- PhD Dissertation Defense

Integrated Cyclic Adsoprtion/Desorption Beds
and Biofiltration System for Treatment of Waste Gas Streams

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• Contents

- Introduction
- Objective
- Research Phases
- Recommendations

•Introduction

Conceptually identical process to the biofilter

- Microbial attachment: Synthetic inorganic or polymeric media
- Intermittent delivery of Nutrient & Buffer to the media

  ✓ **Consistent Nutrient & pH control**

  ✓ **Optimizing the waste utilizing kinetics**

•Trickle-Bed Air Biofilter (TBAB)

- **Consistent**
- **Long-term**
- **High**

Removal Performance

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•Introduction

•for more successful application in industry

•Challenges

•Source Characteristics

- Variation in Concentration
- Variation in Composition
- Non-use periods

•Biofilter Maintenance

- Biomass accumulation

•Load fluctuation

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•Introduction

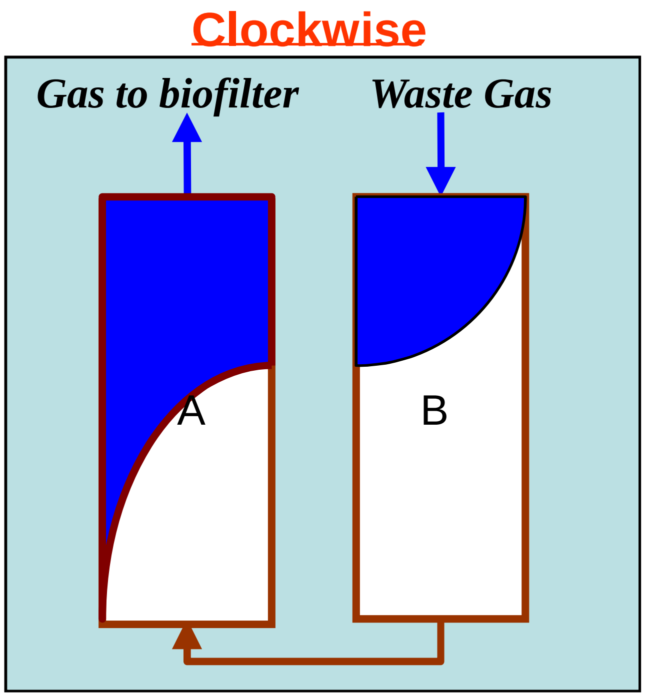
Solution to load fluctuation on Biofilter

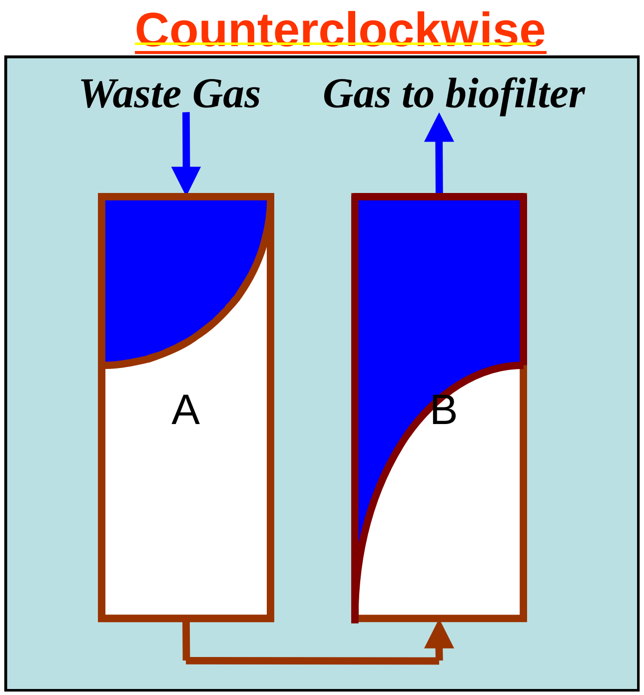
- **Buffer unit : adsorption bed can be a buffer unit to a biofilter.**
  - **Application in industry: single activated carbon bed**
  - **Challenges of single bed**
    - **Lose buffer capacity to high load and large fluctuation**
    - **Starvation period during initial period of operation**
    - **Breakthrough after relative short operating period**

•Introduction

Solution to load fluctuation on Biofilter

- Cyclic adsorption/desorption beds





•Introduction

•2-Bed Adsorption/Desorption Unit

- **Cyclic operation : Shift of air flow direction**
  - **→ Each bed will not be fully saturated with adsorbate**

- **Will Serve as**

➢ **Polishing unit during the initial acclimation period of the biofilter**
➢ **Buffer unit in load fluctuation**
➢ **Feeding source without any feeding phase during non-use periods**

•Objective

Primary Objective

To apply an integrated cyclic adsorption/desorption beds and biofiltration system to remove VOCs from waste gas streams.

Secondary Objectives

- **Effect of interchanging the feed VOCs**
- **Effect of VOCs composition**
- **Characterization of 2-bed unit**
- **Application of integrated system**
- **Microbial diversity study**

•Phase I

Objective

Characterization of TBAB for VOC interchange under step-change loadings

•Materials and Methods

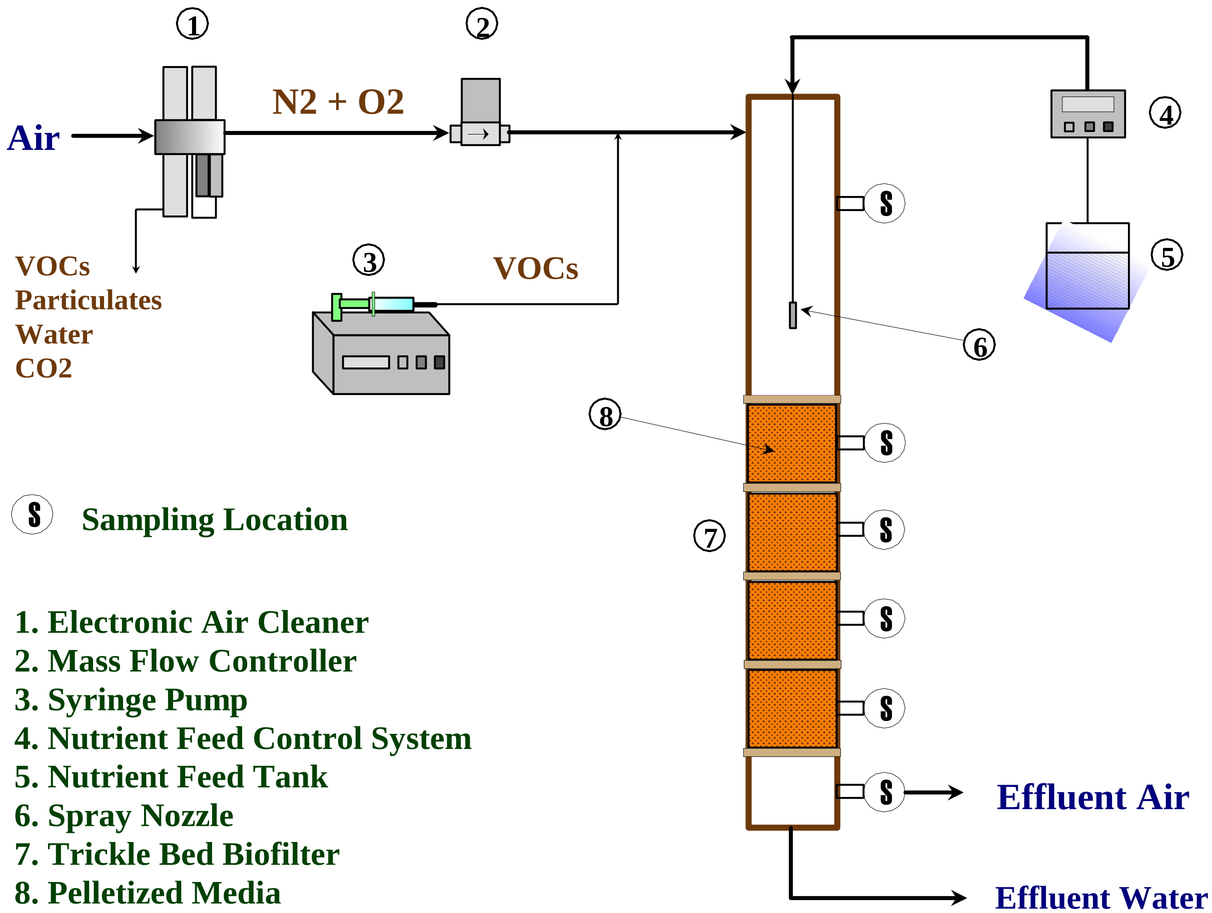
Experimental setup

- ➢ **Reactor : Independent lab-scale TBAB**
  - ✓ **Diameter: 76 mm (ID)**
  - ✓ **Media depth: 60 cm**
  - ✓ **Temperature: 20 °C**
  - ✓ **Co-current**

•Materials and Methods

- **Reactor : Independent lab-scale TBAB**
- **Media: pelletized biological support media**

•Materials and Methods



S Sampling Location

1. Electronic Air Cleaner
2. Mass Flow Controller
3. Syringe Pump
4. Nutrient Feed Control System
5. Nutrient Feed Tank
6. Spray Nozzle
7. Trickle Bed Biofilter
8. Pelletized Media

•Materials and Methods

➢ Feed VOCs

	Aromatic		Oxygenated	
	Toluene	Styrene	Methyl ethyl ketone (MEK)	Methyl isobutyl ketone (MIBK)
K'_H	0.280	0.109	0.00194	0.00062
S	534.8	310	239×10^3	20.4×10^3

K'_H = dimensionless Henry's law constant   S = water solubility, mg/L

•Materials and Methods

➢ Operating Condition

- **Sequence of Feed VOCs**
  - **Study 1:** MEK → Toluene → MIBK → Styrene → MEK
  - **Study 2:** MIBK → Toluene → MEK → Styrene → MIBK
  - **Study 3:** Styrene → MEK → Toluene → MIBK → Styrene

- **Inlet concentration of feed VOCs**

  50 ppmv ~ the critical inlet concentration

- **Flow rate**
  - **Study 1:** Air flow = variable (Different EBRT for each VOC)
  - **Study 2:** Air flow = variable (Different EBRT for each VOC)
  - **Study 3:** Air flow = 1.35 L/min (Constant EBRT = 2.02 min)

- **Biomass control : Periodic in-situ backwashing**

  Frequency: 1 hour of duration / a week

•Summary of Previous Results

Toluene removal

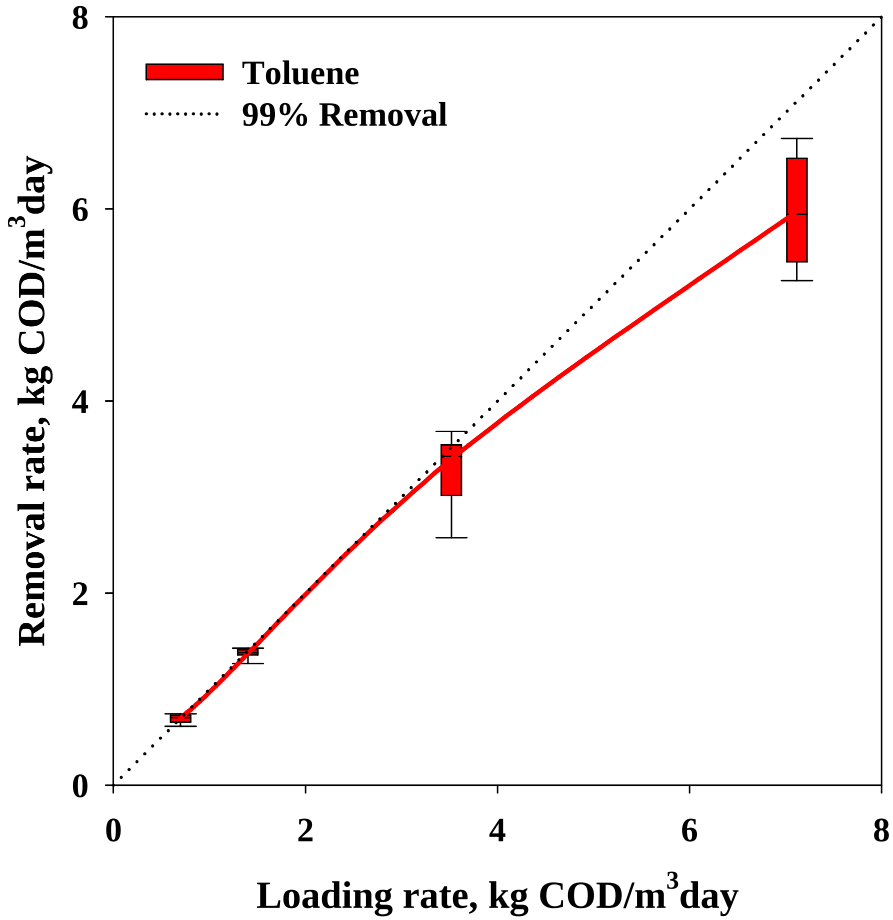
- Critical loading
  3.5 kg COD/m^3·day
  (46.6 g/m^3·hr)

- Maximum removal capacity
  6.0 kg COD/m^3·day
  (79.9 g/m^3·hr)

•EBRT: 1.23 min

•Inlet Conc. = 250 ppmv

•Toluene



•Summary of Previous Results

Styrene removal

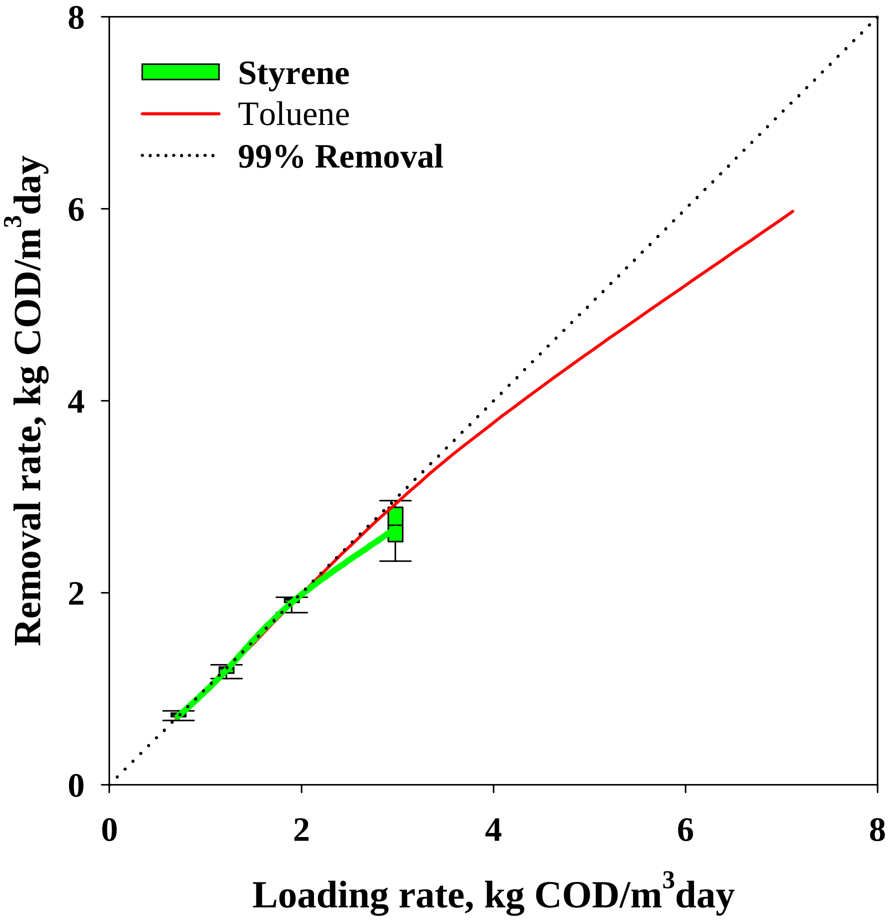
- Critical loading
  1.9 kg COD/m^3·day
  (25.8 g/m^3·hr)

- Maximum removal capacity
  2.7 kg COD/m^3·day
  (36.6 g/m^3·hr)

•EBRT: 2.02 min

•Inlet Conc. = 200 ppmv

•Styrene



•Summary of Previous Results

MEK removal

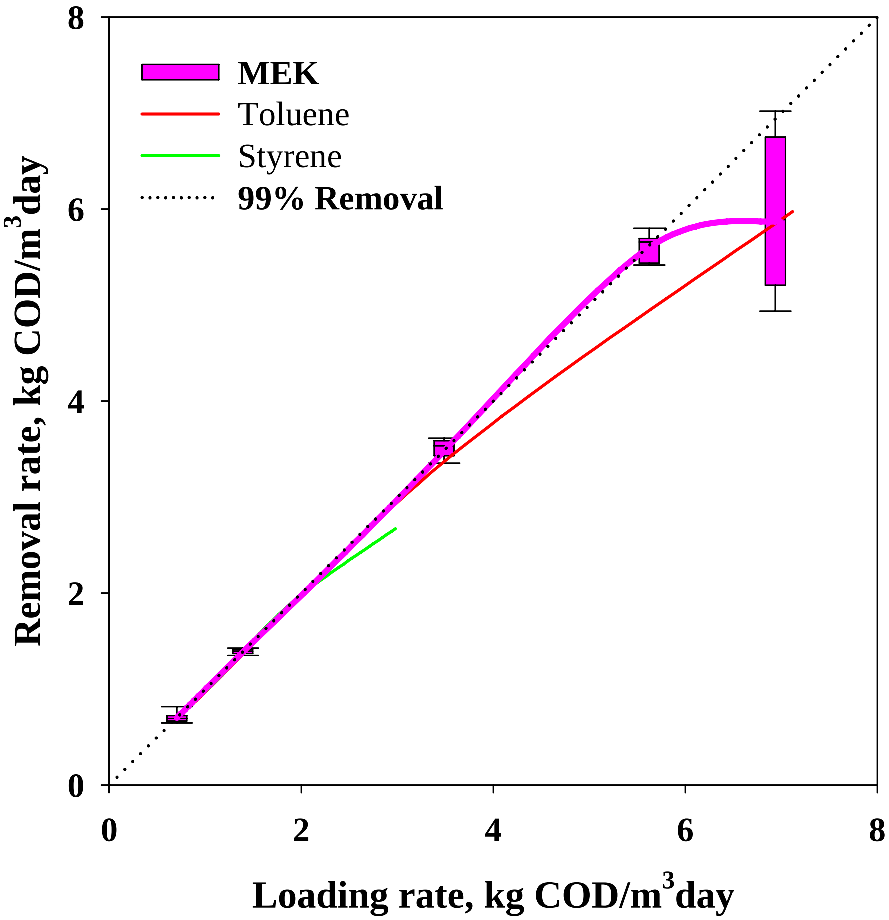
- **Critical loading**
  5.6 kg COD/m³·day
  (95.6 g/m³·hr)

- **Maximum removal capacity**
  5.9 kg COD/m³·day
  (100.7 g/m³·hr)

•EBRT: 0.76 min

•Inlet Conc. = 400 ppmv

•MEK



•Summary of Previous Results

MIBK removal

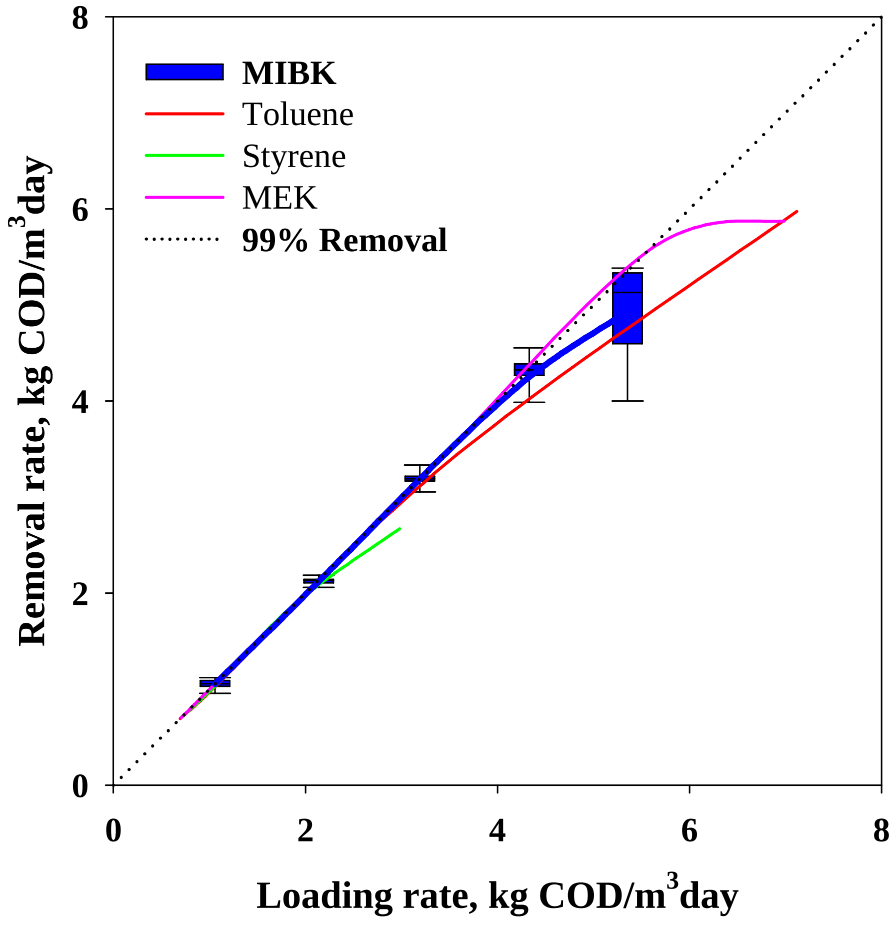
- **Critical loading**
  4.3 kg COD/m³·day
  (65.9 g/m³·hr)

- **Maximum removal capacity**
  4.9 kg COD/m³·day
  (75.1 g/m³·hr)

