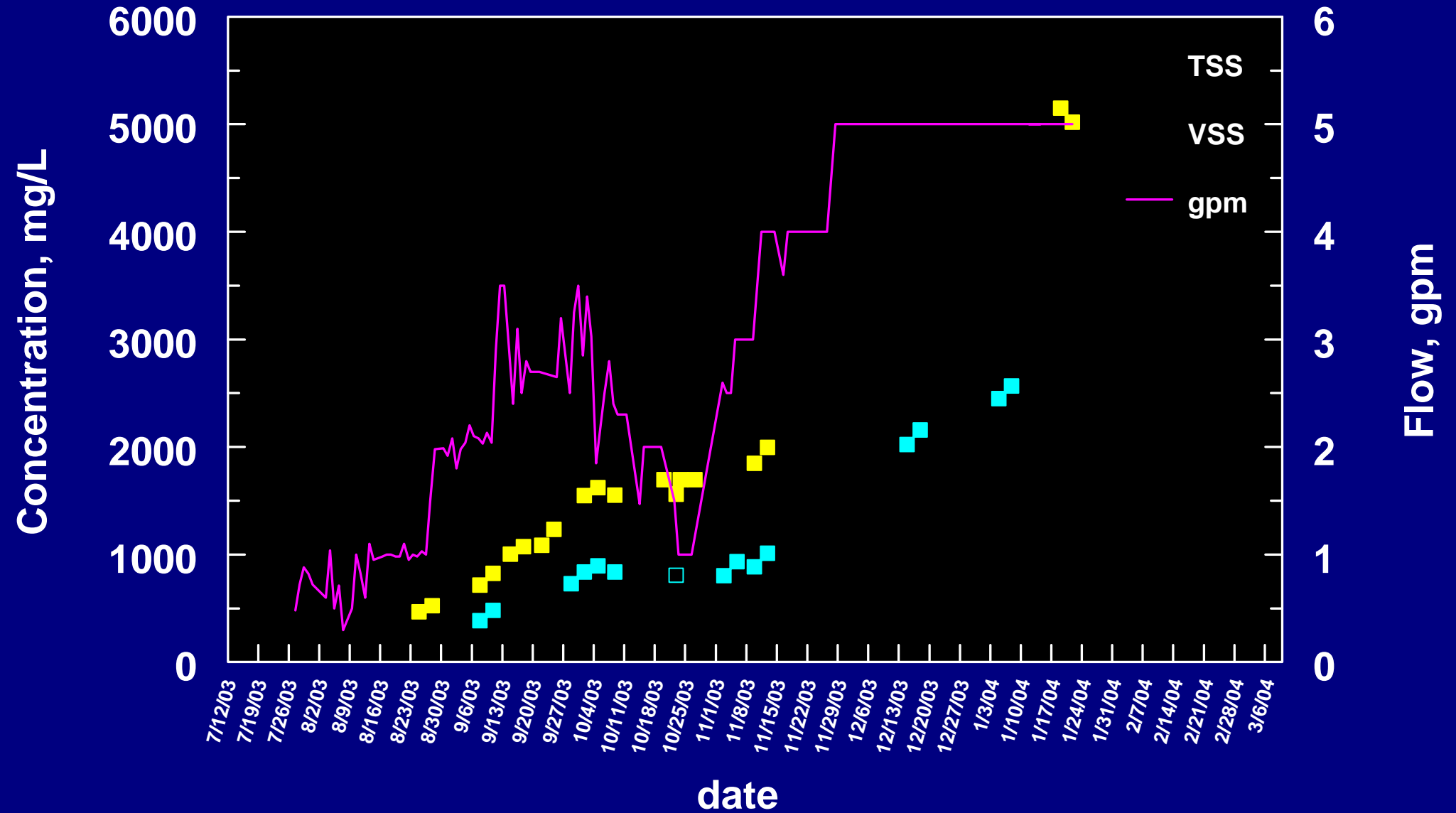
Benzene, Toluene, Ethylbenzene



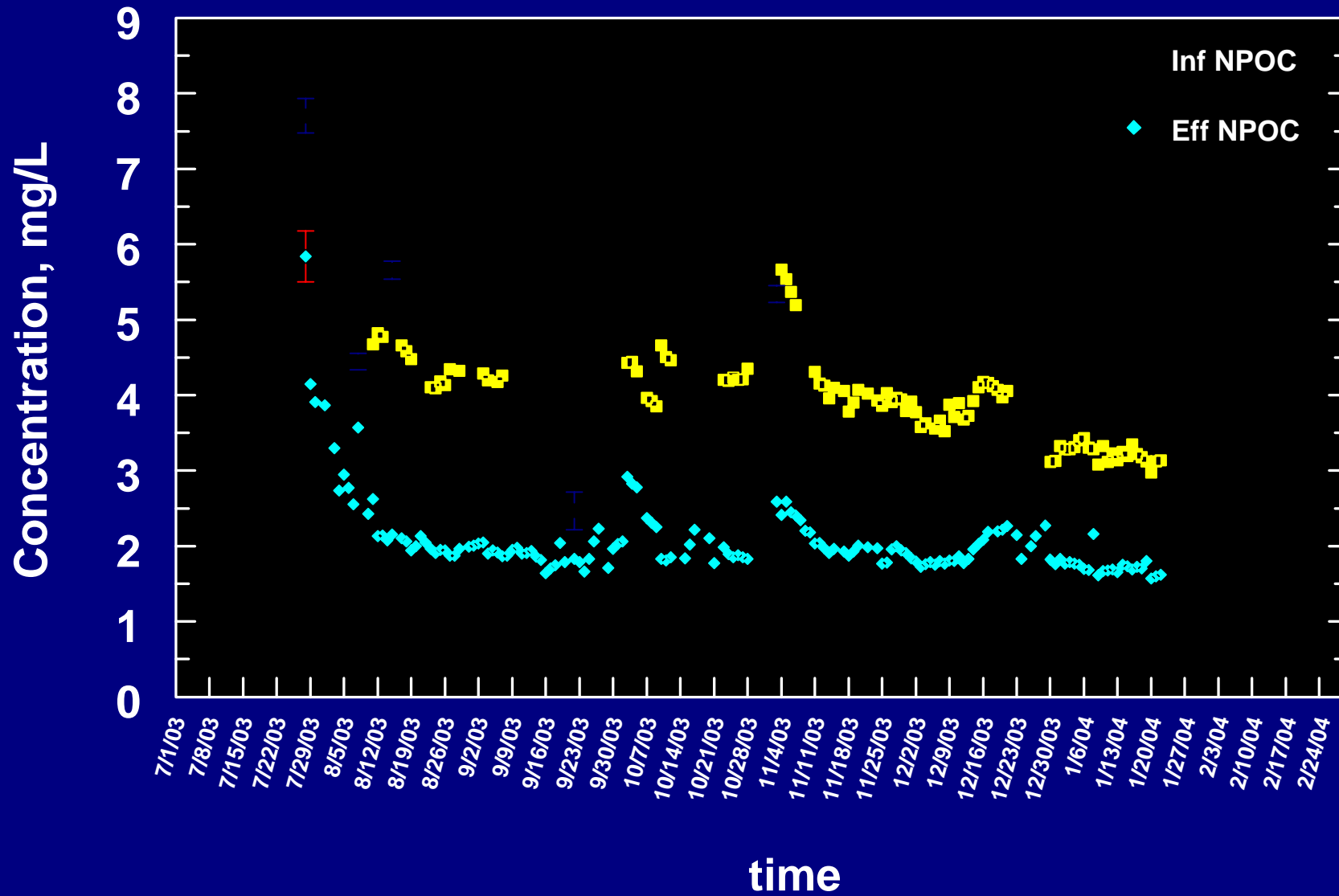
o-, m-, p-Xylenes



Pascoag Reactor Solids



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 Ex-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
 - **UCL₉₅ for final 4 months = 6.1 µg/L**
 - **UCL₉₅ 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 CO₂ and H₂O 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