Carbonaceous Adsorbents with Unique Bulk and Nanostructured Properties and their Applications to Improve Air Quality

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Outline

- **Introduction: Rood Research Group**
- **Capture and Recovery or Disposal of Organic Gases**
  - Activated Carbon Monolith (ACM)
  - Activated Carbon Bead (ACB)
  - Activated Carbon Fiber Cloth (ACFC)
- **Adsorption of Toxic Industrial Chemicals with Novel Carbons**
- **Trace Multi-pollutant Capture**
- **Summary**

Introduction: Rood Research Group

- Carbon Based Materials to Purify Gas Streams for Reuse or Efficient Disposal
  - Capture and Recovery or Disposal of Organic Gases
    - Electrothermal Swing Adsorption of unique morphology
  - Adsorption of Toxic Industrial Chemicals with Novel Carbons
  - NO Oxidation by Catalytic Carbon Materials
  - Trace Multipollutant Capture NO Oxidation by Catalytic Carbon Materials
  - Novel Synthesis Process for Iron-Impregnated Porous Carbon Spheres
  - Bioaerosol and Toxic Gas Capture and Destruction
- Outdoor and Laboratory Aerosol Characterization
  - Optical Remote Sensing
    - Digital images to determine plume opacity
    - LIght Detection And Ranging to determine particulate mass emission factors from unique sources
  - Impact of Humidity on the Optical Properties of Climate Relevant Aerosol at Relative Humidities up to 98%

Air Quality Research Laboratories

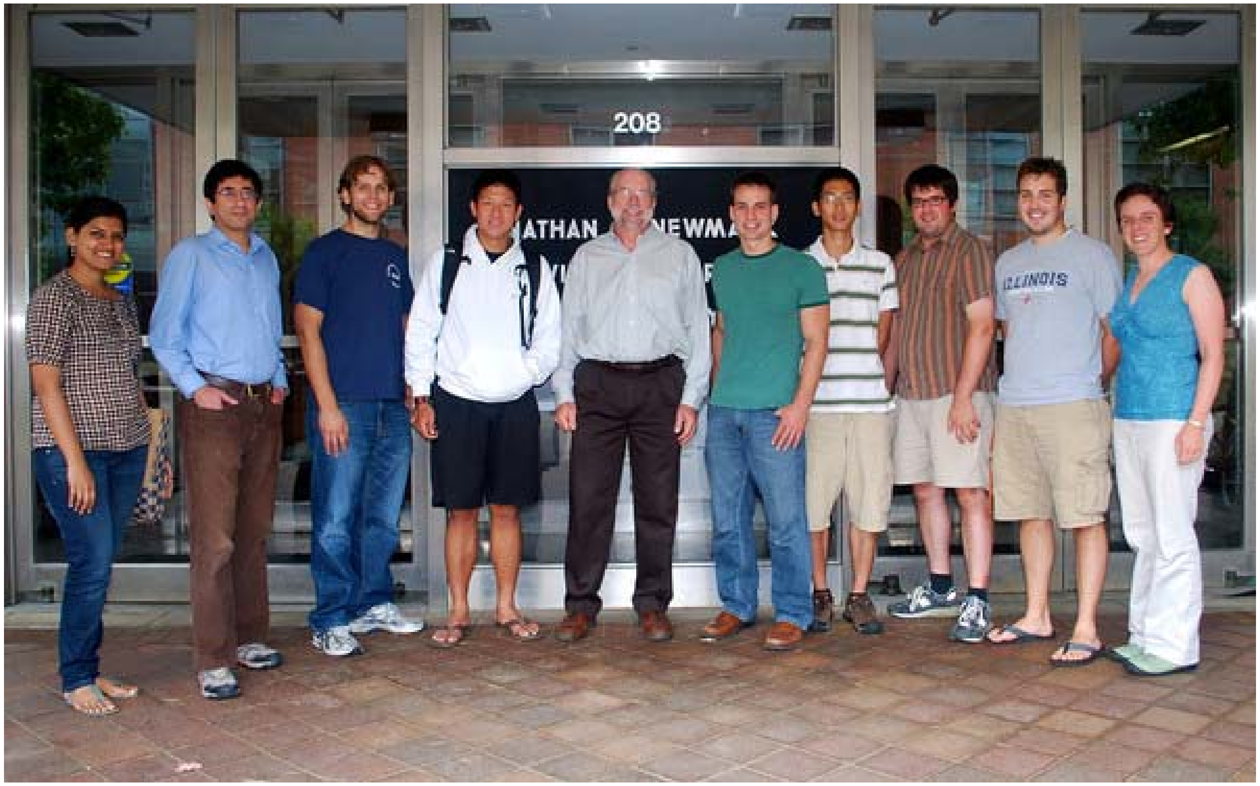
Air Quality Clean Room

Paul Dusenberry Air Quality Laboratory

Ivan Racheff Controlled Temperature and Humidity Laboratory

Pilot-Scale VaPRRS in Shipping Container

Human Innovation and Resources!