•EBRT: 0.76 min

•Inlet Conc. = 150 ppmv

•MIBK

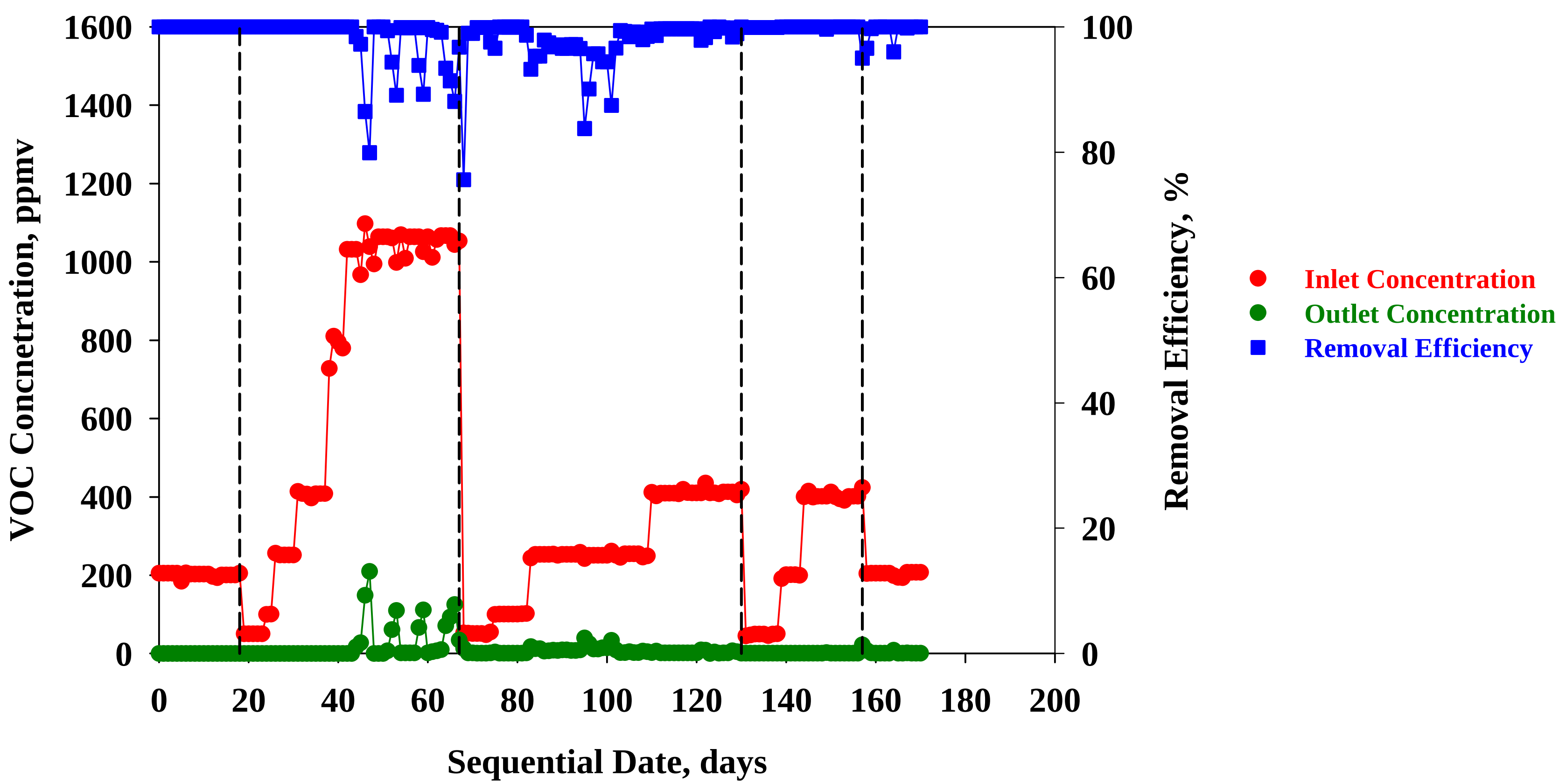


•Results

- Interchange of the feed VOCs
  - ✓ TBAB performance with respect to VOC removal
  - ✓ Effluent response corresponding to interchanging of feeding VOCs
    - → Removal efficiency
    - → CO_2 production

•Results •: Study 3 (Constant EBRT)

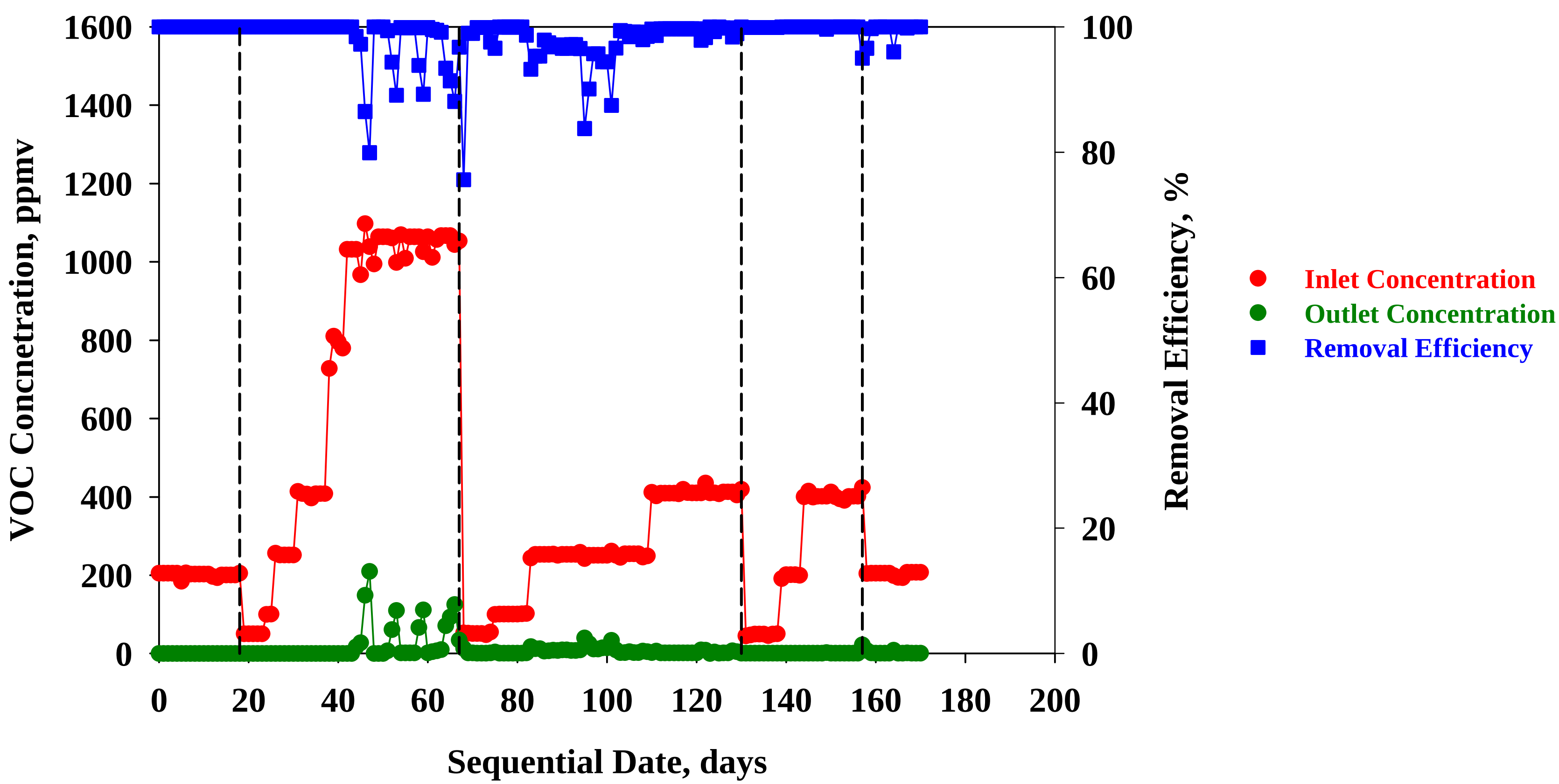
➢ **TBAB performance with respect to VOC removal**



•Results •: Study 3 (Constant EBRT)

•Styrene

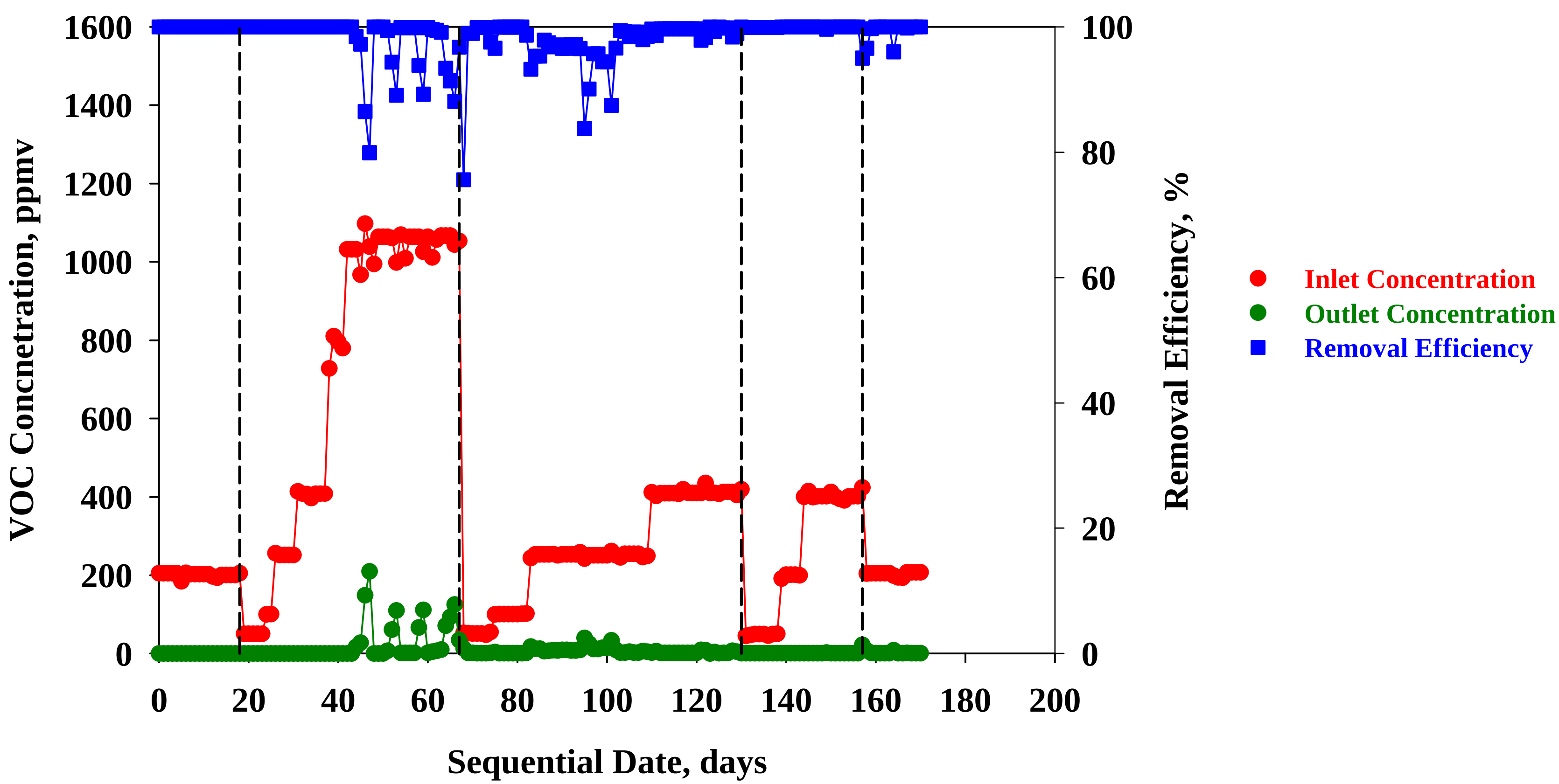
- Inlet: 200 ppmv



•Results •: Study 3 (Constant EBRT)

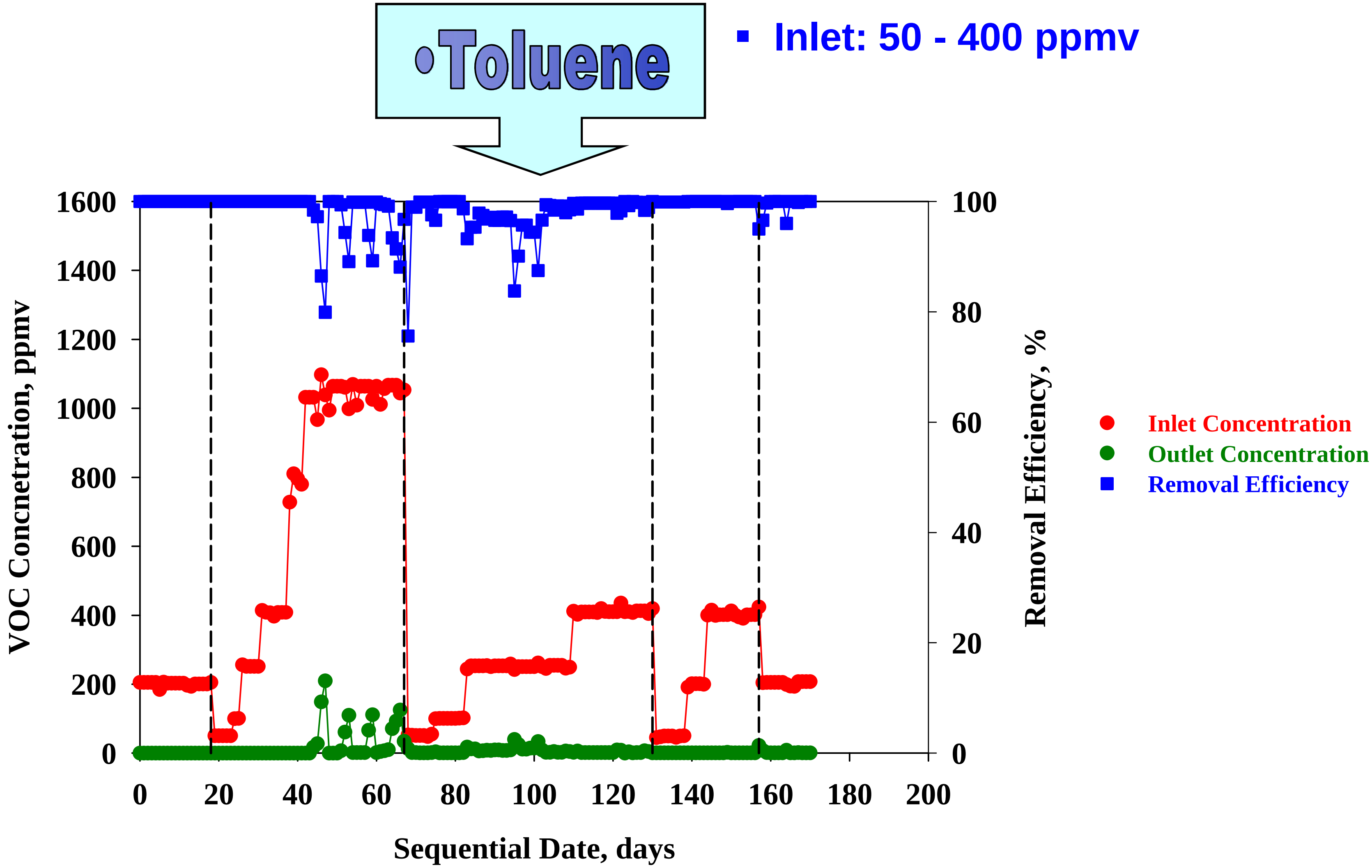
•MEK

- Inlet: 50 - 1080 ppmv



•Results •: Study 3 (Constant EBRT)

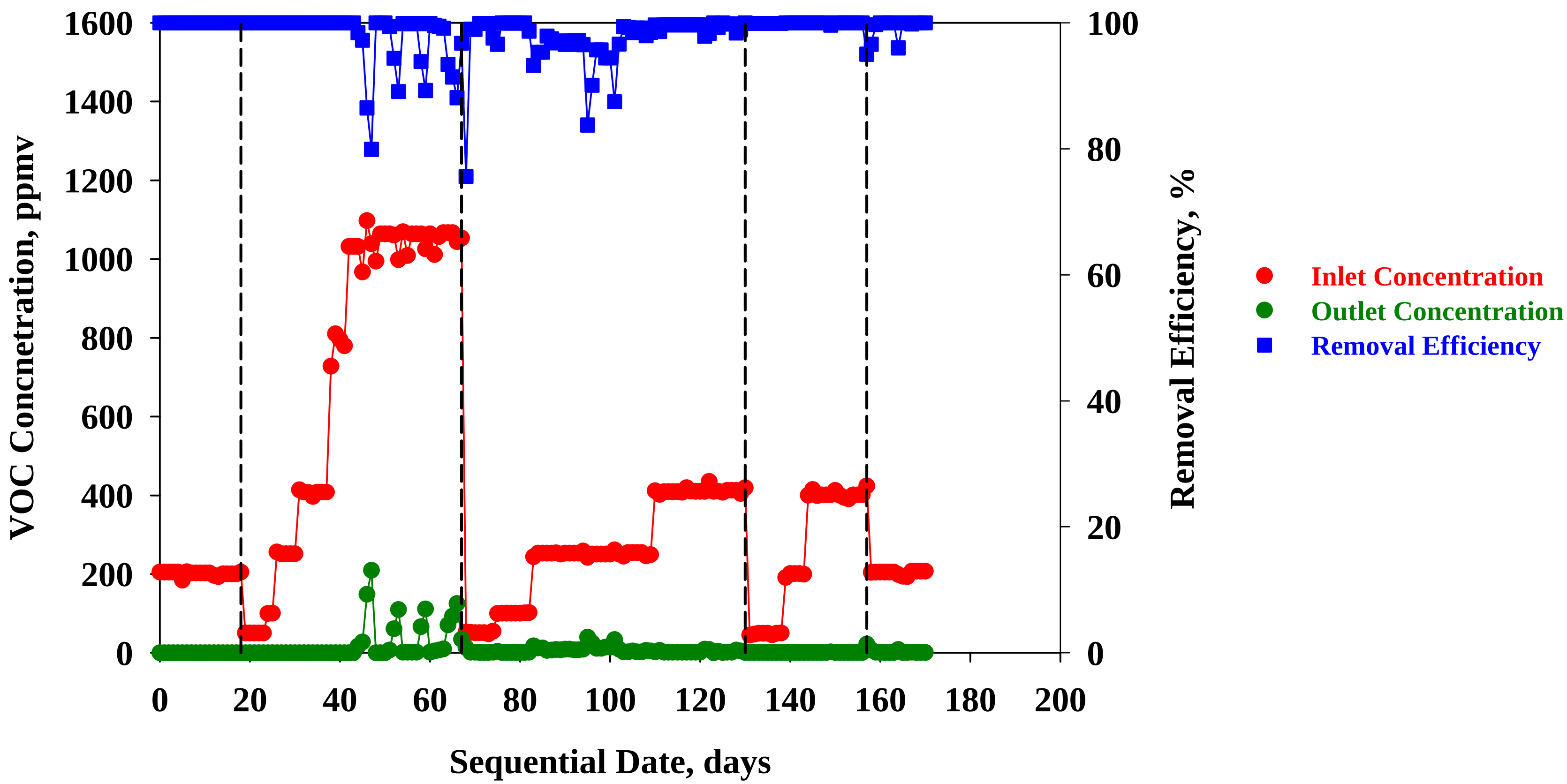
- Inlet: 50 - 400 ppmv



•Results •: Study 3 (Constant EBRT)

•MIBK

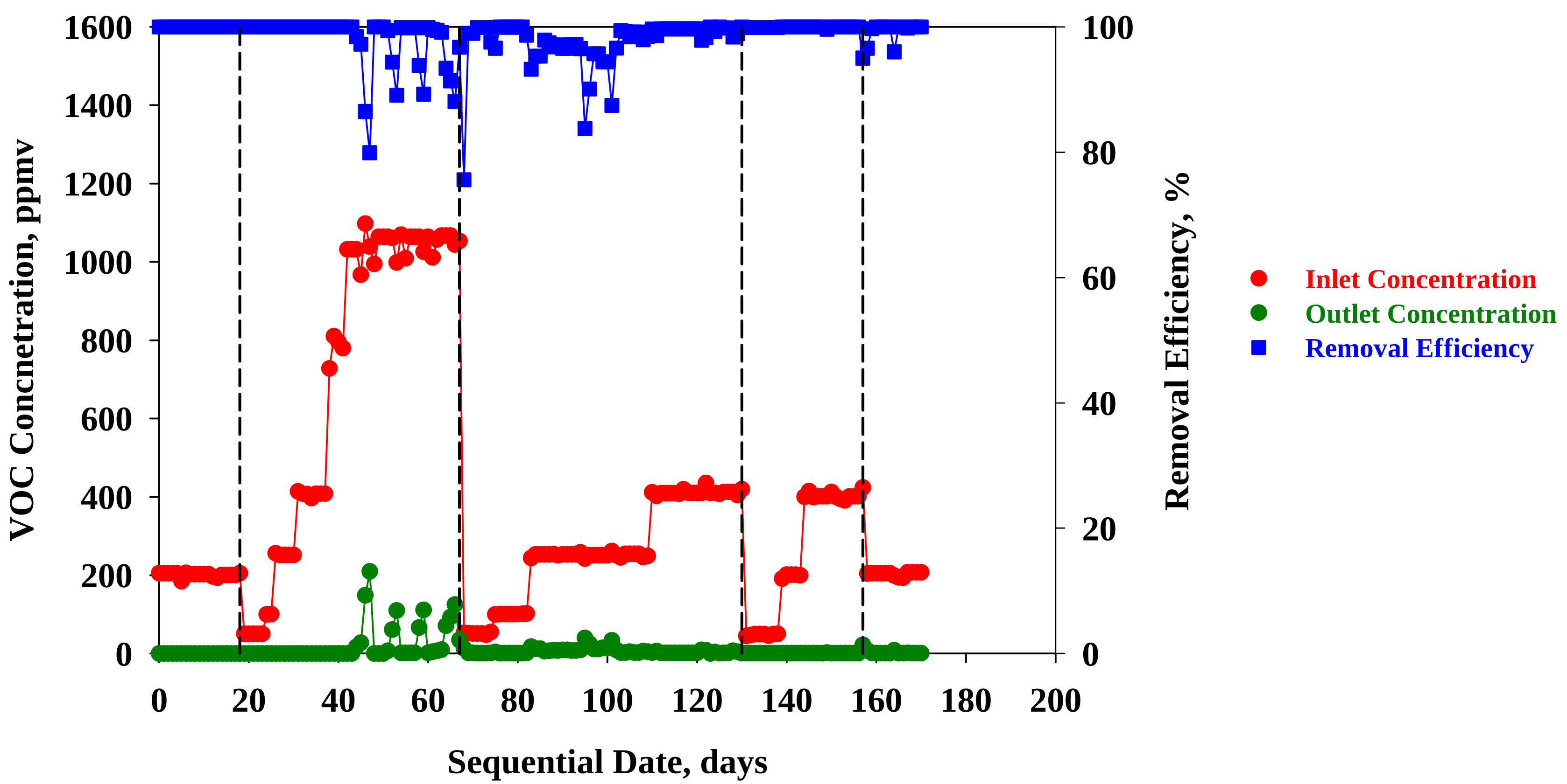
- Inlet: 50 - 400 ppmv



•Results •: Study 3 (Constant EBRT)

•Styrene

- Inlet: 200 ppmv



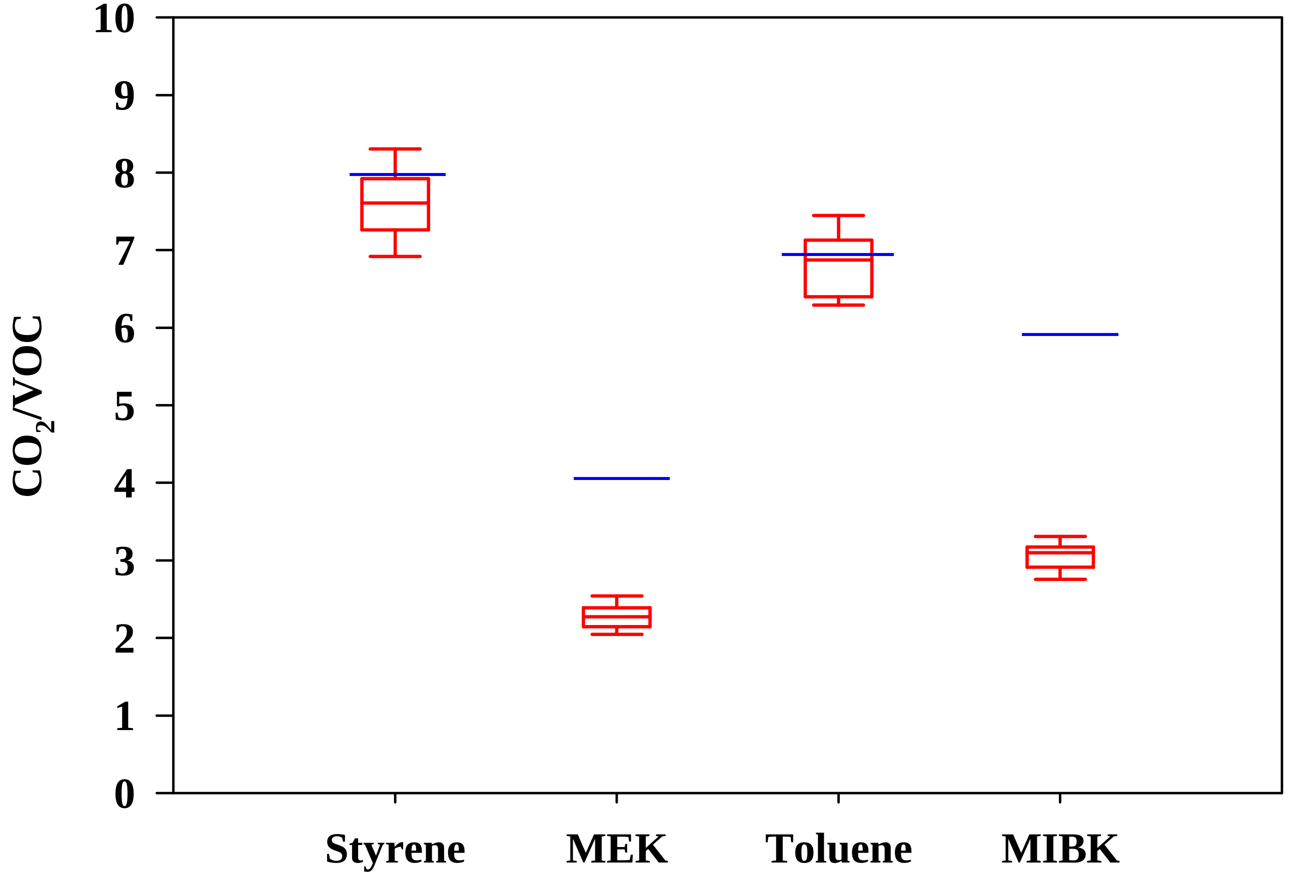
•Results •: Study 3 (Constant EBRT)

➢ **Biofilter Immediate Response after interchanging VOCs**

Time, min	Styrene to MEK	MEK to Toluene	Toluene to MIBK	MIBK to Styrene
30	99.9	55.4	99.4	61.2
60	99.9	58.2	99.9	77.3
300	99.9	65.6	99.9	91.8
600	99.9	73.5	99.9	96.8
1200	99.9	75.6	99.9	95.0
2880	99.9	99.0	99.9	96.6

•Results

➢ CO_2 Production



•Conclusions

- High removal performances were observed in the interchanging VOC-fed TBAB.