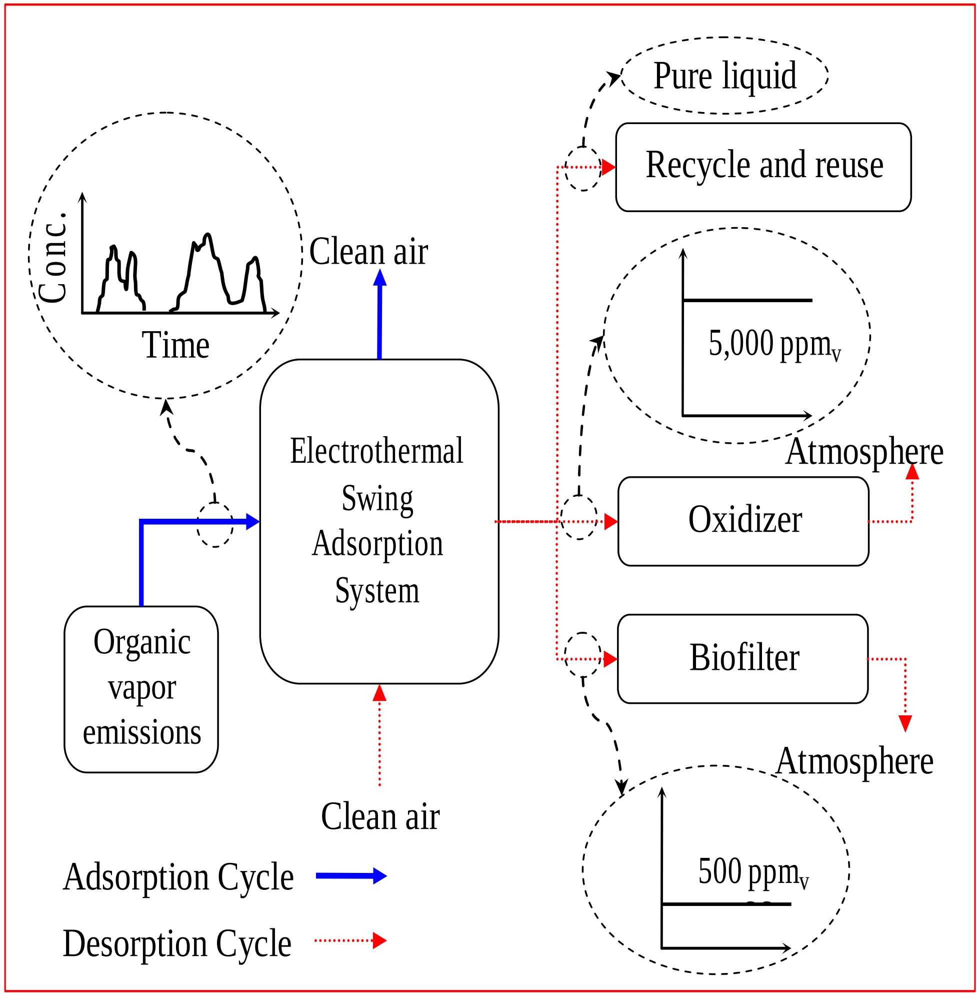


Rood Research Group
(AQES)

Capture and Recovery or Disposal of Organic Gases

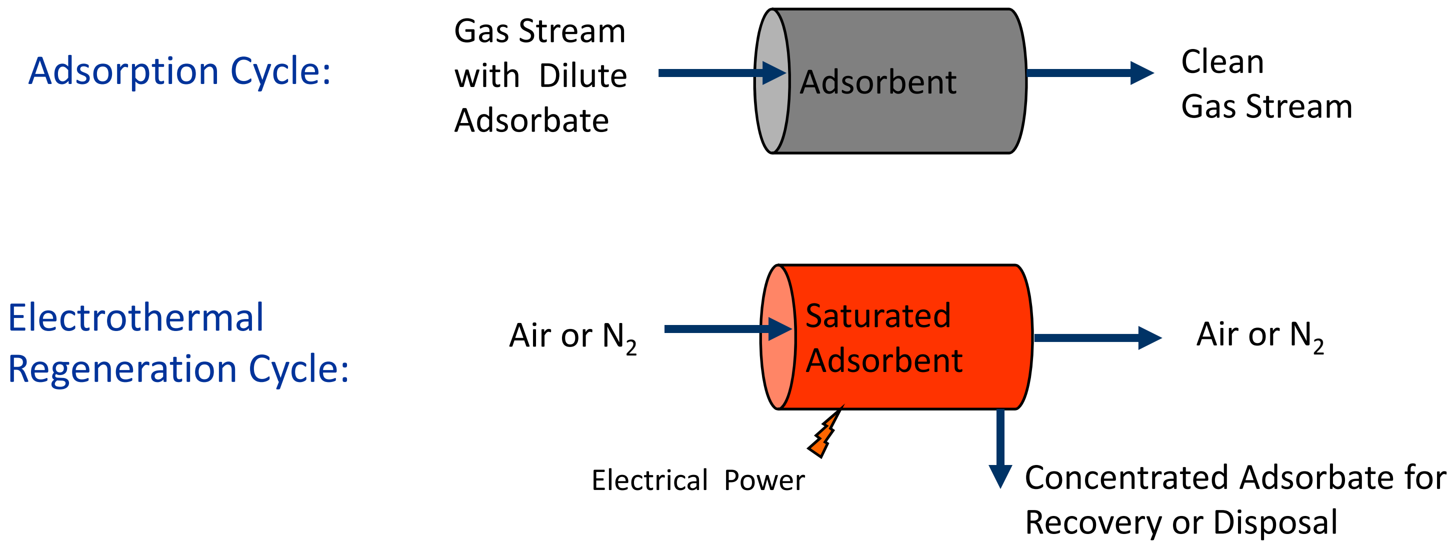
Electrothermal Swing Adsorption (ESA) Technologies

- **Vapor Phase Removal and Recovery System (VaPRRS):**
  - organic vapors are recovered as a liquid
- **Gas Phase Removal and Recovery System (GaPRRS):**
  - organic gases are recovered as a liquid
- **Steady State Tracking (SST) system:**
  - organic vapors/gases are exhausted at a specified steady-state concentration and flow rate for disposal by a much smaller oxidizer or biofilter



Electrothermal Swing Adsorption

- Activated carbon adsorbents are widely used to capture hazardous and valuable gases that are used with industrial sources
- Electrothermal Swing Adsorption (ESA): adsorbent is an electrical resistor to heat and regenerate the adsorbent (Joule heating)



Adsorption Cycle:

Gas Stream with Dilute Adsorbate

Adsorbent

Clean Gas Stream

Electrothermal Regeneration Cycle:

Air or N_2

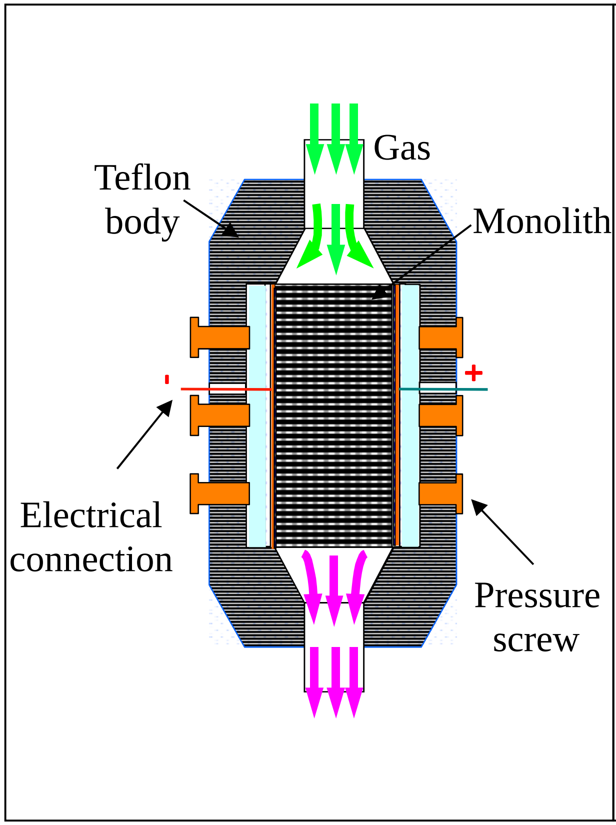
Saturated Adsorbent

Air or N_2

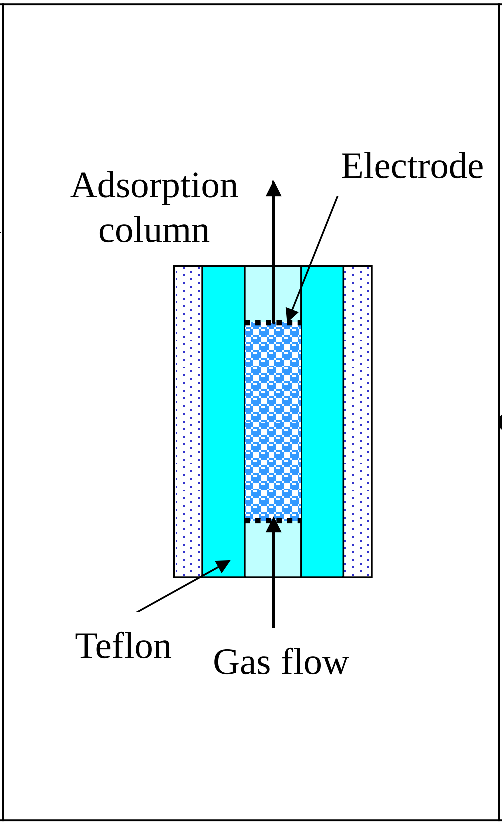
Electrical Power

Concentrated Adsorbate for Recovery or Disposal

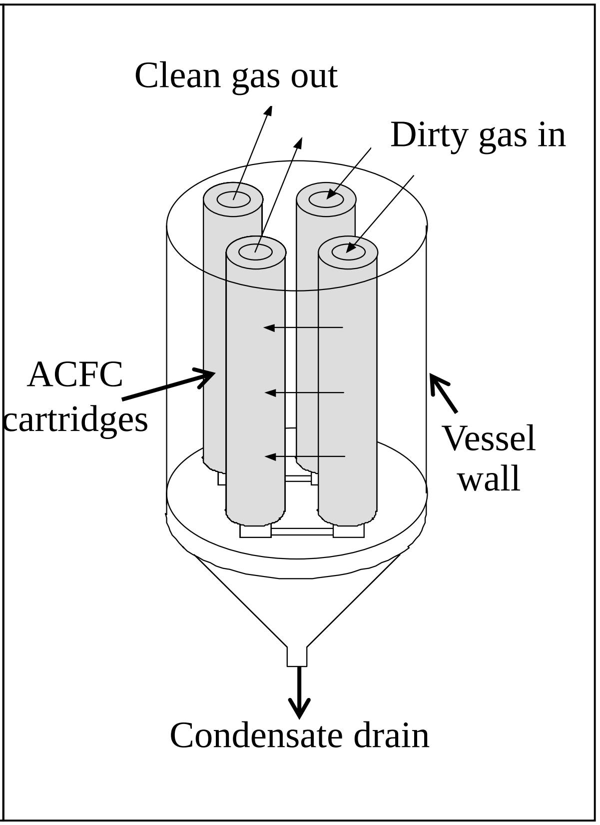
ACM, ACB, and ACFC Adsorption Vessels