- Prolonged EBRT had no apparent effect on the biofilter performance for MEK and MIBK, while the prolonged EBRT improved the biofilter performance of styrene and toluene significantly.

- The initial compound did not have apparent effect on performance of VOC interchanging in the biofilter.

•Conclusions

- TBAB easily acclimated to MEK & MIBK, while TBAB acclimations to Toluene & Styrene were delayed for about 2 days.

- The destructed toluene and styrene were eliminated exclusively by aerobic biodegradation, however, the destructed MEK and MIBK were eliminated by aerobic biodegradation and possible denitrification.

•Phase II

Objective

Characterization of TBAB for VOC mixture

•Materials and Methods

- **Feed VOC Mixtures**
  - **Feeding condition to Biofilter A: Equal Molar Ratio**
    - **Toluene: Styrene: MEK: MIBK = 1: 1: 1: 1**
  - **Feeding condition to Biofilter B: Emission Ratio Based on *EPA 2003 toxic release report* for chemical industries**
    - **Toluene: Styrene: MEK: MIBK = 0.448: 0.260: 0.234: 0.058**

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•Materials and Methods

➢ Operating Conditions

- **Inlet concentration of feed VOCs**
  - **50 ppmv ~ 1000 ppmv for Biofilter A**
  - **50 ppmv ~ 500 ppmv for Biofilter B**

- **Flow rate**
  - **Air flow = 1.35 L/min (Constant EBRT = 2.02 min)**

- **Biomass control**
  - **Backwashing : 1 hour of duration / week**
  - **Starvation: two days / week**
    - ✓ **VOC feeding shut off, only air and nutrient solution passing through**

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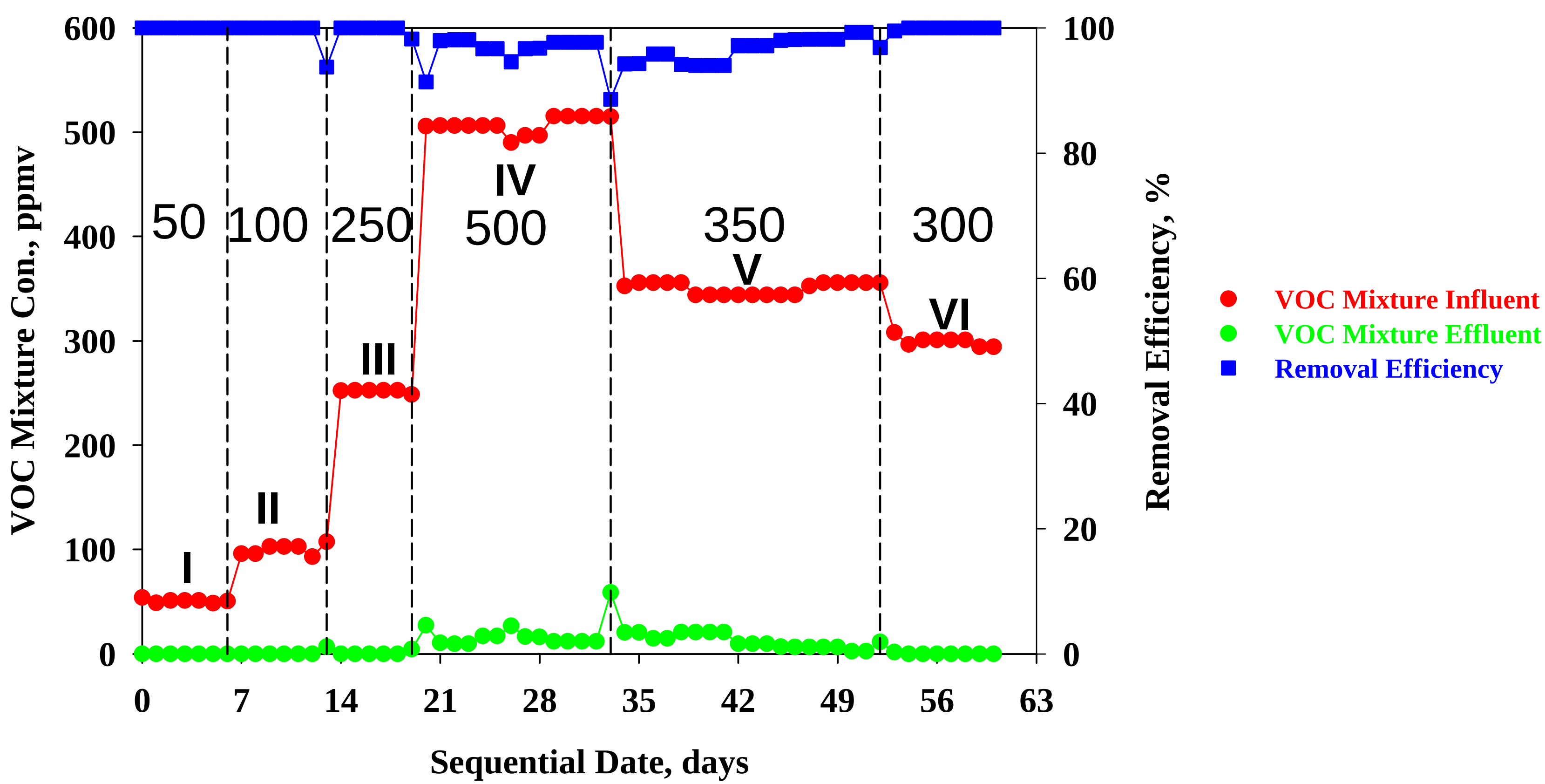
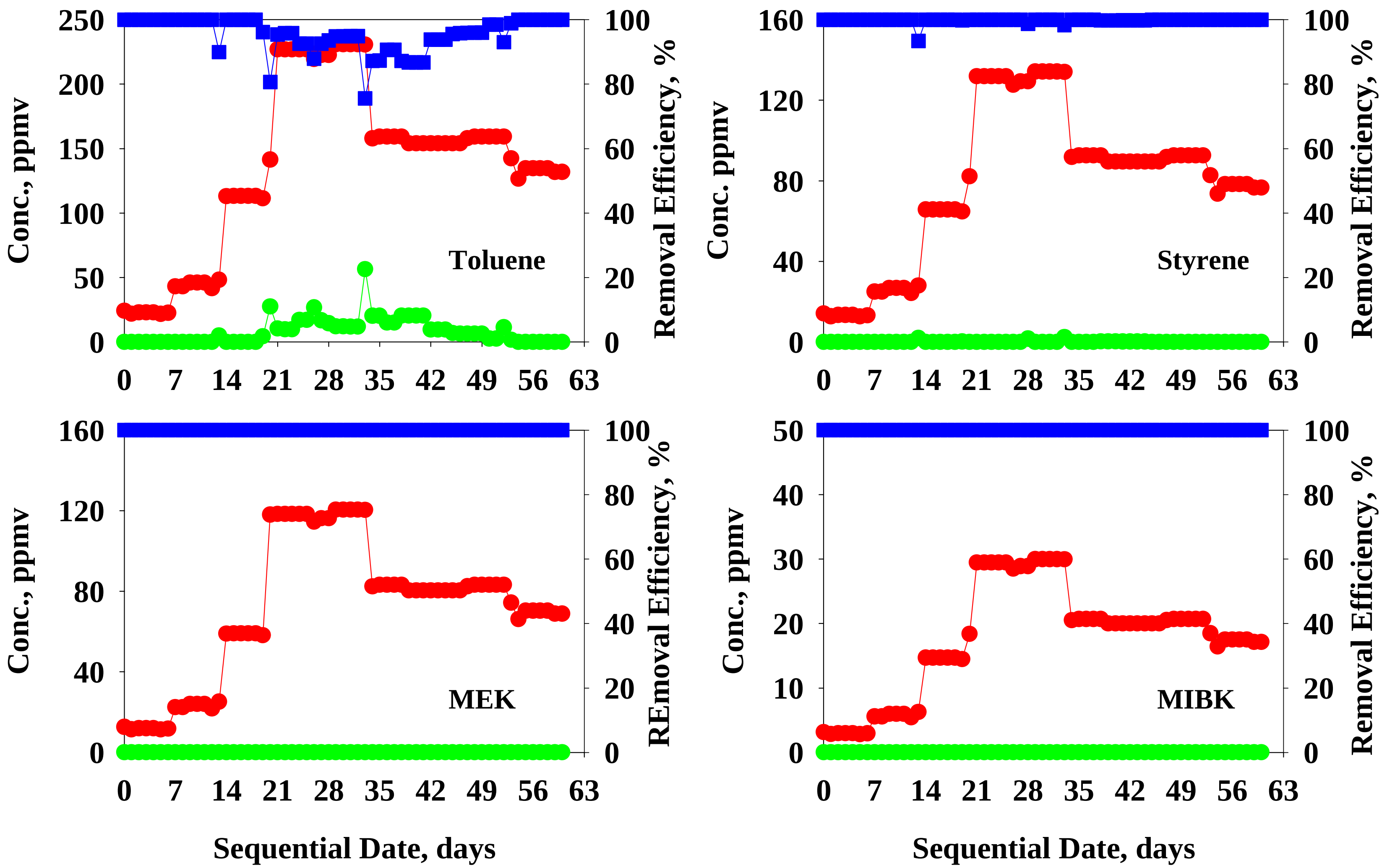
•Results

➢ **TBAB performance with respect to VOC removal**

Toluene: Styrene: MEK: MIBK = 0.448: 0.260: 0.234: 0.058



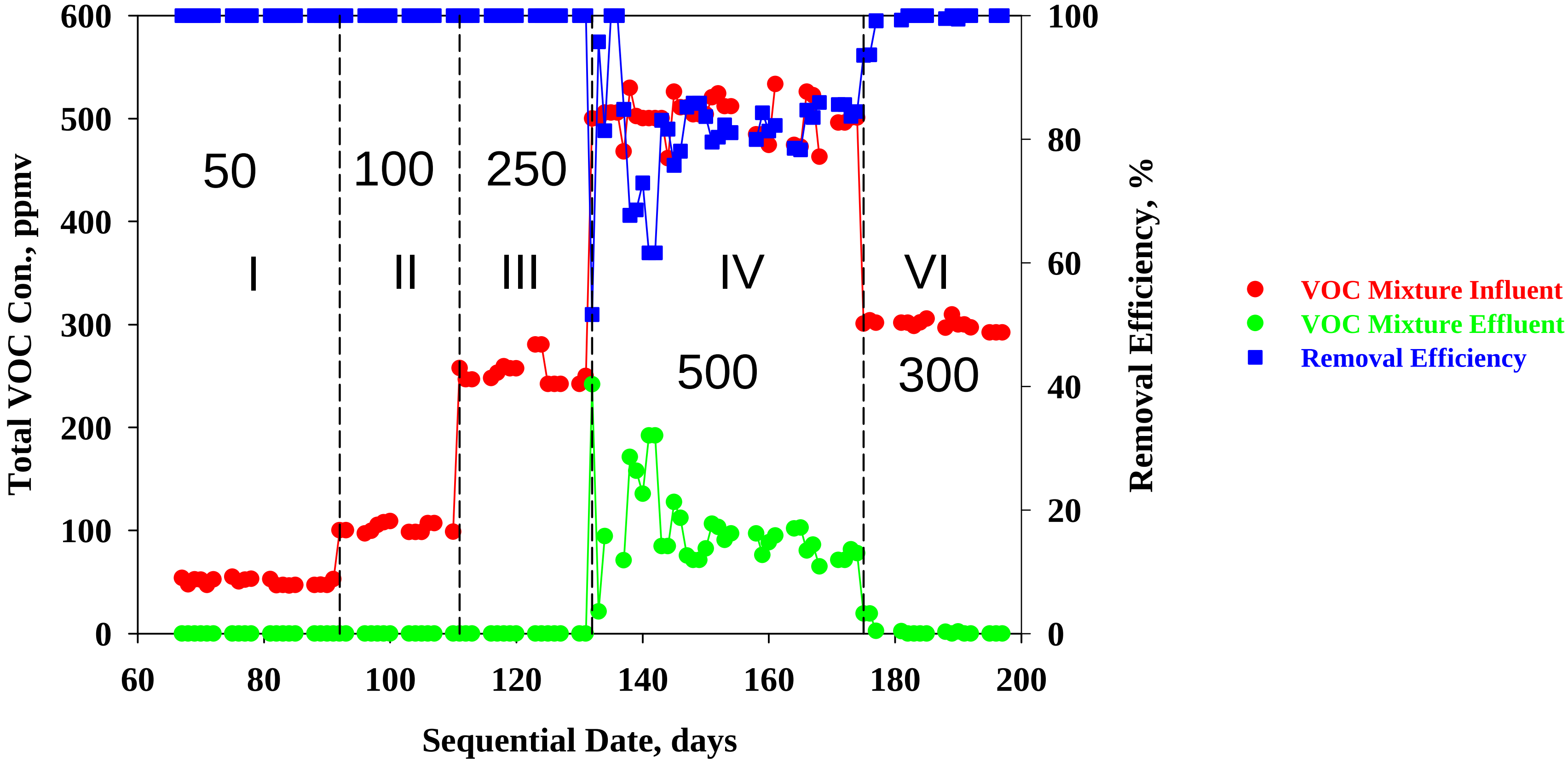
•Results



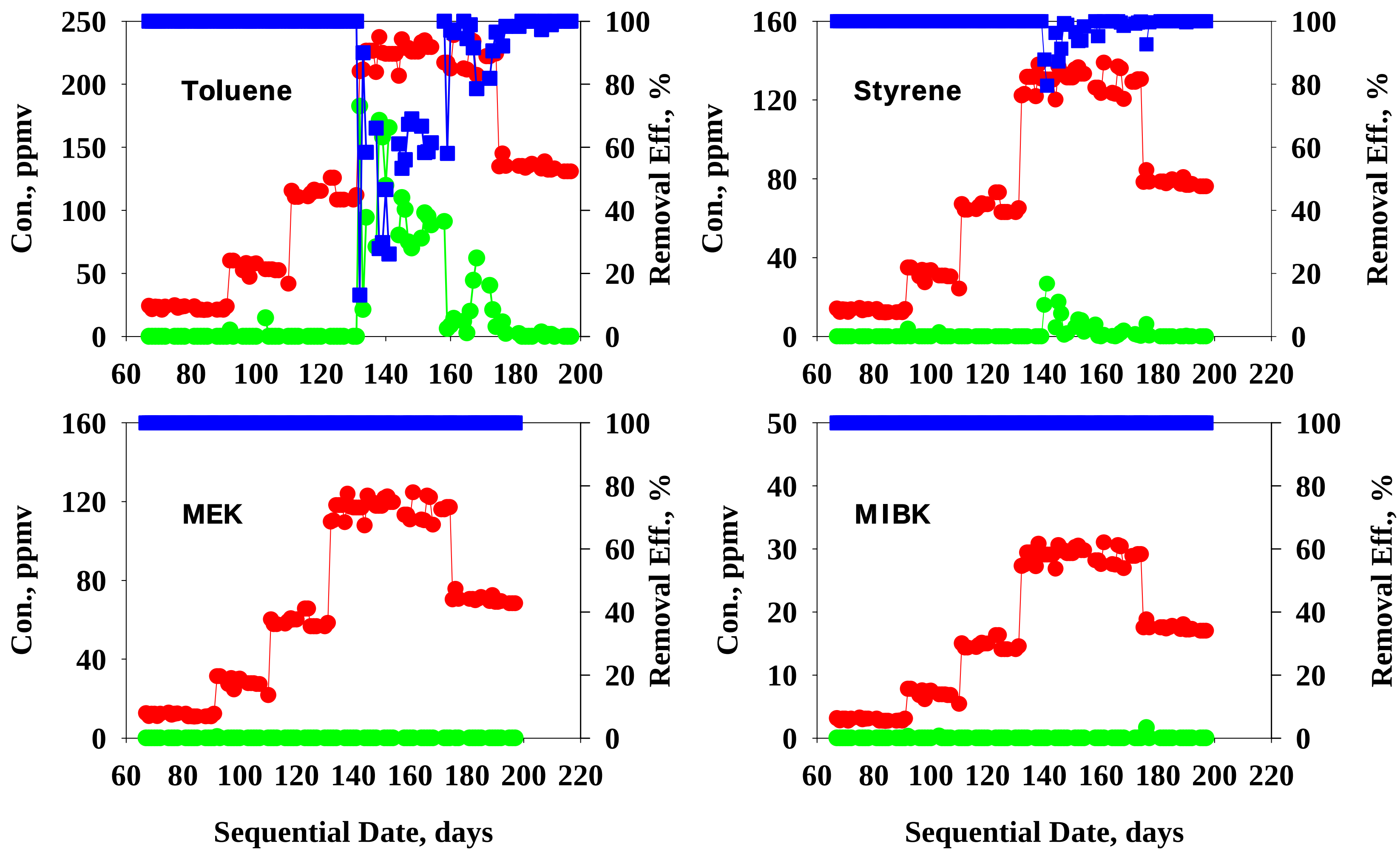
Toluene
Styrene
MEK
MIBK
Conc., ppmv
Conc. ppmv
Removal Efficiency, %
REmoval Efficiency, %
250
200
150
100
50
0
160
120
80
40
0
50
40
30
20
10
100
80
60
40
20
0 7 14 21 28 35 42 49 56 63
Sequential Date, days
Sequential Date, days

•Results

➤ **TBAB performance with respect to VOC removal**

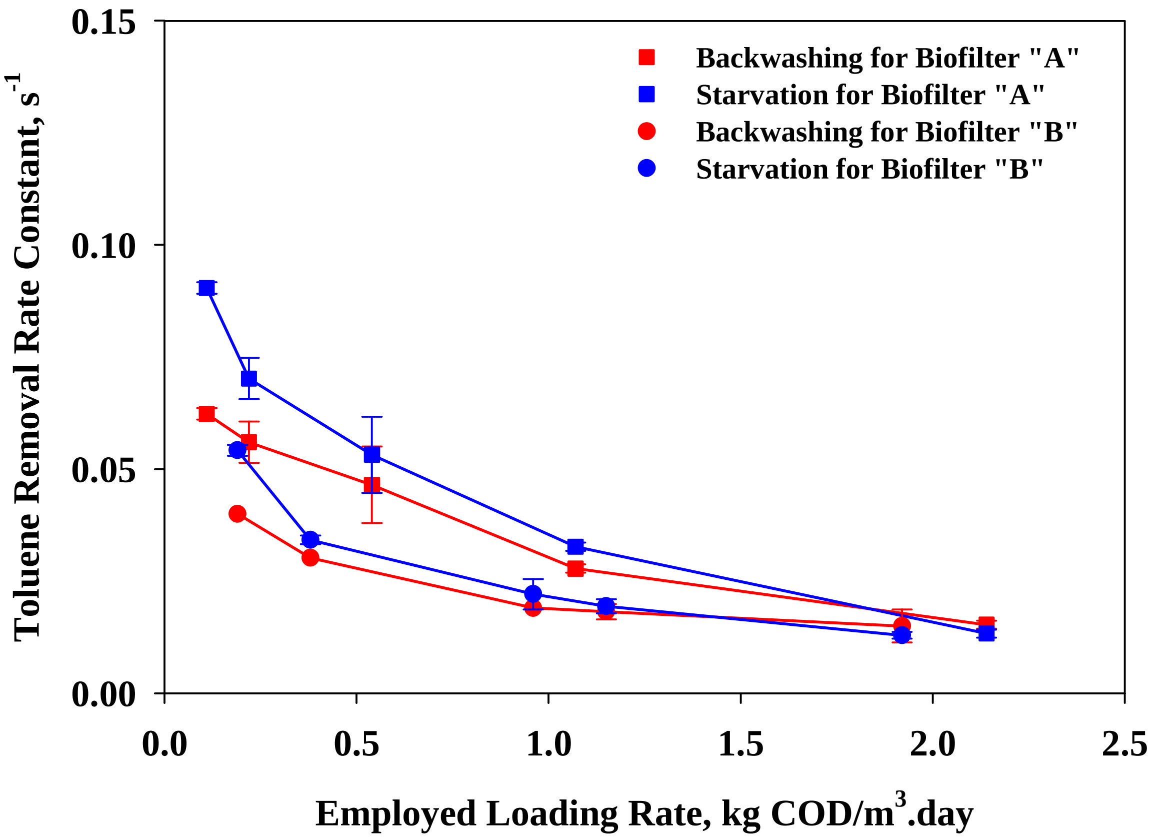


•Results


Toluene
Styrene
MEK
MIBK
Con., ppmv
Removal Eff., %
Sequential Date, days
250
200
150
100
50
0
160
120
80
40
60
80
100
120
140
160
180
200
220
50
40
30
20
10

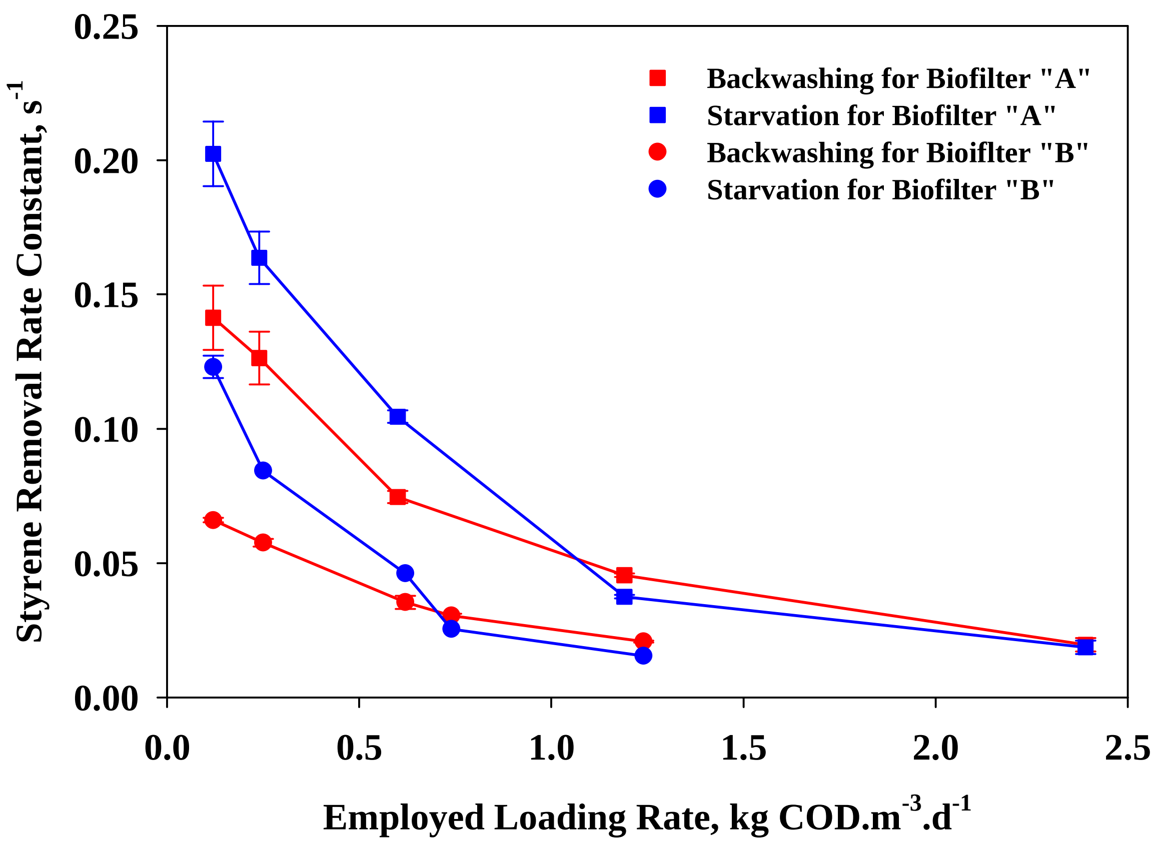
•Results

Toluene



•Results

Styrene



•Conclusions

- Over 99% removal efficiency could be maintained at inlet concentrations up to 500 ppmv for mixture 1 and 300 ppmv for mixture 2 under backwashing operating conditions.