ACM



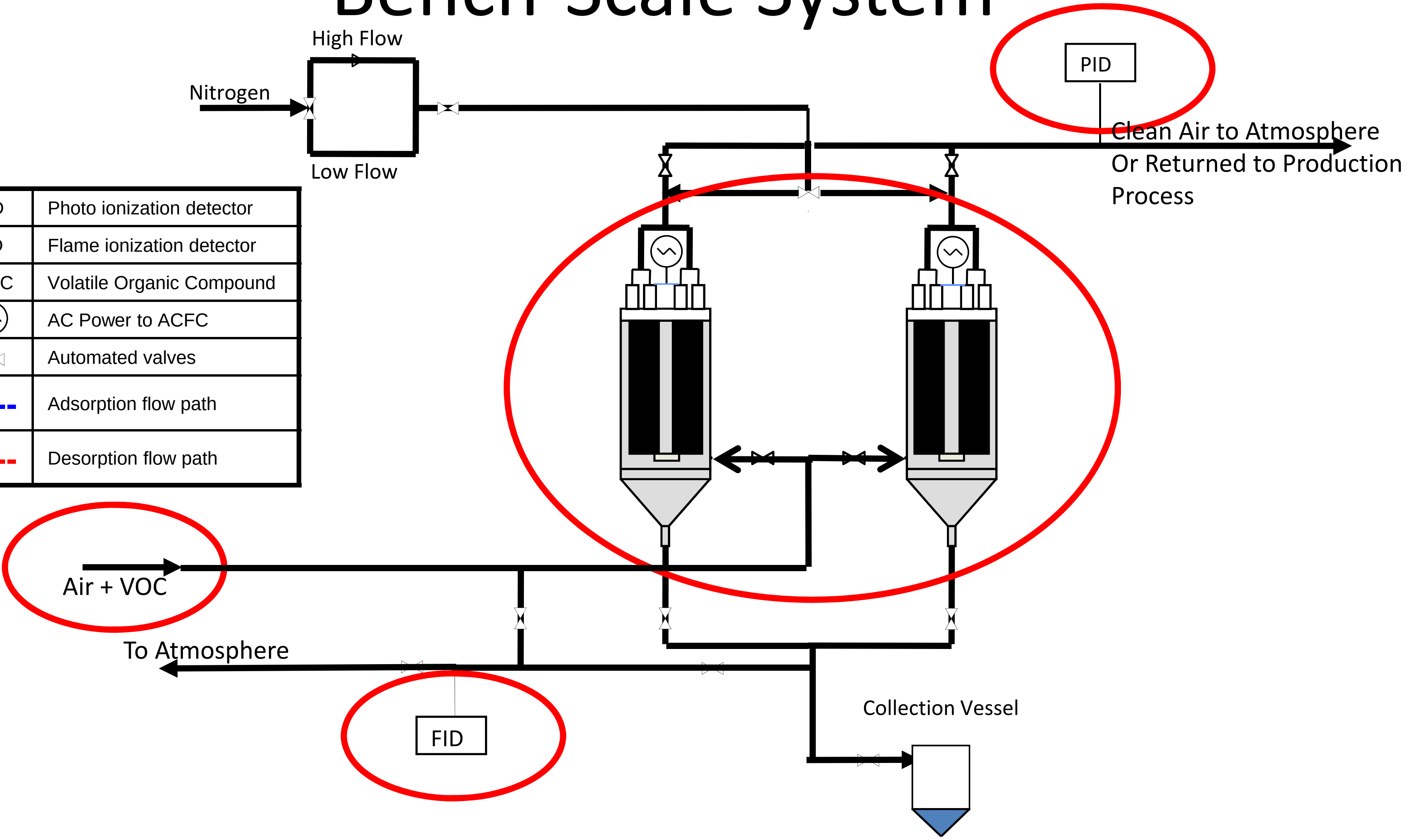
ACB



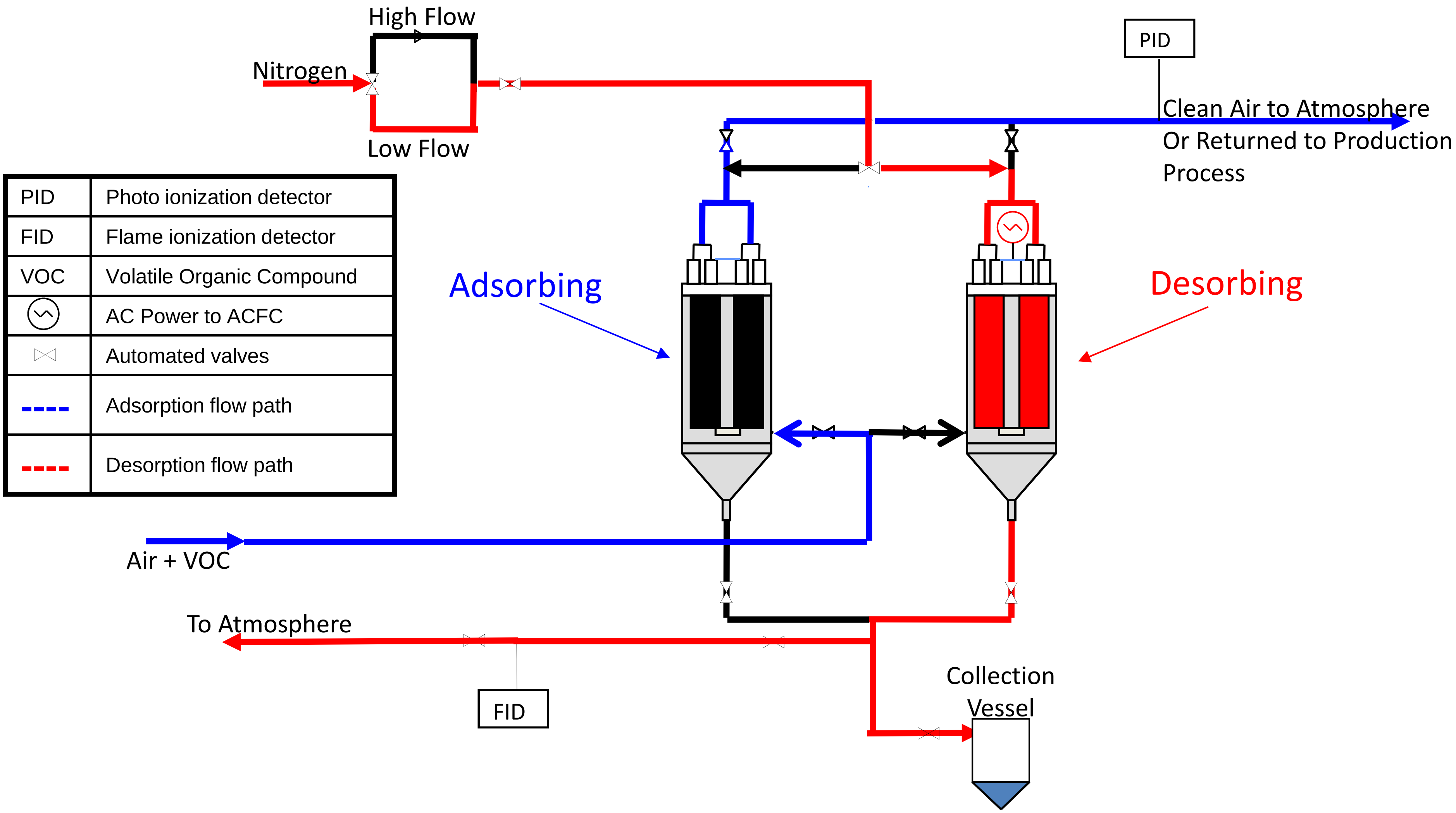
ACFC

Experimental Setup: Bench-Scale System

PID	Photo ionization detector
FID	Flame ionization detector
VOC	Volatile Organic Compound
∿	AC Power to ACFC
⋈	Automated valves