- Starvation operation helped in maintaining high level performance and could be used as another means of biomass control provided the inlet concentration did not exceed 250 ppmv (2.01 kg COD/m3-d) and 300 ppmv for mixture 1 and mixture 2, respectively.

- Re-acclimation was delayed for both mixtures with increase of inlet concentrations. The biofilter performance for mixture 2 required longer time to recover than that mixture 1 due to higher toluene content in mixture 2.

- Toluene content in the mixture played a major role in the biofilter overall performance. The removal efficiency of toluene decreased with increase of content of MEK and MIBK in the mixtures.

- Biofilter depth utilization increased with increase of inlet mixture concentration.

•Phase III

Objective

Characterization of cyclic 2-bed adsorption unit

•Materials and Methods

•Adsorption Unit

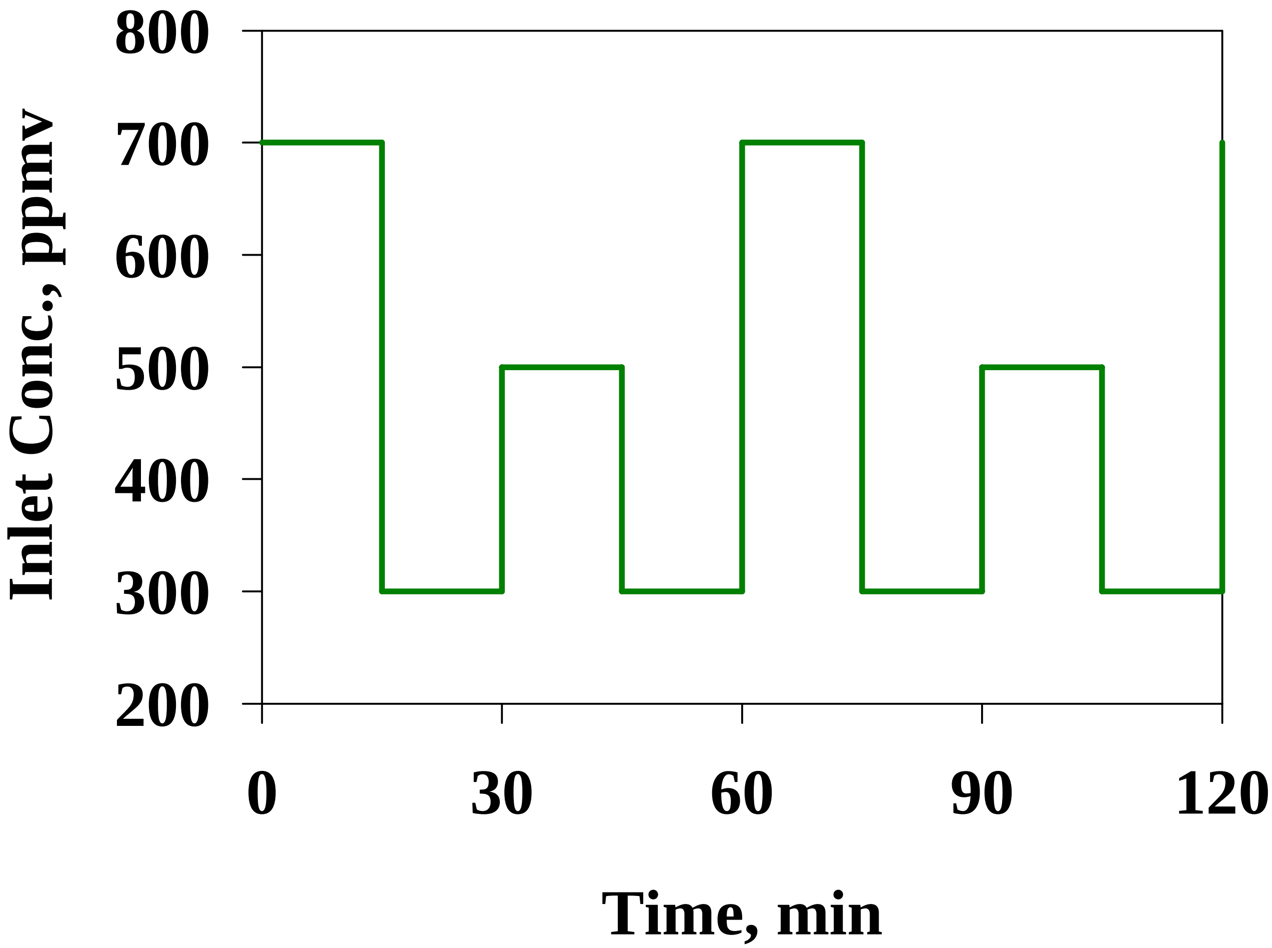
- 2 Beds
- Dimension : 2.5 cm (D) × 20 cm (L)
- Duration of one cycle : 8 hours
- EBRT: 9.1 sec (1.35 L/min)

- Absorbent : GAC (BPL 6 × 16)

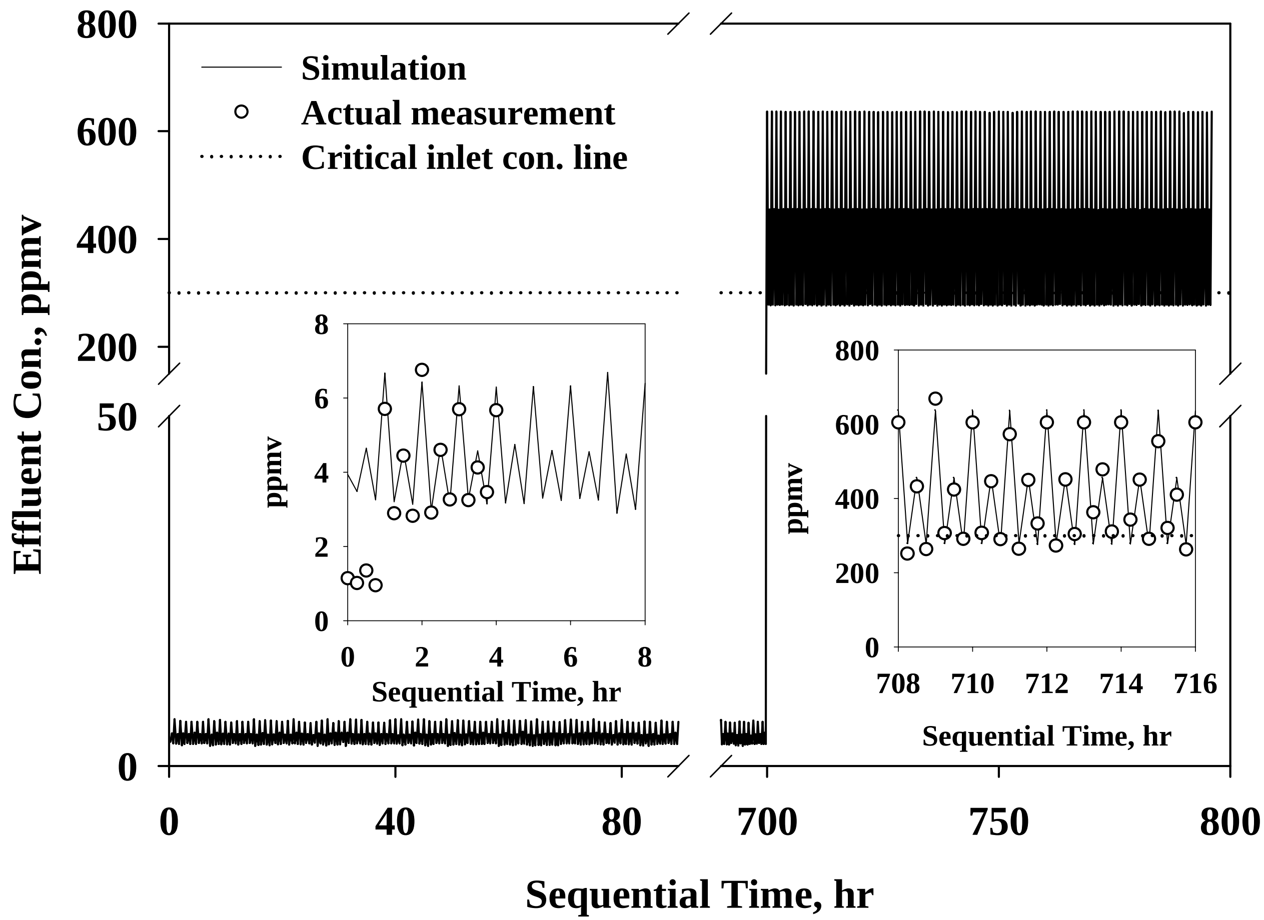
•Materials and Methods

Feeding condition: mixture based on EPA emission report

Toluene: Styrene: MEK: MIBK = 0.448: 0.260: 0.234: 0.058

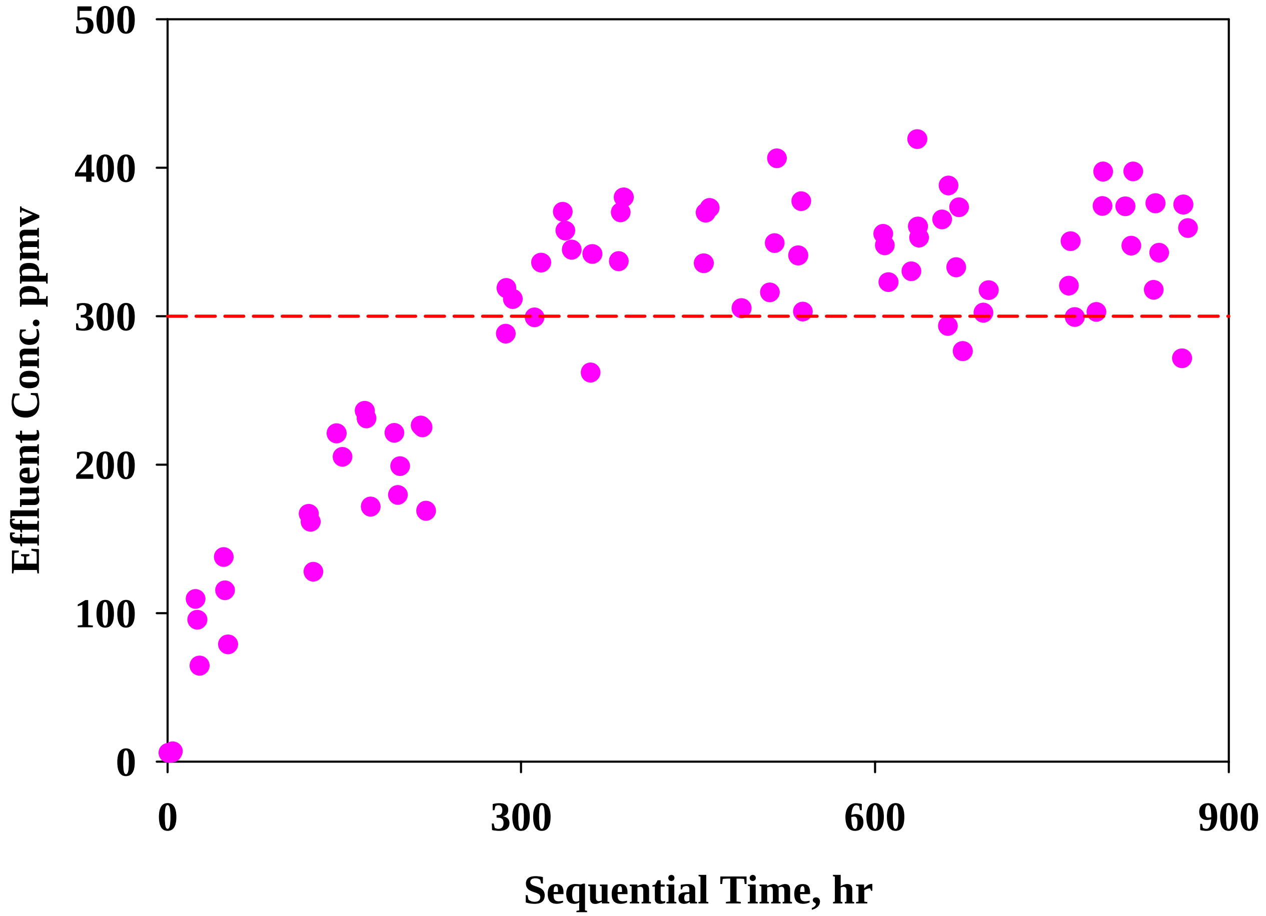


•Results



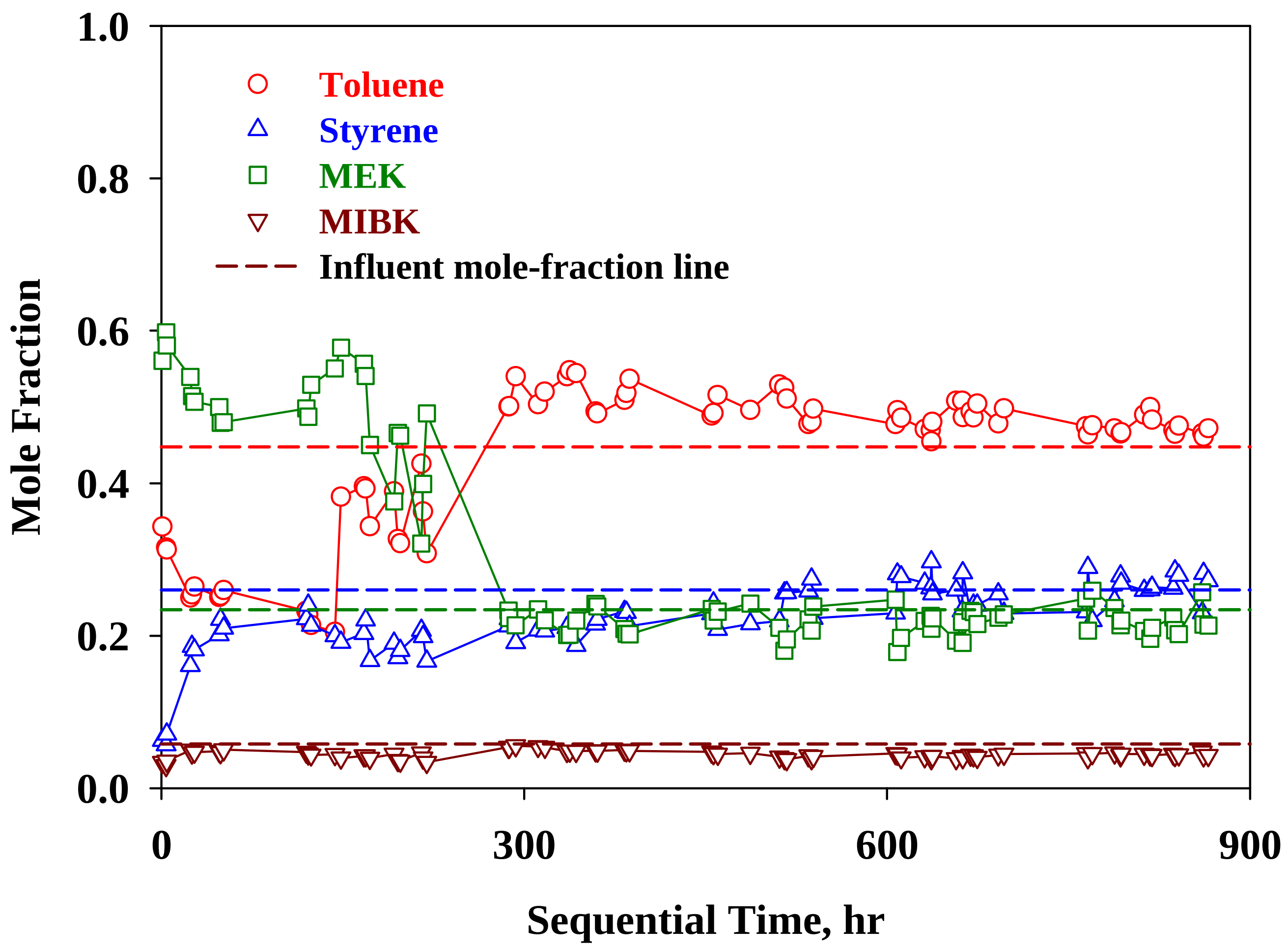
Simulation
Actual measurement
Critical inlet con. line
Effluent Con., ppmv
Sequential Time, hr
800
600
400
200
50
0
40
80
700
750
ppmv
Sequential Time, hr
0
2
4
6
8
ppmv
Sequential Time, hr
708
710
712
714
716

•Results



Effluent Conc. ppmv
500
400
300
200
100
0
0
300
600
900
Sequential Time, hr

•Results



1.0
0.8
0.6
0.4
0.2
0.0
Mole Fraction
Toluene
Styrene
MEK
MIBK
Influent mole-fraction line
0
300
600
900
Sequential Time, hr

•Conclusions

- A single adsorption bed failed to act as a buffering unit to the followed biofilter during the initial acclimation period and also failed to attenuate fluctuation in inlet concentrations after breakthrough.
- The 2-bed adsorption unit with cyclic operation succeeded in providing low effluent that will help the initial acclimation of a followed biofilter and also attenuating significantly the fluctuation in inlet concentration after stabilization.
- Competitive adsorption occurred in the adsorption bed for the different components in the mixture due to their differences in physicochemical properties.

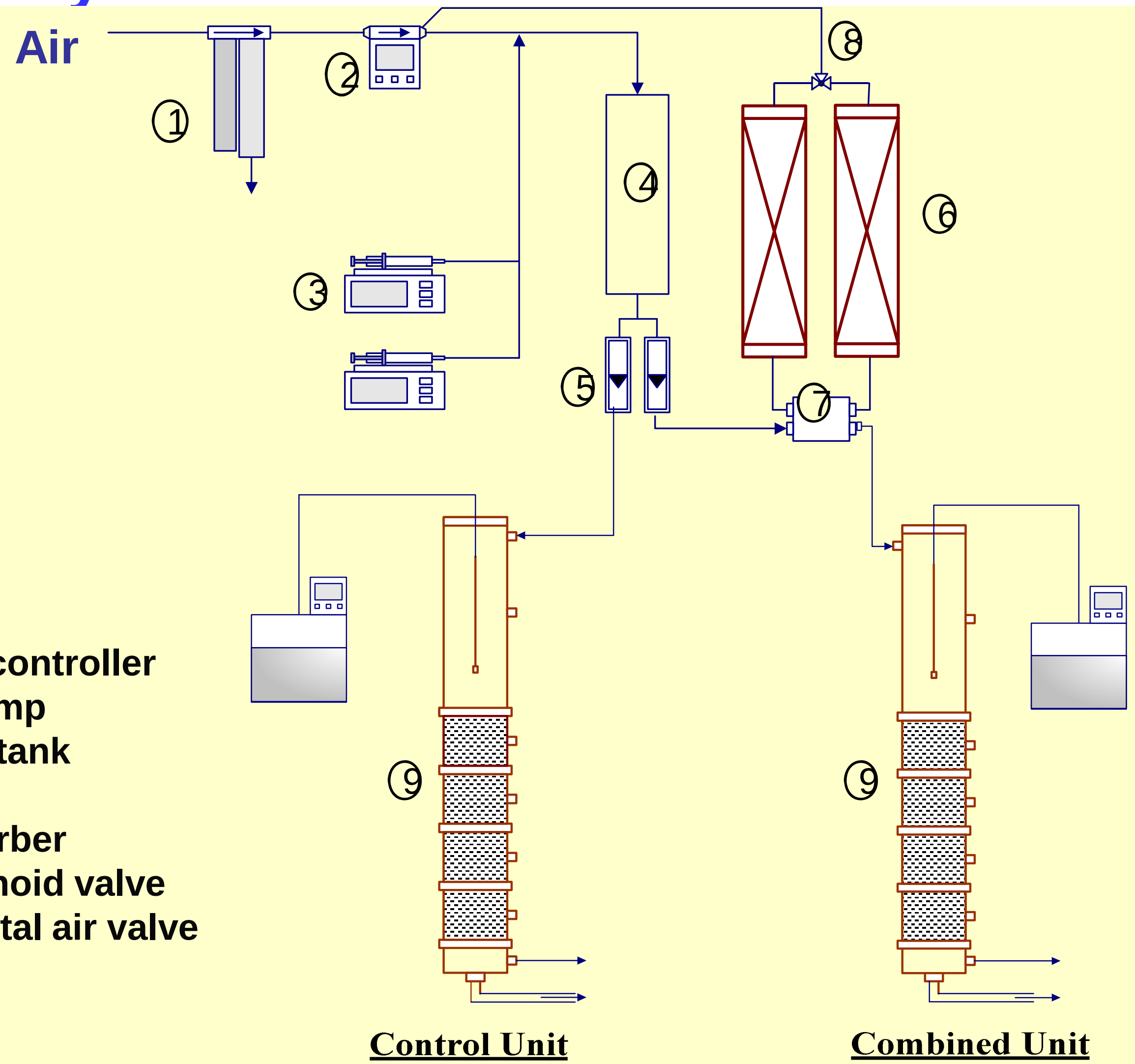
•Phase IV

Objective

Application of the integrated system on removal of VOC mixture

•Materials and Methods

➢ Combined system for VOCs mixture



1. Air cleaner
2. Mass flow controller
3. Syringe pump
4. Equalizing tank
5. Flow meter
6. 2-bed adsorber
7. 4-way solenoid valve
8. Supplemental air valve
9. Biofilter

•Materials and Methods

➢Operating conditions

Square Wave Change
- Base = 250 ppmv
- Peak = 700 ppmv (7 mins / hour)
- Average concentration : 300 ppmv

Square Wave Change
- Base = 250 ppmv
- Peak = 500 ppmv (12 mins / hour)
- Average concentration : 300 ppmv

Square Wave Change
- Base = 250 ppmv
- Peak = 500 ppmv (2 ×12 mins / hr)
- Average concentration : 350 ppmv

Square Wave Change
- Base = 300 ppmv
- Middle = 500 ppmv (15 mins/hour)
- Peak = 700 ppmv (15 mins / hour)
- Average concentration : 450 ppmv

•Materials and Methods

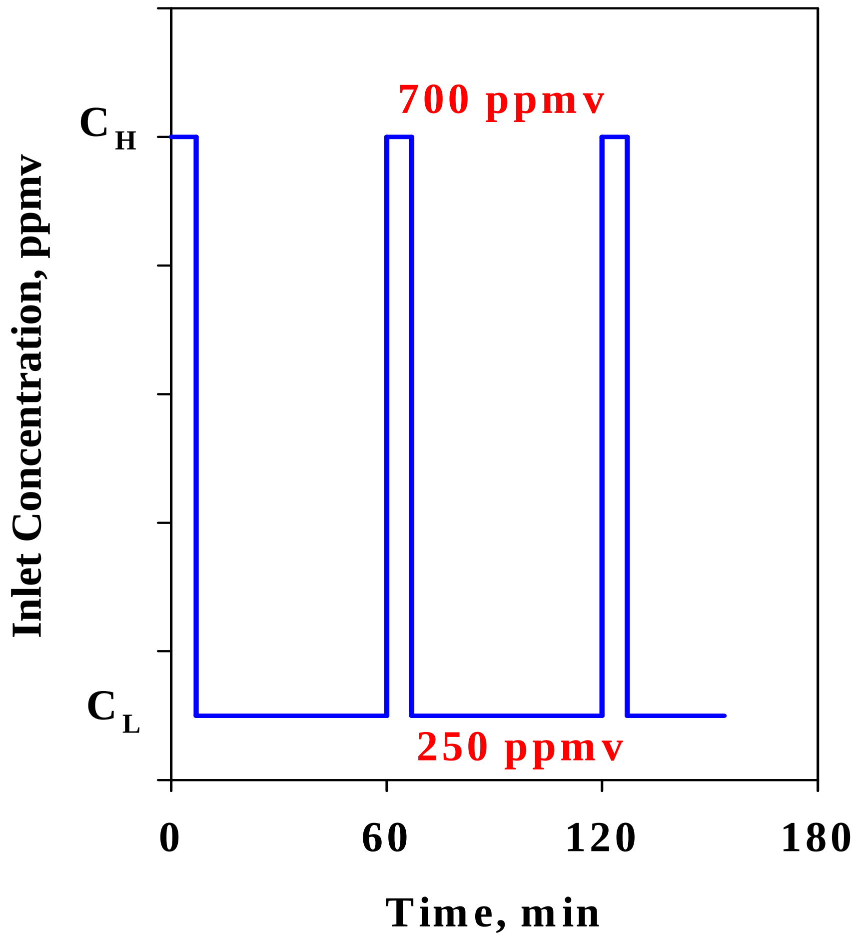
- Air flow: 1.35L/min (EBRT: 2.02 min)

- Biomass control
  - Backwashing : 1 hour of duration / week
  - Starvation: two days / week

•Results

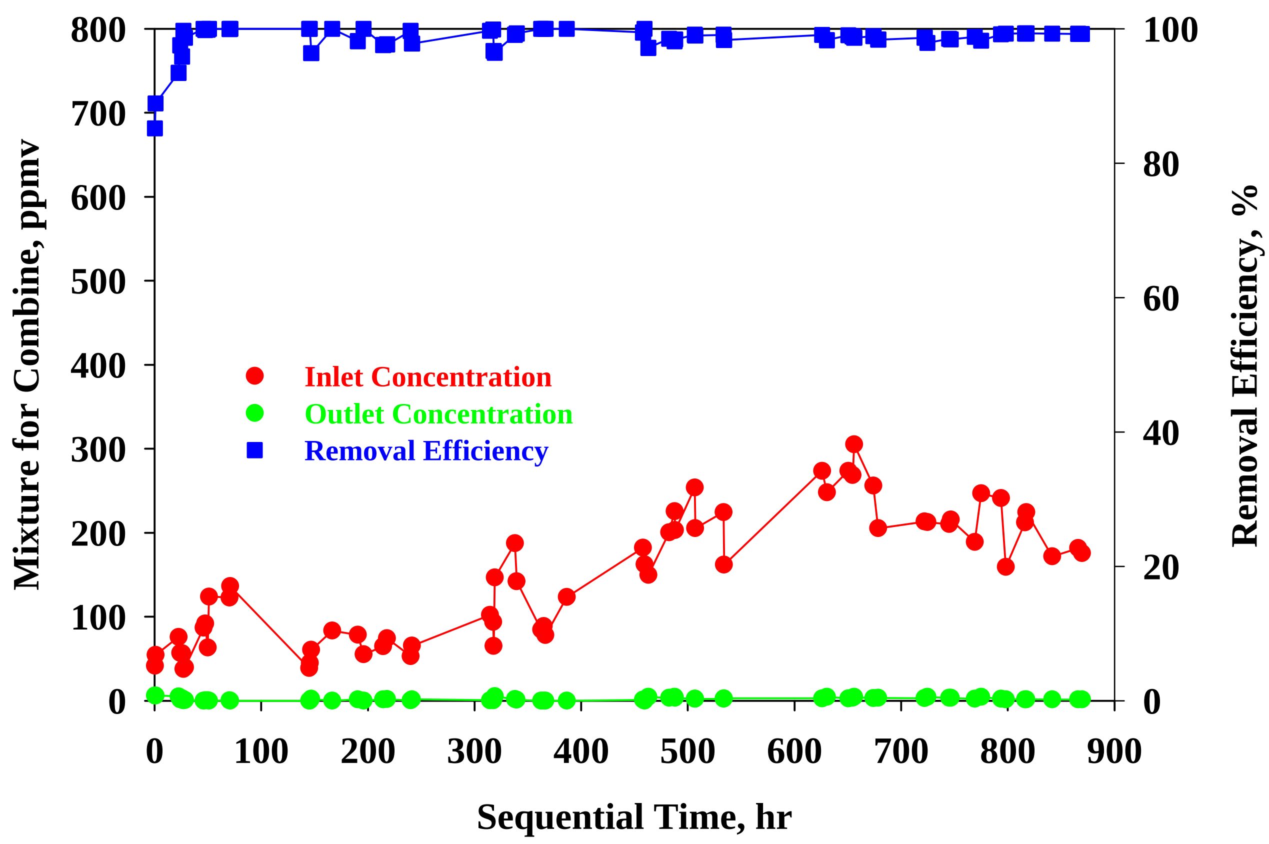
Square Wave Change

- Base = 250 ppmv
- Peak = 700 ppmv (7 mins / hour)
- Average concentration : 300 ppmv
- Average Total Loading = 34.0 g/m^3.hr
- Toluene Loading = 15.4 g/m^3.hr
- Styrene Loading = 10.1 g/m^3.hr
- MEK Loading = 6.3 g/m^3.hr
- MIBK Loading = 2.2 g/m^3.hr

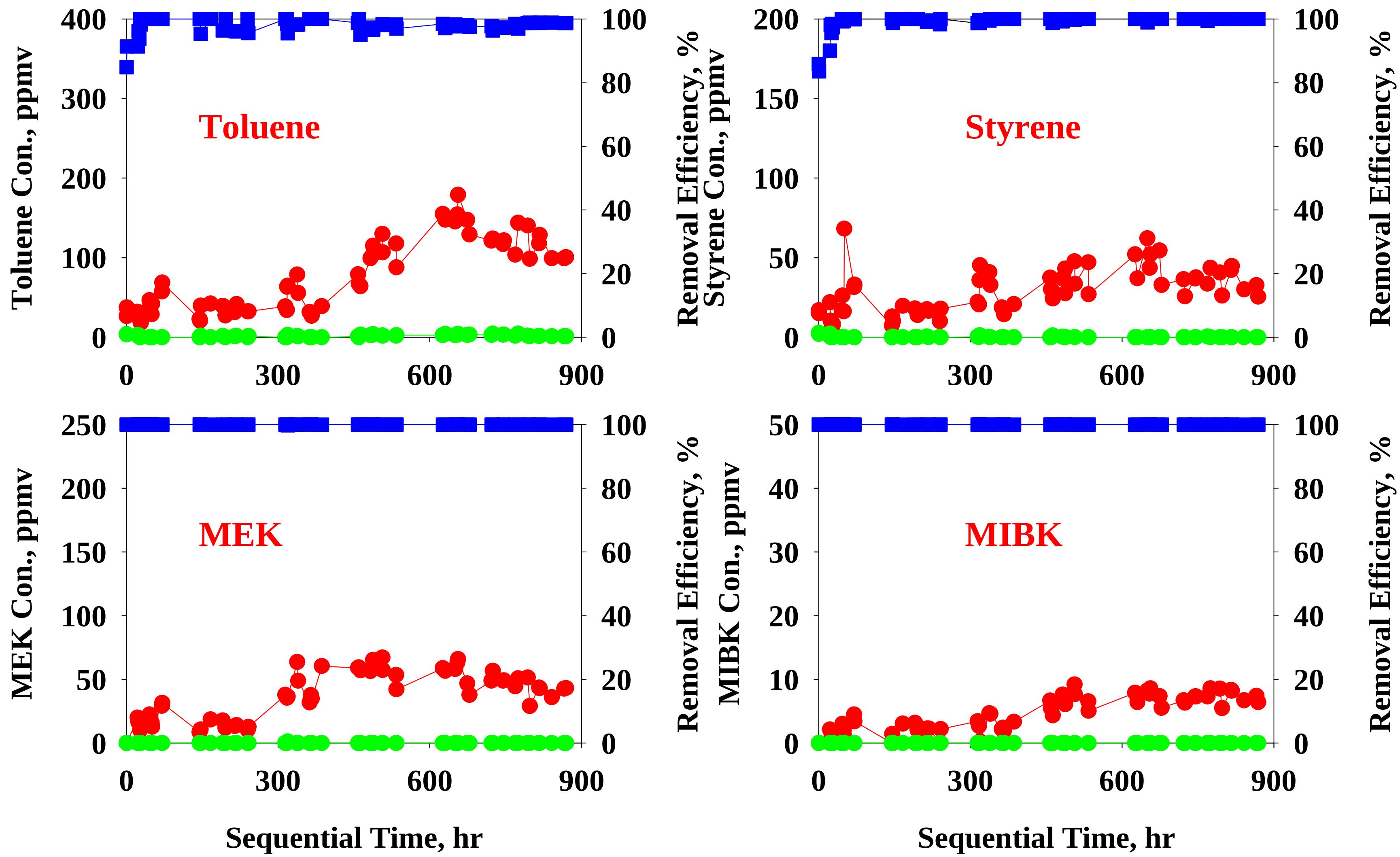


•Results

Biofilter Performance in Combined System



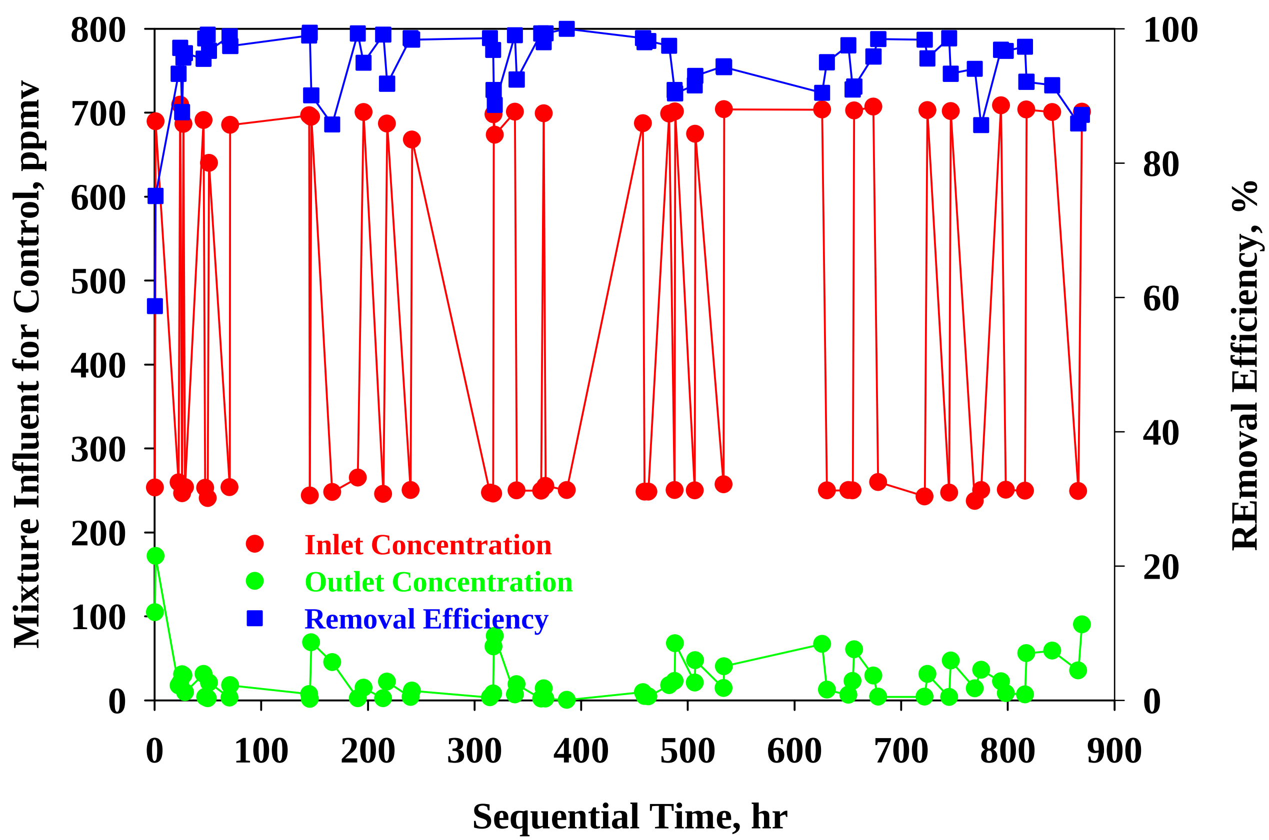
•Results



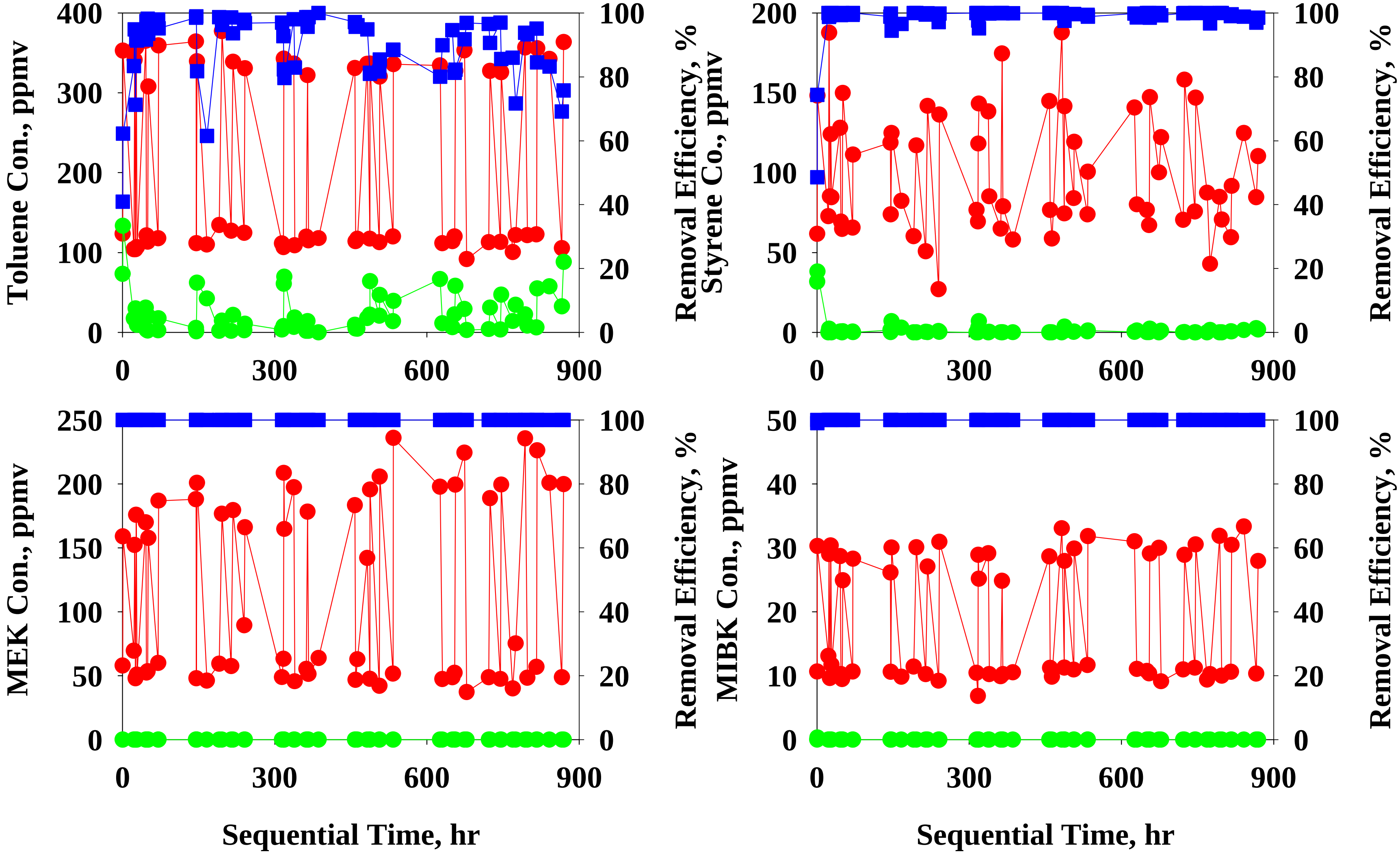
Toluene
Toluene Con., ppmv
Removal Efficiency, %
400
300
200
100
0
100
80
60
40
20
0
0
300
600
900
Styrene
Styrene Con., ppmv
Removal Efficiency, %
200
150
100
50
0
100
80
60
40
20
0
0
300
600
900
MEK
MEK Con., ppmv
Removal Efficiency, %
250
200
150
100
50
0
100
80
60
40
20
0
0
300
600
900
Sequential Time, hr
MIBK
MIBK Con., ppmv
Removal Efficiency, %
50
40
30
20
10
0
100
80
60
40
20
0
0
300
600
900
Sequential Time, hr

•Results

Biofilter Performance in Control System

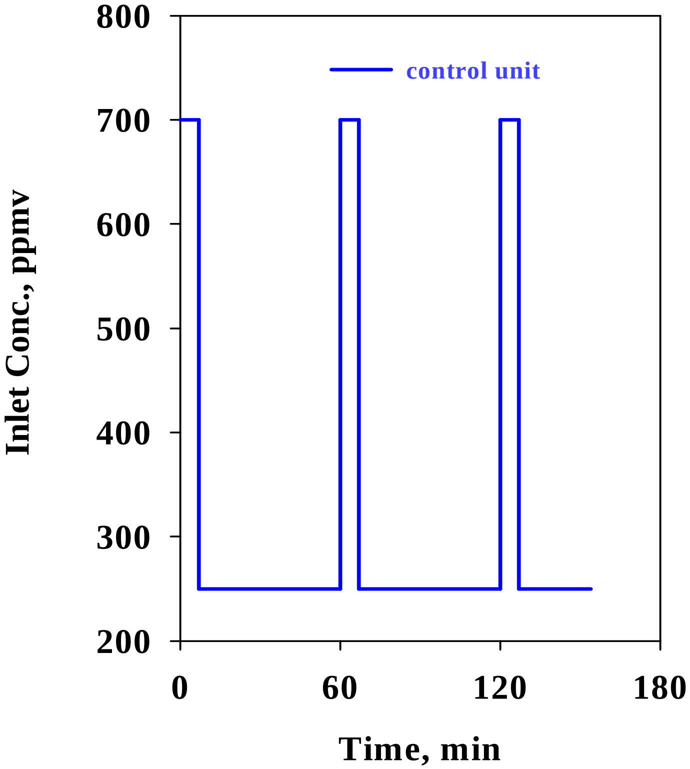


•Results

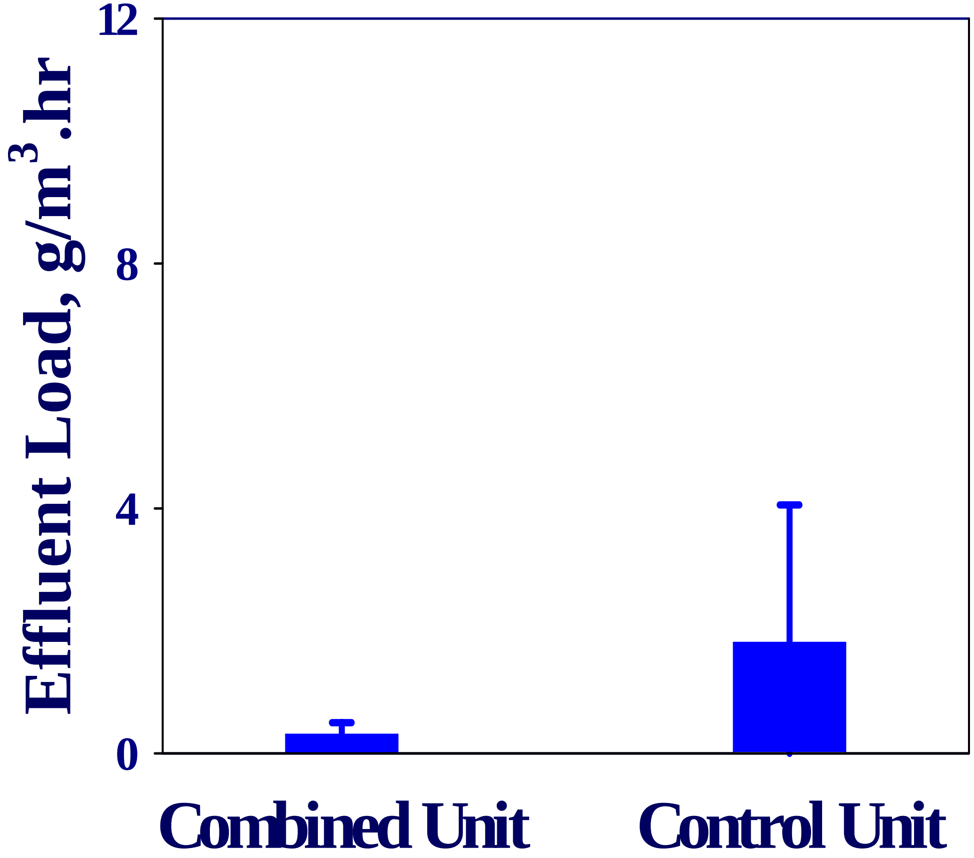


Toluene Con., ppmv
Removal Efficiency, %
Styrene Co., ppmv
Removal Efficiency, %
MEK Con., ppmv
Removal Efficiency, %
MIBK Con., ppmv
Removal Efficiency, %
Sequential Time, hr
Sequential Time, hr