----	Adsorption flow path
----	Desorption flow path



Concurrent Adsorption/Desorption



PID	Photo ionization detector
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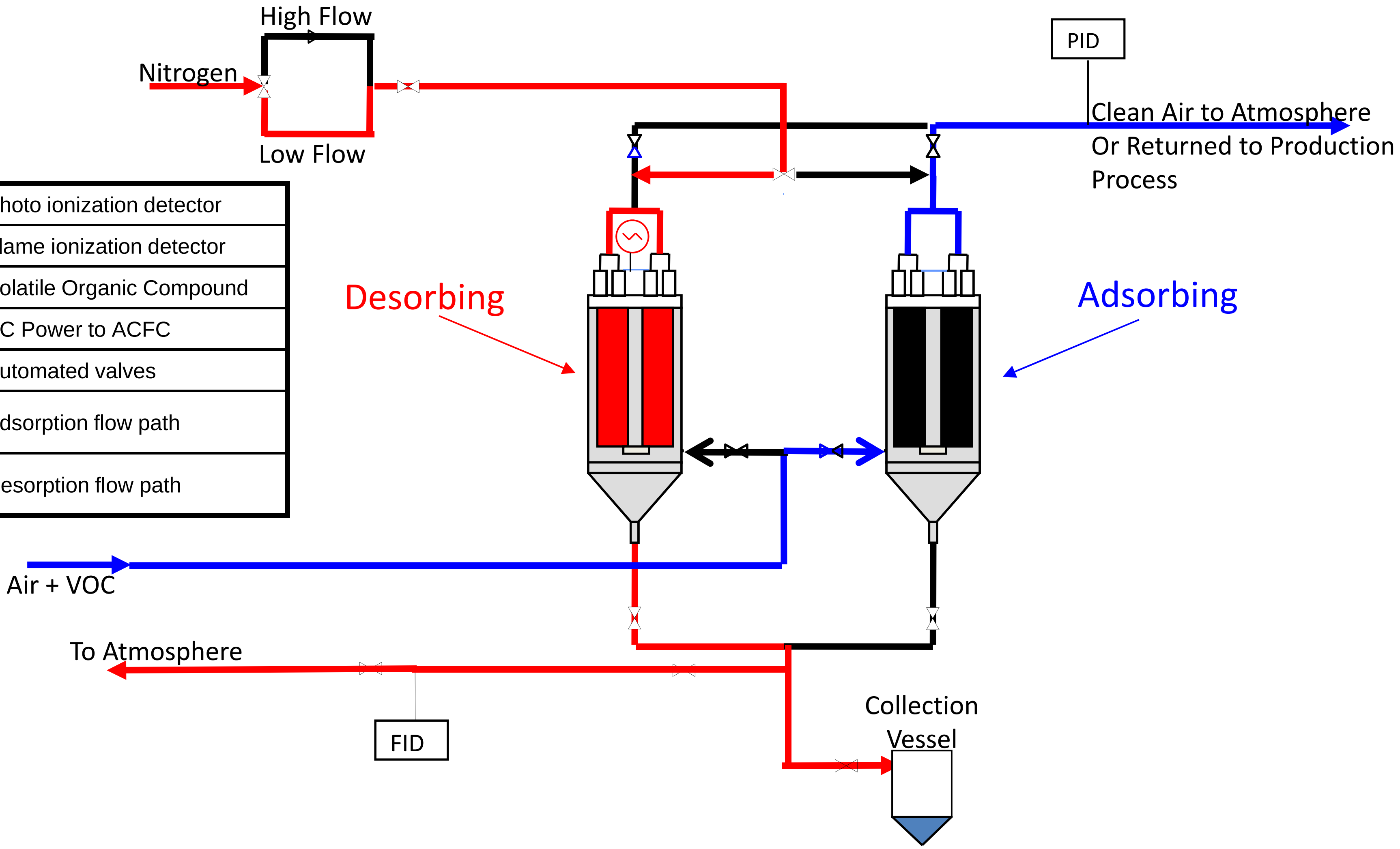
Controlled automatically using LabView^{TM}