•Results



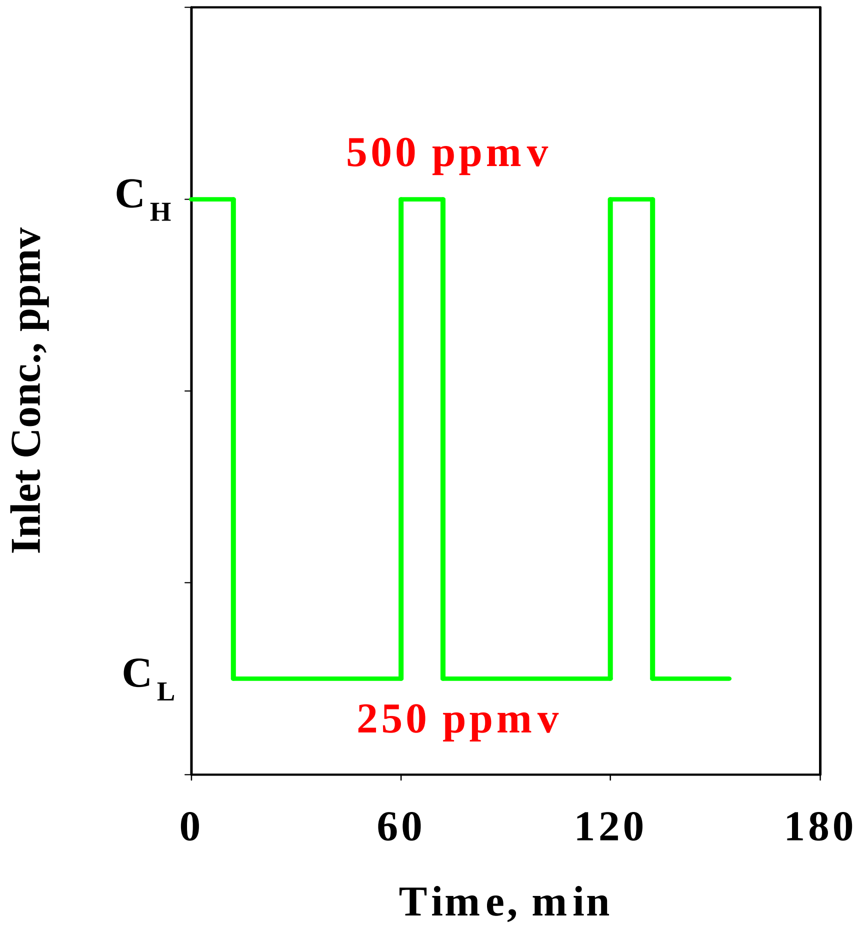
Combined	Ave	SD
ppmv	204.4	30.8



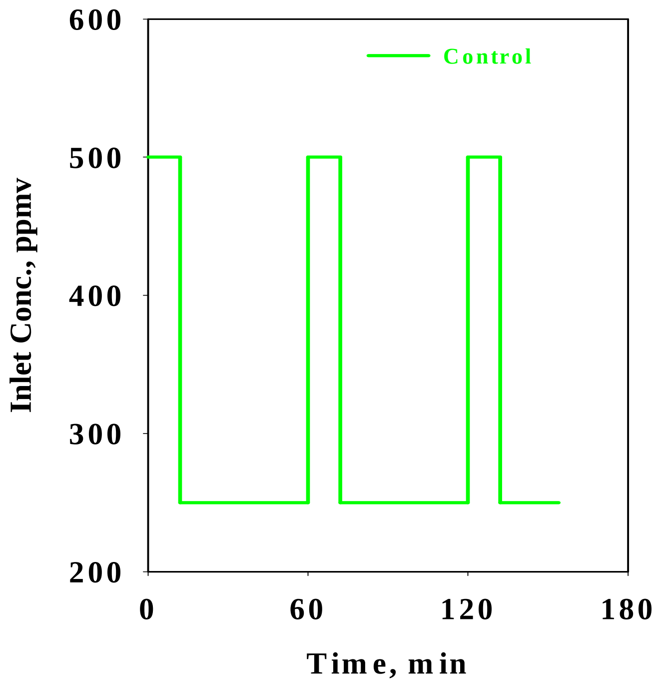
•Results

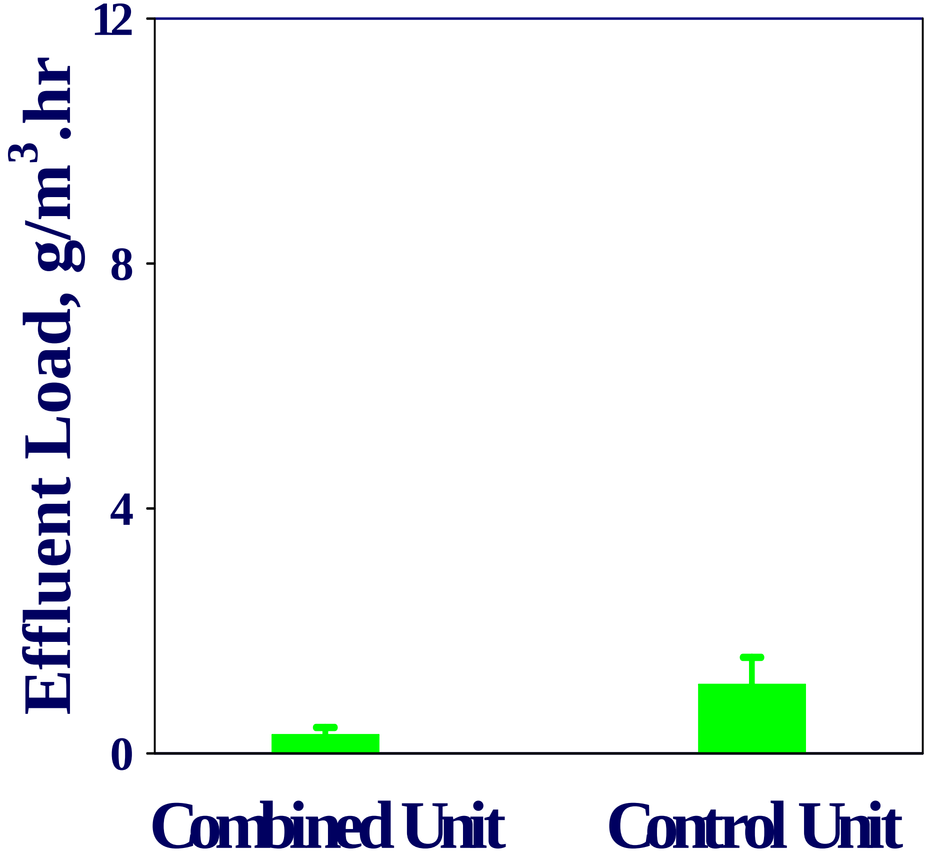
Square Wave Change

- Base = 250 ppmv
- Peak = 500 ppmv (12 mins / hour)
- Average concentration : 300 ppmv
- Average Total Loading = 34.0 g/m^3.hr
- Toluene Loading = 15.4 g/m^3.hr
- Styrene Loading = 10.1 g/m^3.hr
- MEK Loading = 6.3 g/m^3.hr
- MIBK Loading = 2.2 g/m^3.hr



•Results



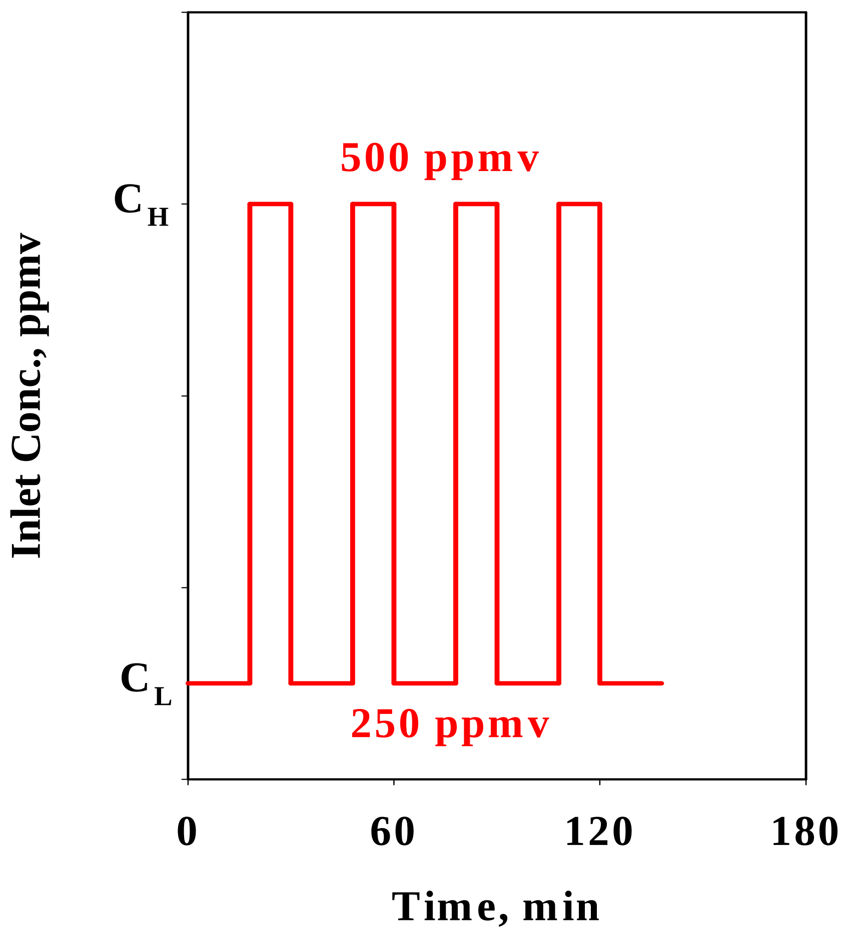


Combined	Ave	SD
ppmv	188.6	19.2

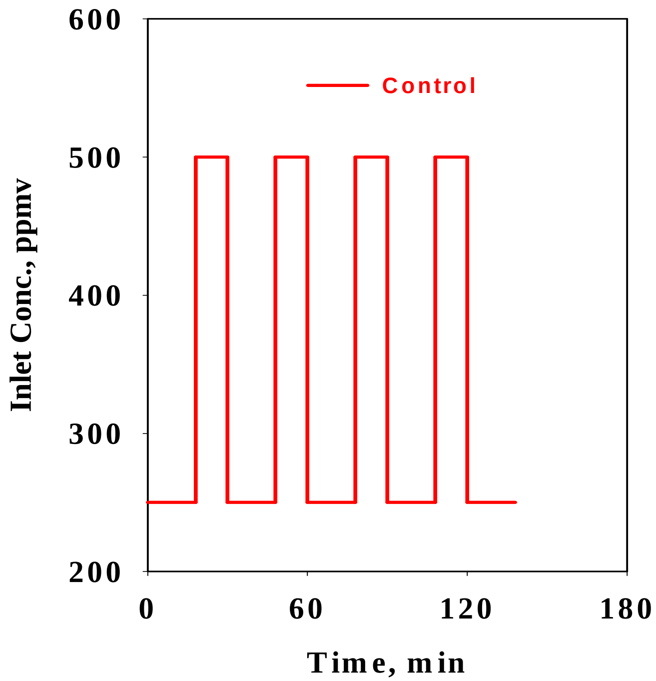
•Results

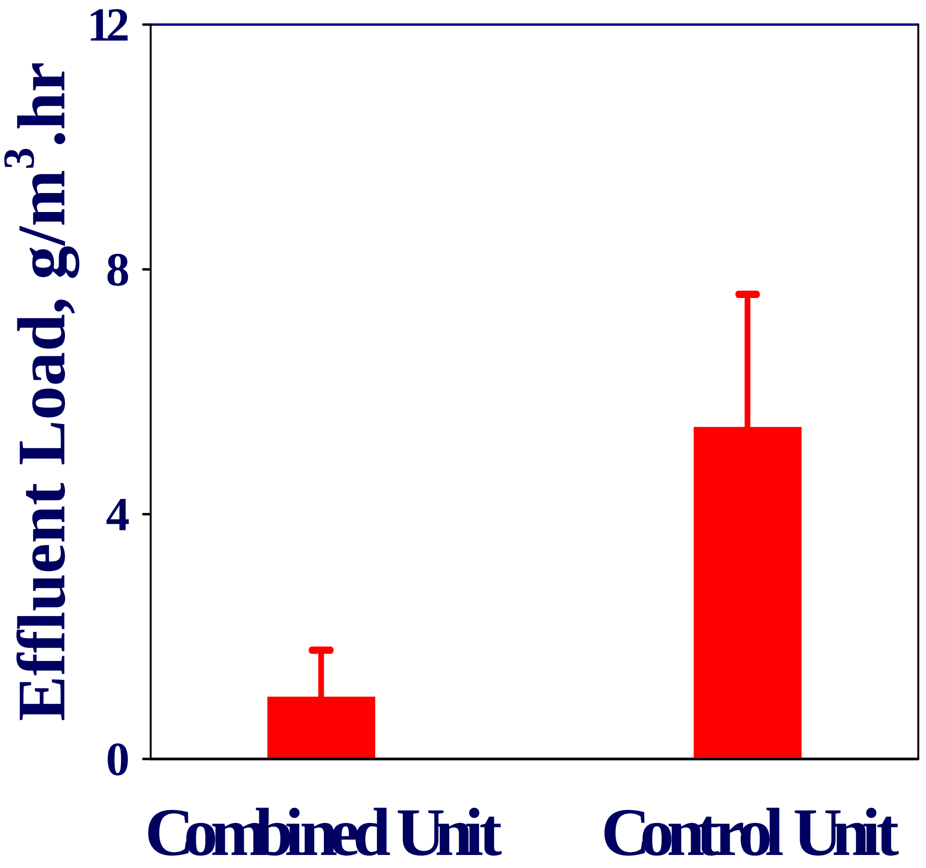
Square Wave Change

- Base = 250 ppmv
- Peak = 500 ppmv (2 × 12 mins / hr)
- Average concentration : 350 ppmv
- Average Total Loading = 39.6 g/m^3.hr
- Toluene Loading = 17.9 g/m^3.hr
- Styrene Loading = 11.8 g/m^3.hr
- MEK Loading = 7.4 g/m^3.hr
- MIBK Loading = 2.5 g/m^3.hr



•Results



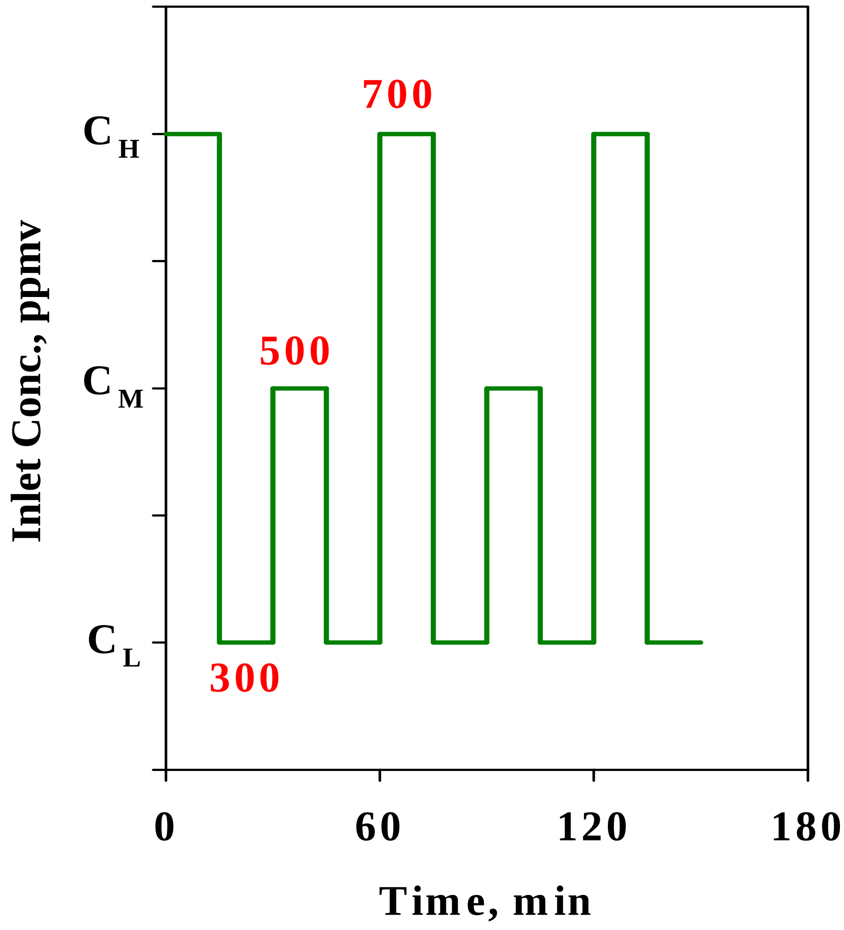


Combined	Ave	SD
ppmv	230.1	25.2

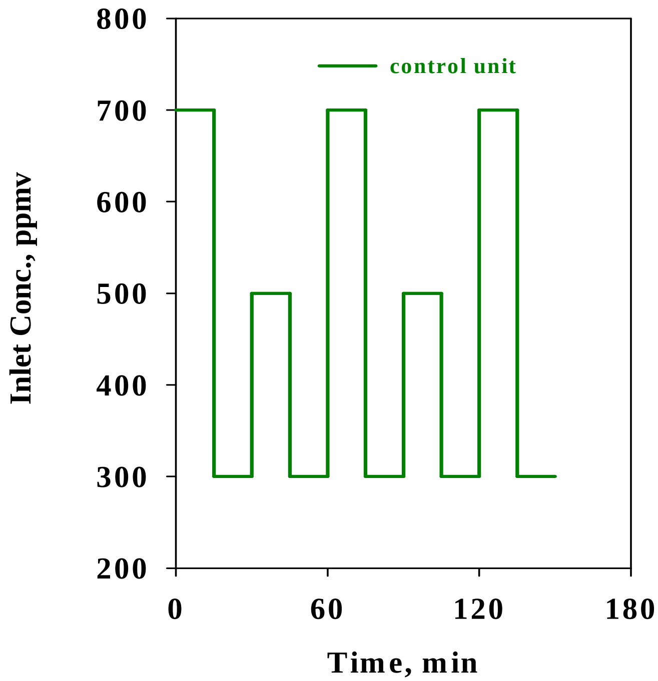
•Results

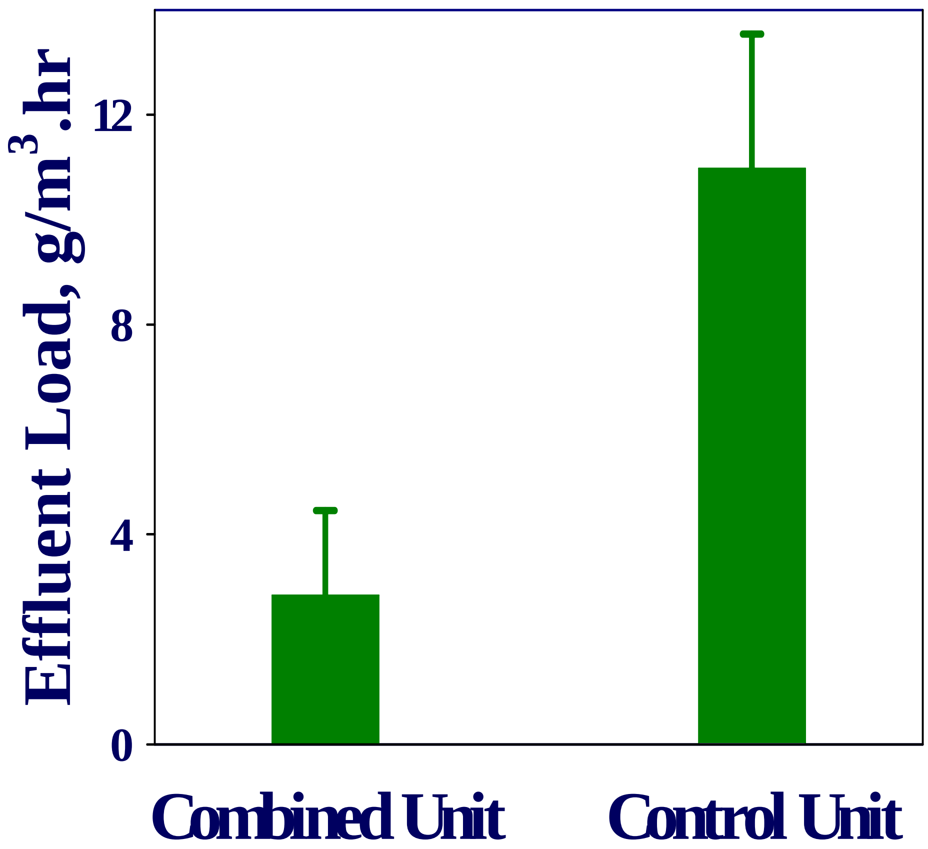
Square Wave Change

- Base = 250 ppmv
- Middle = 500 ppmv (15 mins/hour)
- Peak = 700 ppmv (15 mins / hour)
- Average concentration : 450 ppmv
- Average Loading = 50.9 g/m^3.hr
- Toluene Loading = 23.0 g/m3.hr
- Styrene Loading = 15.1 g/m3.hr
- MEK Loading = 9.5 g/m3.hr
- MIBK Loading = 3.3 g/m3.hr



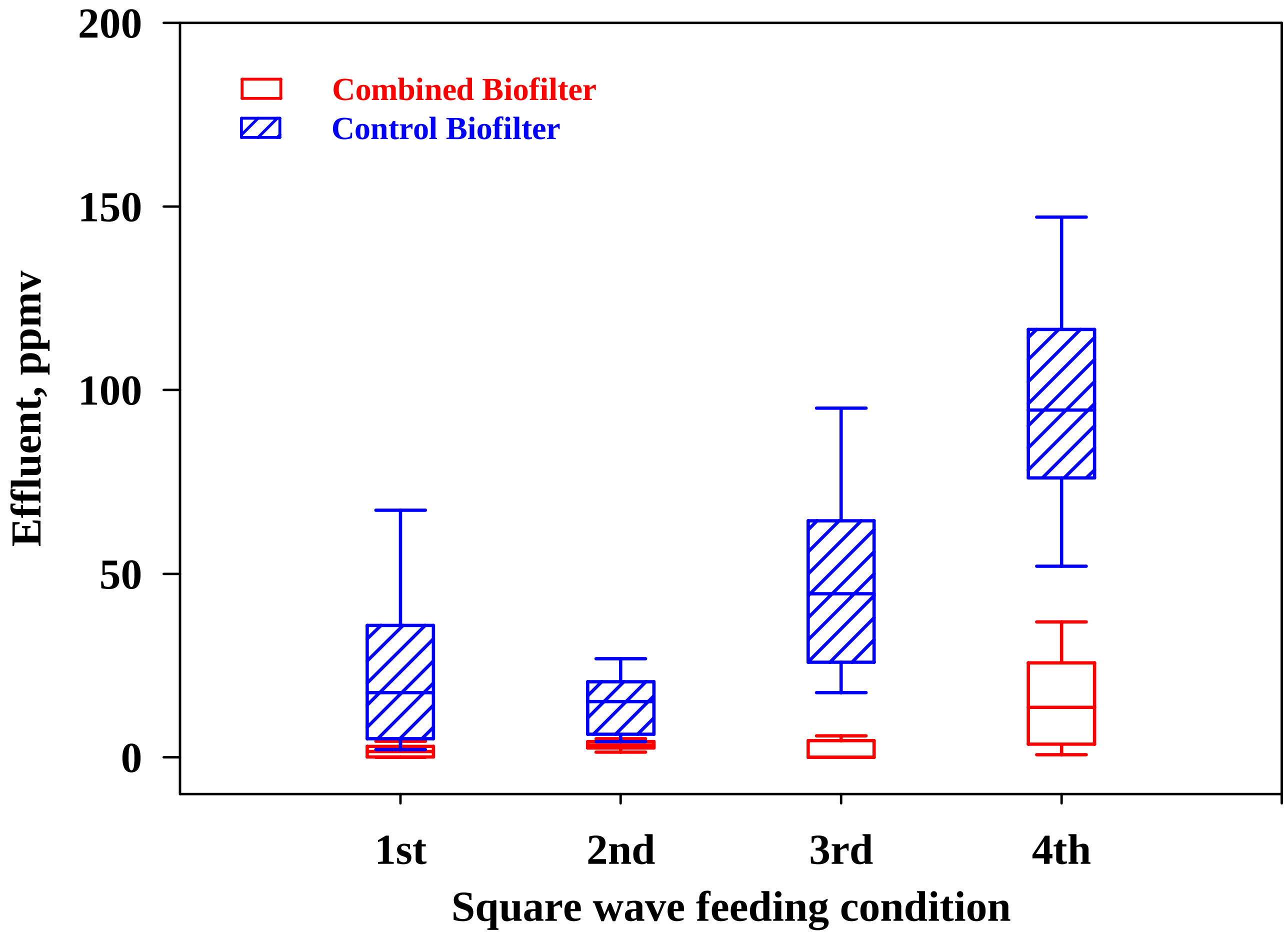
•Results





Combined	Ave	SD
ppmv	338.1	21.2

•Results

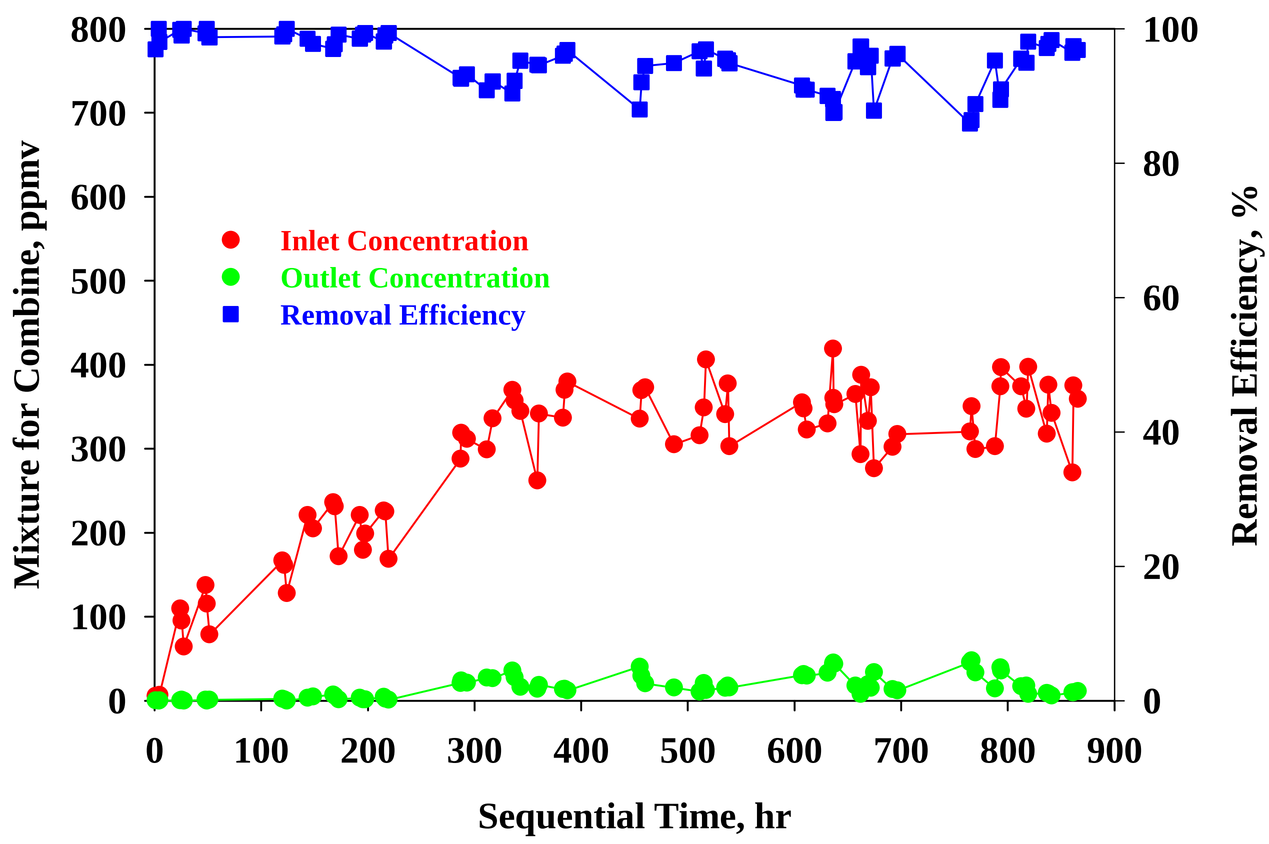


Combined Biofilter
Control Biofilter
200
150
100
50
0
Effluent, ppmv
1st
2nd
3rd
4th
Square wave feeding condition