Concurrent Adsorption/Desorption



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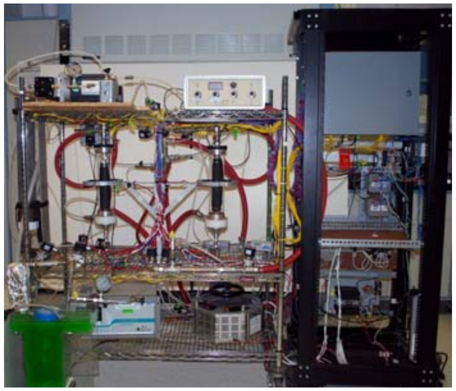
Existing ESA Systems at UofI

Bench-scale VaPRRS and SST systems at UofI



Bench-scale GaPRRS system at UofI

Bench-scale bioaerosol removal/inactivation system at UofI

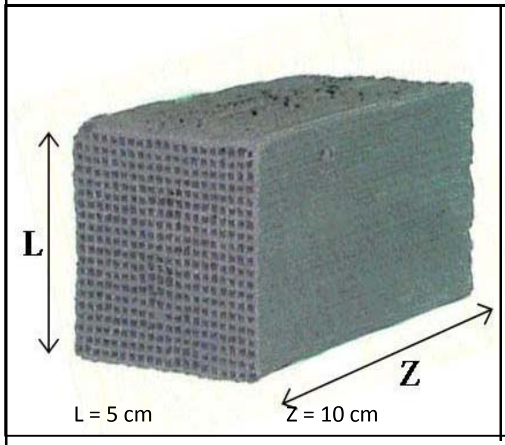
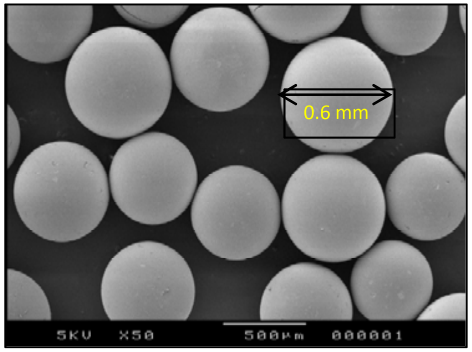
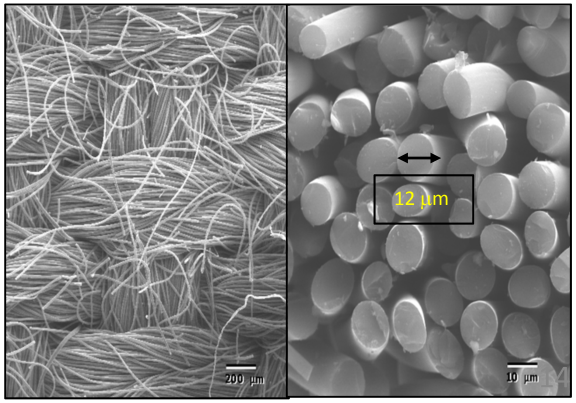
Pilot-scale VaPRRS at Utah USA

Full-scale mobile VaPRRS in Wisconsin USA

Full-scale SST system in Busan Korea

Morphology of Activated Carbons for ESA

- **Activated Carbon Monolith (ACM)**: organized structure, parallelepiped shape, 400 open channels, square section (2 mm per side), wall thickness (0.5 mm)
- **Activated Carbon Bead (ACB)**: synthetic spheres, ash free to inhibit fires, high resistance to mechanical attrition
- **Activated Carbon Fiber Cloth (ACFC)**: wide range of morphologies, shapeable, high carbon content, ash free to inhibit fires

ACM	ACB	ACFC
		

Physical Properties of Select Carbons

Adsorbent	**Precursor**	**N_2 BET-Surface Area (m^2/g)**	**Micropore Volume (cm^3/g)**	**Porosity**	**Shape**
ACM	Coal	603	0.21	0.64	Open channels x_{wall} = 0.5 mm
ACB (Ambersorb 572)	Styrene di-vinylbenzene resin	1,100	0.41	0.51	Spherical beads d_{bead} = 0.6 mm
ACFC (ACC-5092-20)	Novoloid phenolic resin	1,600	0.75	0.93	Woven cloth d_{fiber}= 12 μm