• Results

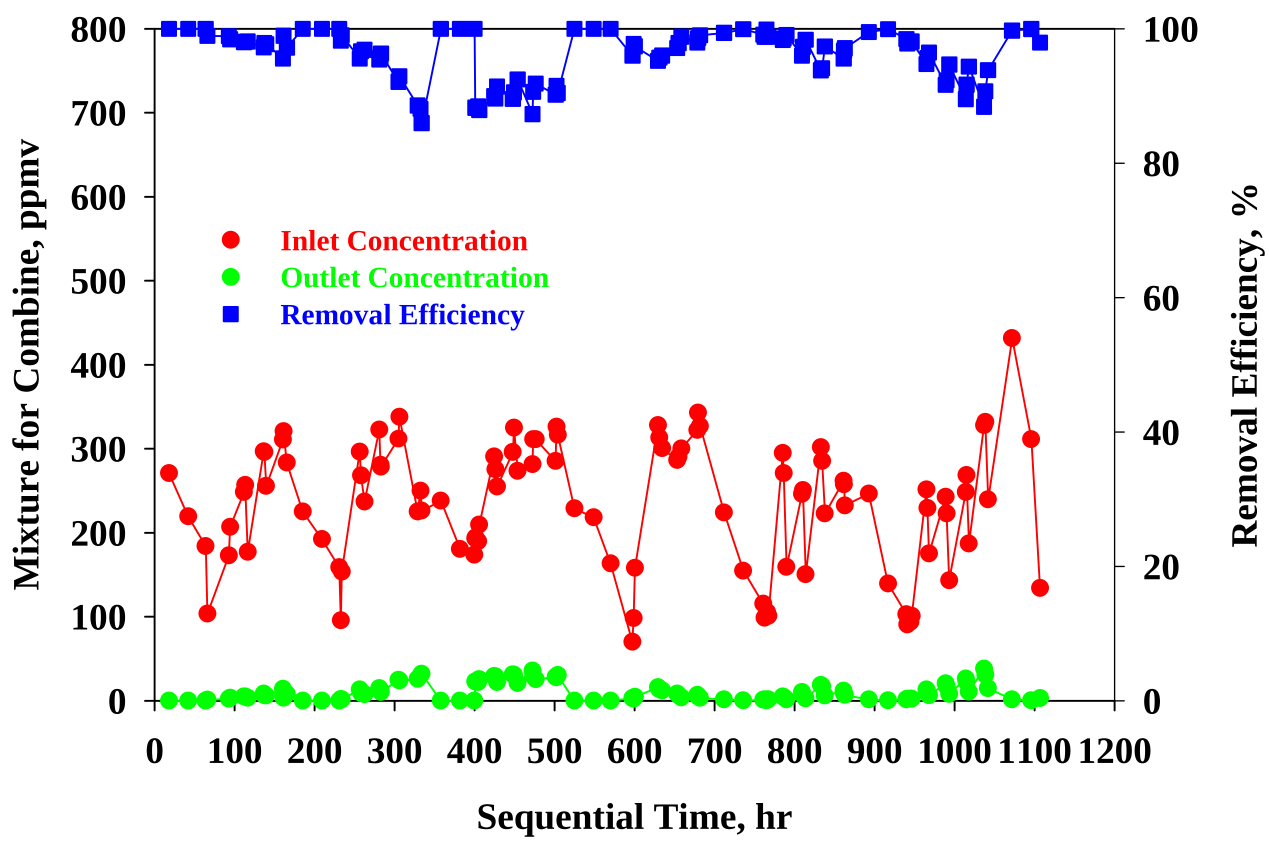
•Results

Biofilter Performance in Combined System-Backwashing



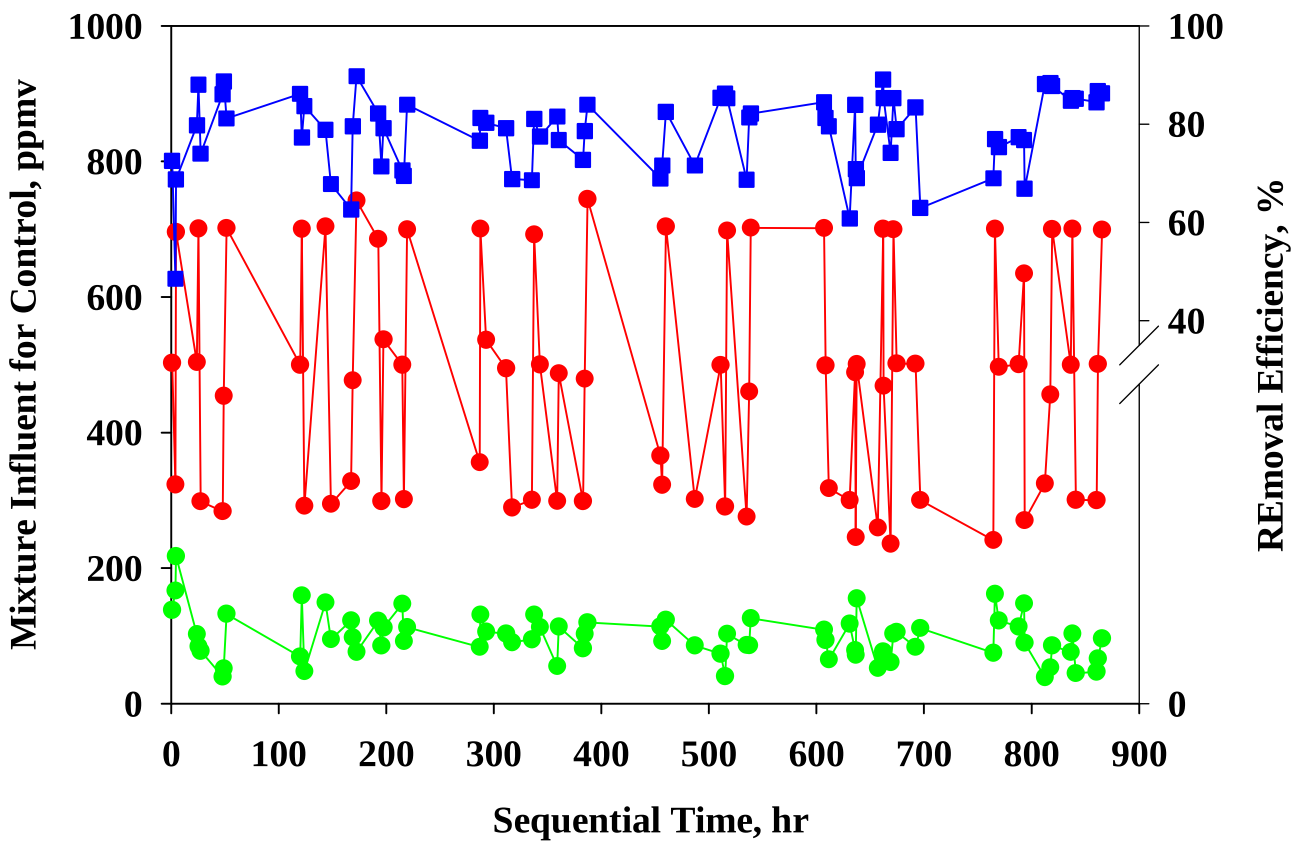
•Results

Biofilter Performance in Combined System-Starvation



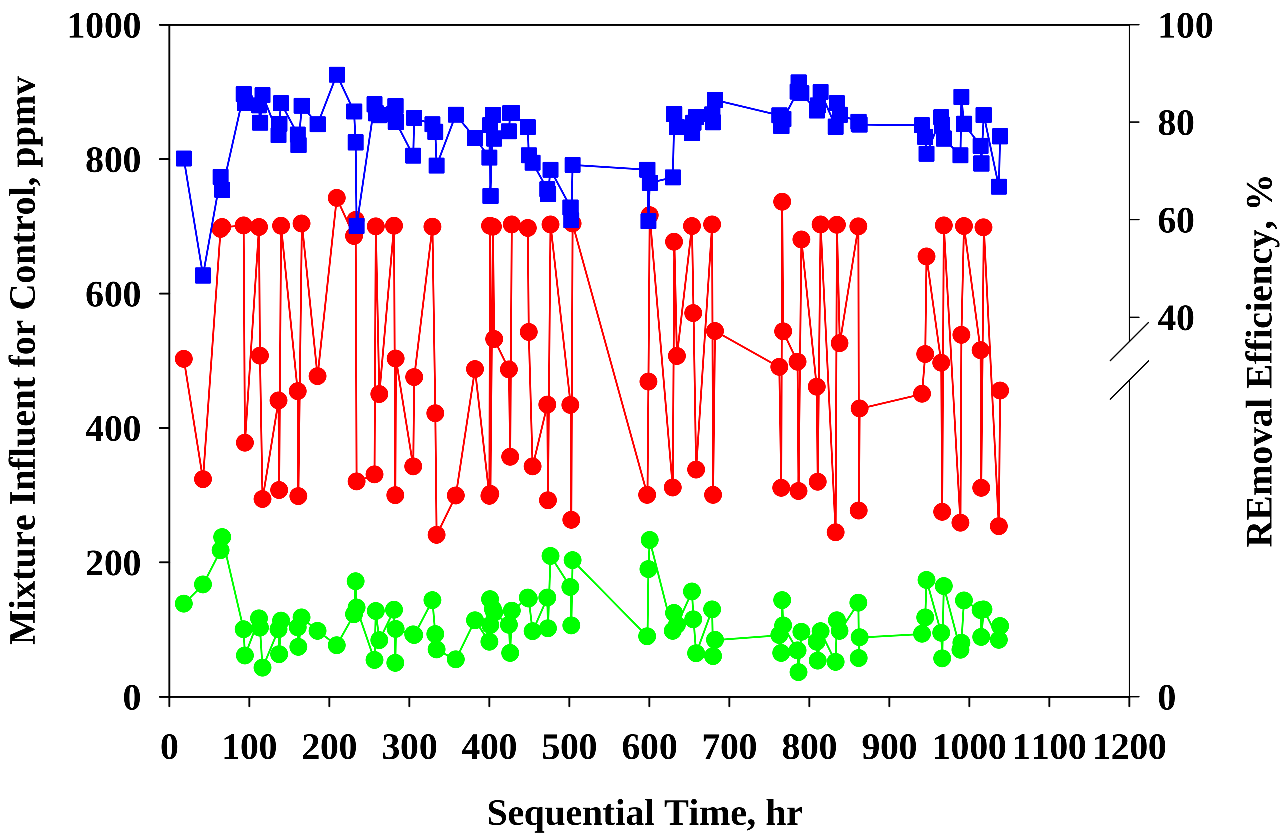
•Results

Biofilter Performance in Control System-Backwashing



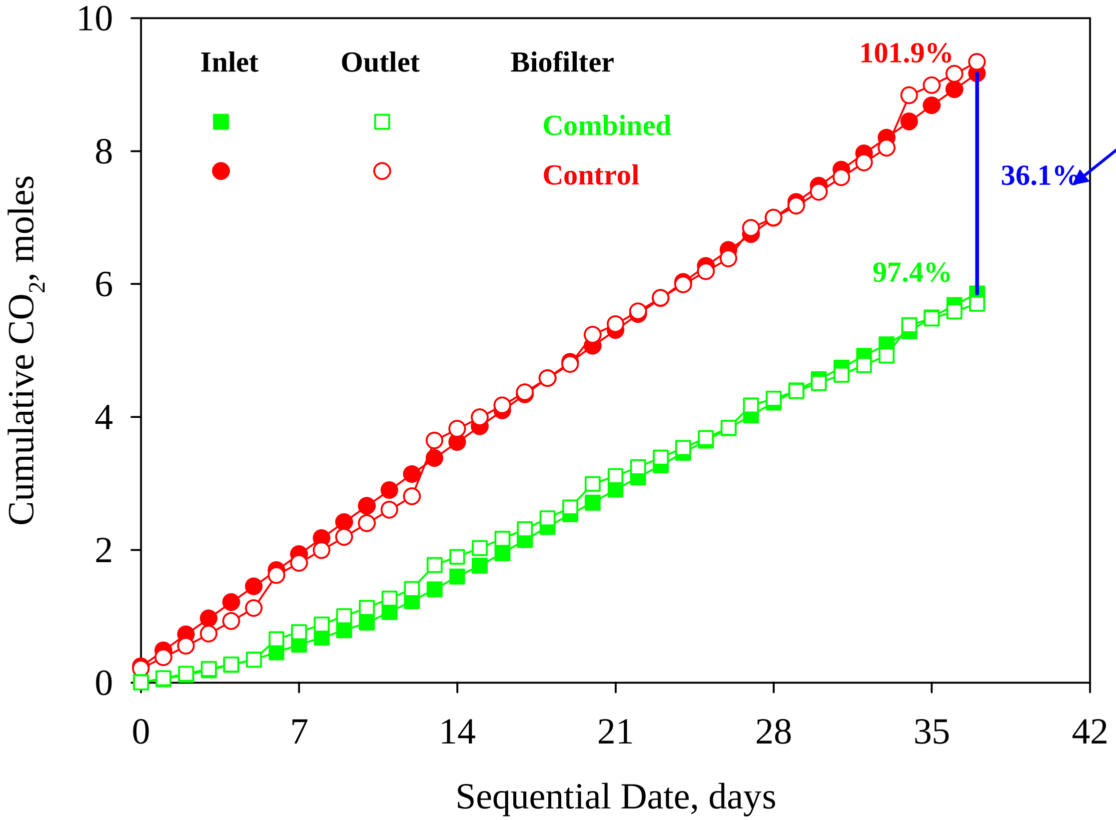
•Results

Biofilter Performance in Control System-Starvation



•Results

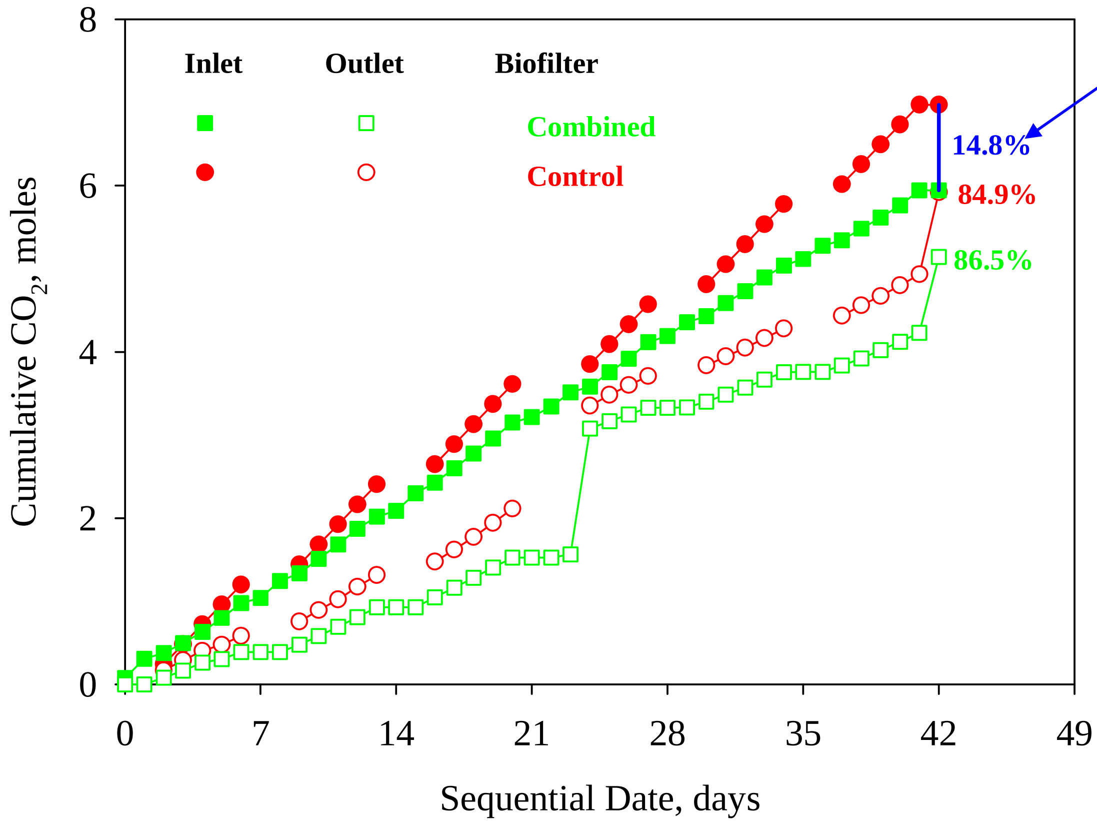
Carbon Mass Balance for Backwashing



Carbon accumulation in the two beds

•Results

Carbon Mass Balance for Starvation

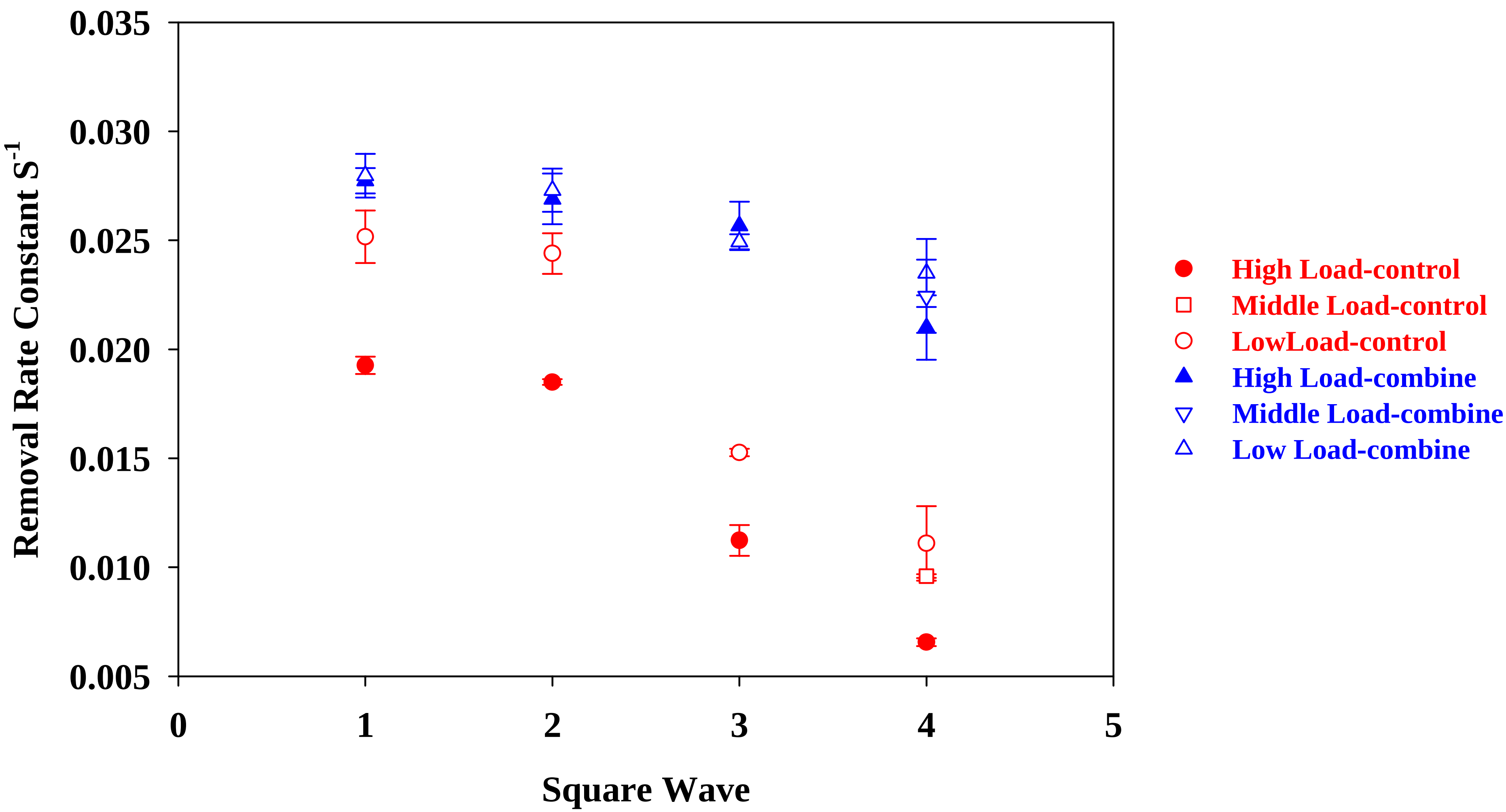


Carbon accumulation

in the two beds

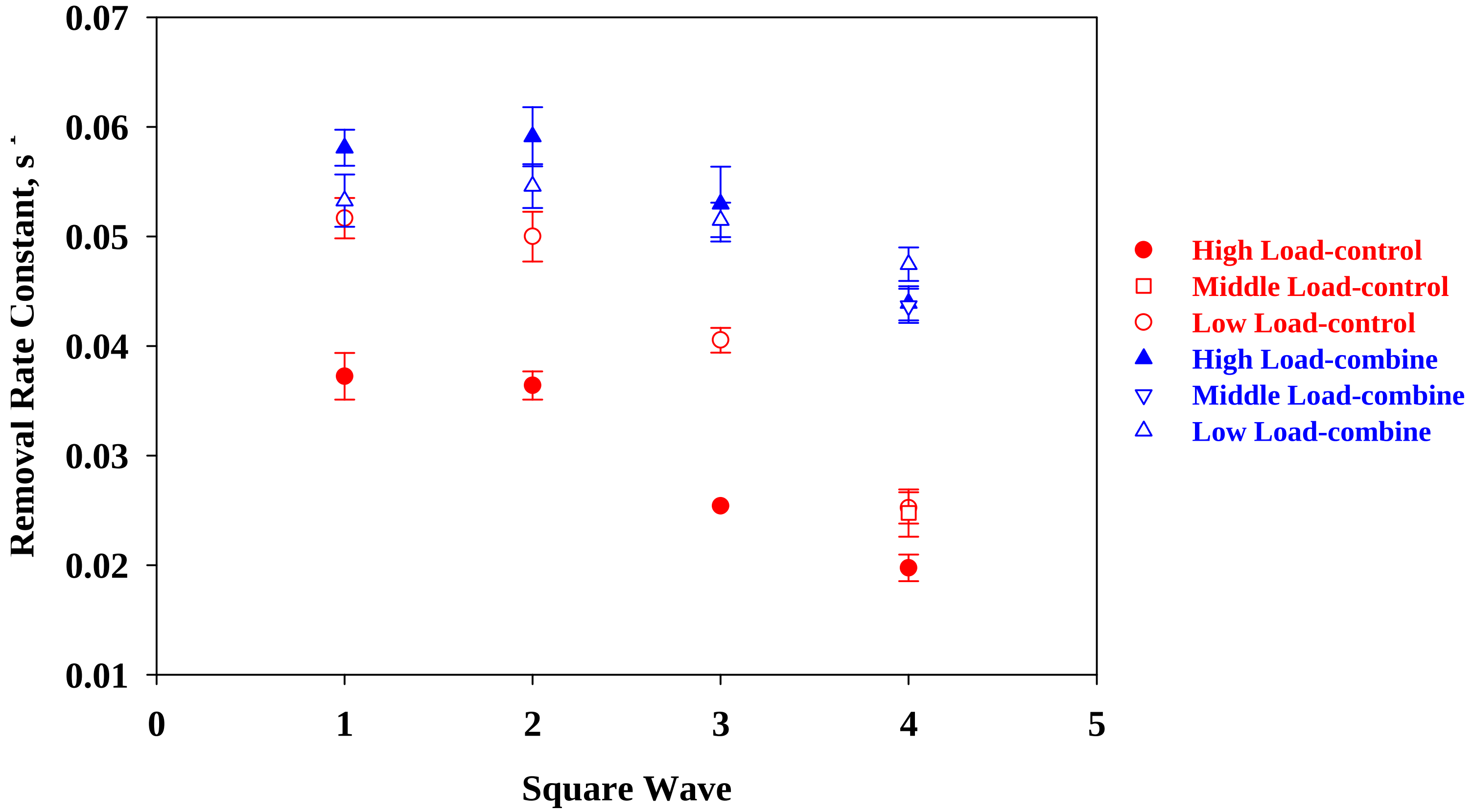
•Results

Toluene removal kinetics in mixture



•Results

Styrene removal kinetics in mixture



•Conclusions

- **Cyclic 2-bed adsorption/desorption unit successfully dampened loading fluctuation of VOCs mixture to the followed biofilter.**
- **Integrated trickling biofilter with cyclic 2-bed adsorption/desorption unit could maintain long-term high level removal efficiency.**
- **Integrated system showed more apparent efficacy to more frequent or/and higher magnitude fluctuation in feeding conditions.**
- **Cyclic 2-bed unit successfully functioned as feeding source to the followed biofilter during starvation period.**

UNIVERSITY OF Cincinnati

•Phase V

Objective

Microbial diversity investigation

•Materials and Methods

- **Microbial Analysis**

  DGGE of PCR-amplified 16S rDNA

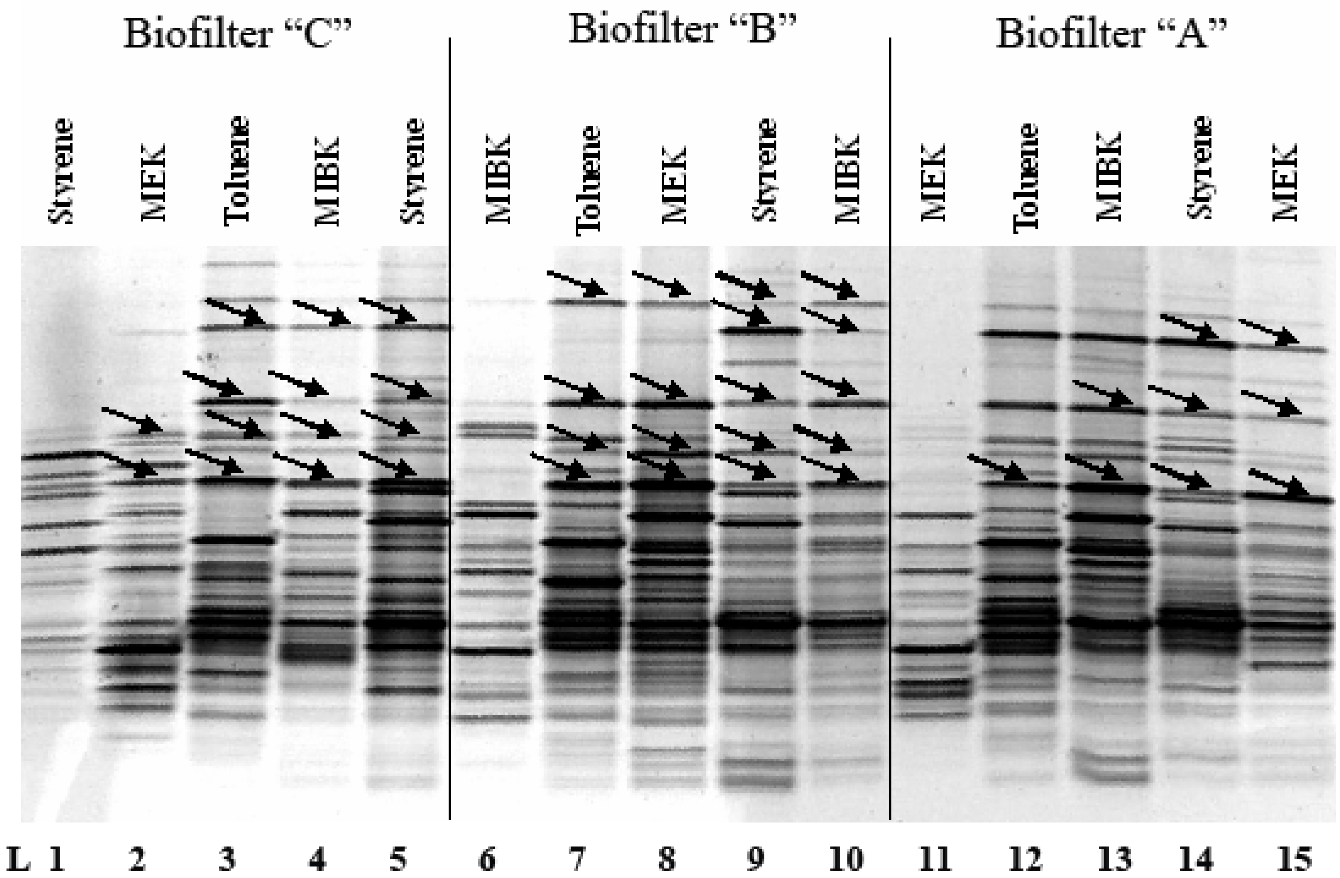
•Materials and Methods

- **Microbial Analysis**

- **DNA extract**
- **PCR**
  - ✓ **Polymerase chain reaction**
  - ✓ **To “grow up” extra copies of a target nucleic acid sequence**
- **DGGE**
  - ✓ **Separate microbial species**

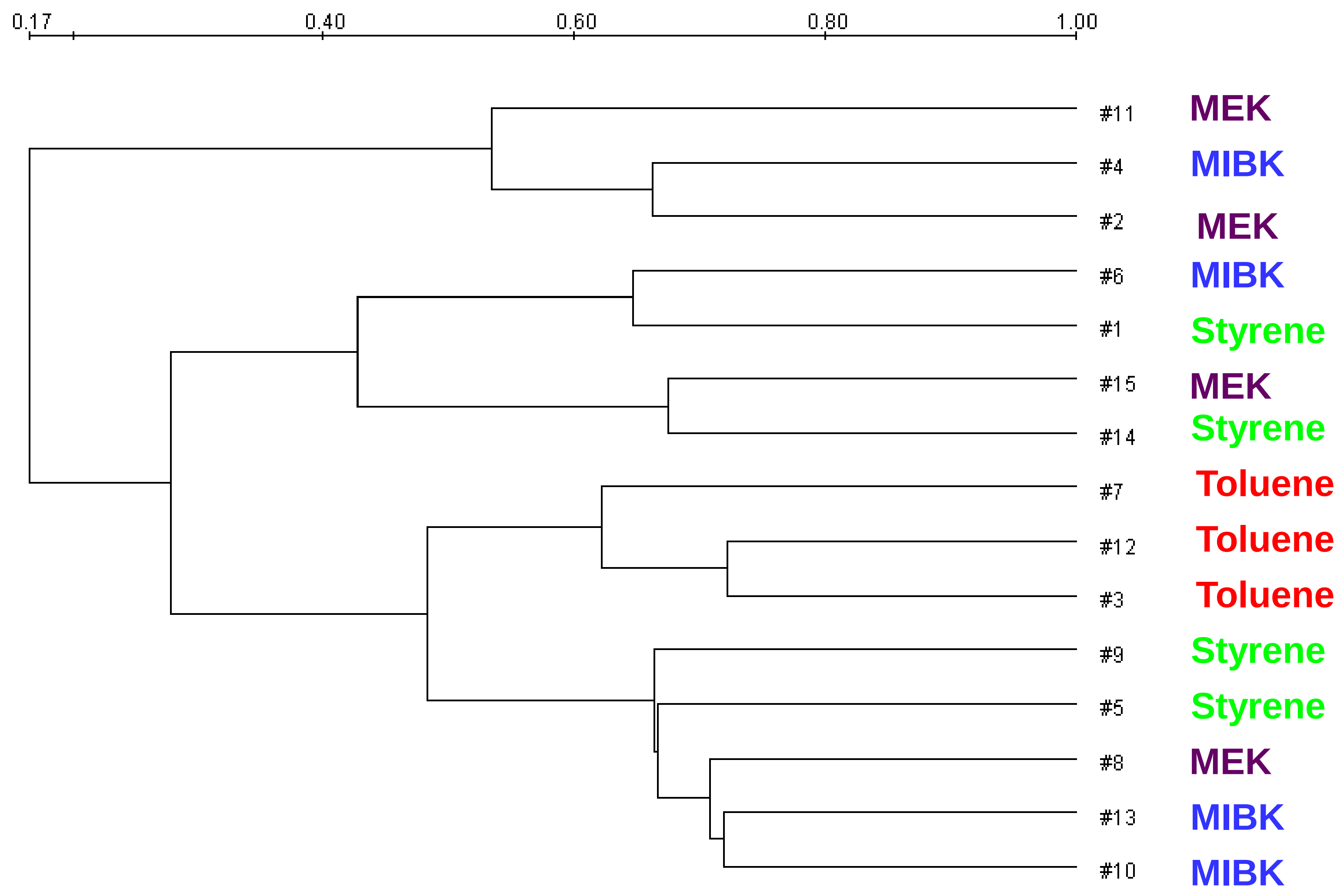
•Results

➢ DGGE for VOC Interchange



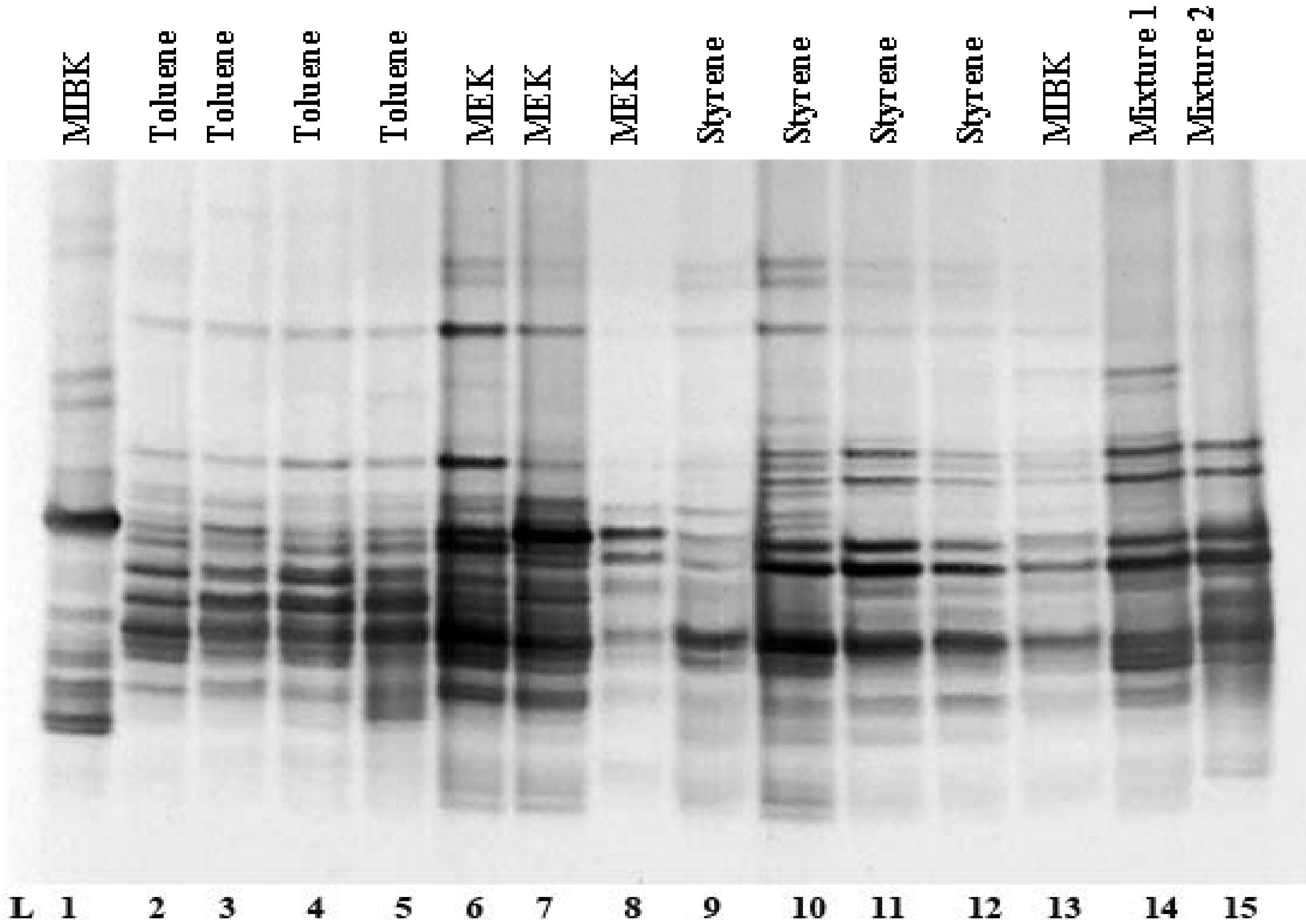
•Results

➢ **Dendrograms of PCR-DGGE fingerprints for VOC Interchange**



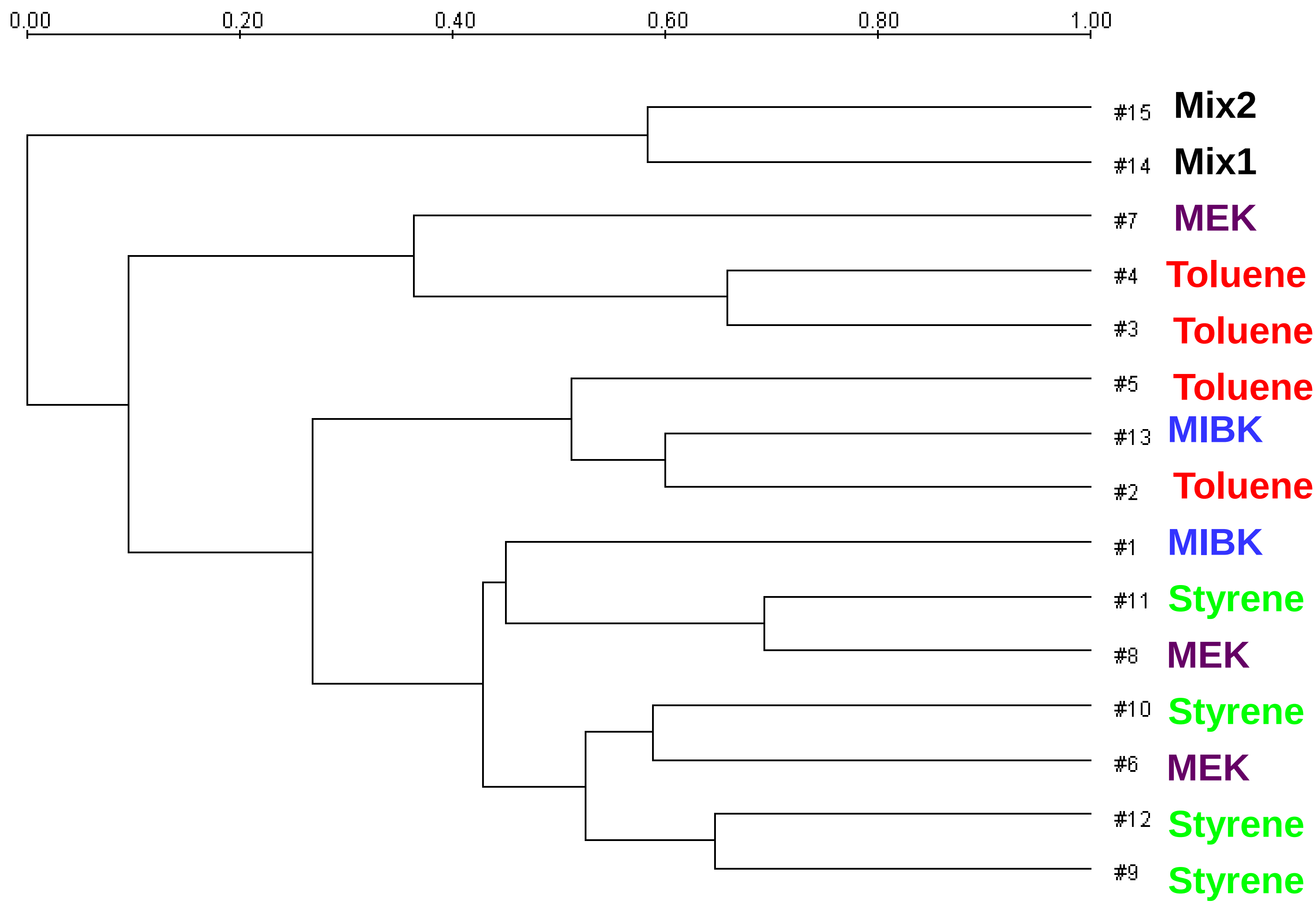
•Results

➢ DGGE for Biofilter “B” in VOC Interchange and VOC mxitures



•Results

➢ **Dendrograms of PCR-DGGE fingerprints**



•Conclusions

- The microbial diversity showed consistent transition for the interchanged VOC.
- The community structure for VOC mixtures show high independency to the component content in the mixture.
- The microbial diversity for toluene did not show significant association with the other VOCs studied unlike the behavior of the other three VOCs studied.
- The community structure in the biofilter did not show a clear relation to the biofilter performance.

•Recommendations for Future Study

- Expanded studies applied to other VOCs with much lower solubility
- Model simulation for the behavior of the cyclic 2-bed adsorption unit
- Investigation on the effect of VOCs toxicity on biofilter performance
- Further investigation in the microbiology in the biofilters

Acknowledgement

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- Dr. Margaret J. Kupferle
- Dr. Daekeun Kim, my research partner
- Environmental Chemistry Lab,
  University of Cincinnati

- PhD Dissertation Defense

- Integrated Cyclic Adsoprtion/Desorption Beds
- and Biofiltration System for Treatment of Waste Gas Streams

Questions?