Sources: Saysset, 1999; Lo, 2002; Yu et al., 2004

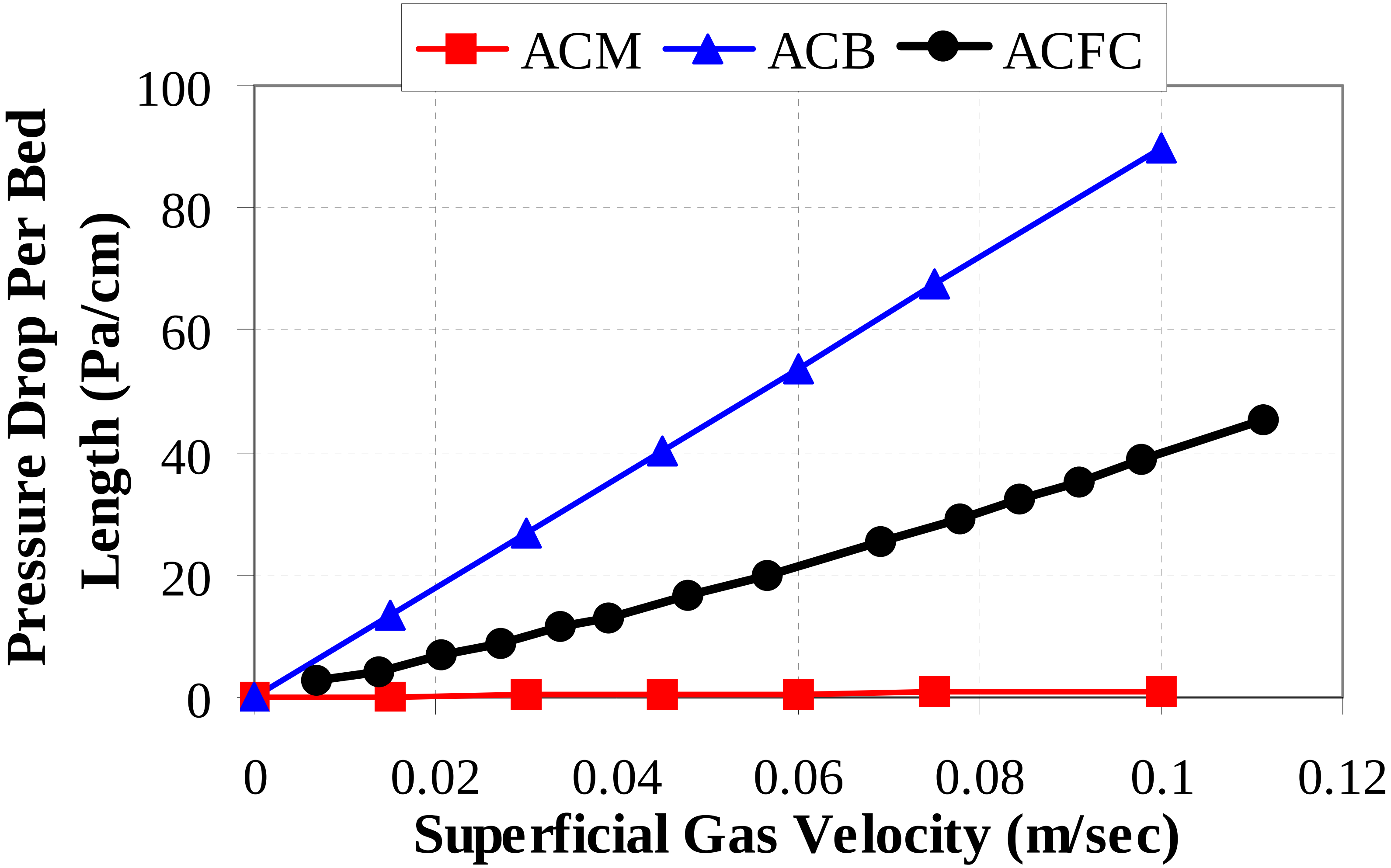
Permeability of Selected Carbons

Porous Material	Permeability (m^2)
Berl saddles	2.6×10^{-7}
ACM*	**1.8×10^{-8}**
Hair felt	1.0×10^{-9}
Wire crimps	6.9×10^{-9}
Cork board	9.1×10^{-10}
ACB*	**2.0×10^{-10}**
Sand (loose beds)	1.0×10^{-10}
Fiber glass	3.8×10^{-11}
ACFC*	**1.9×10^{-11}**
Sandstone	1.5×10^{-12}
Brick	1.1×10^{-13}
Silica powder	3.2×10^{-14}

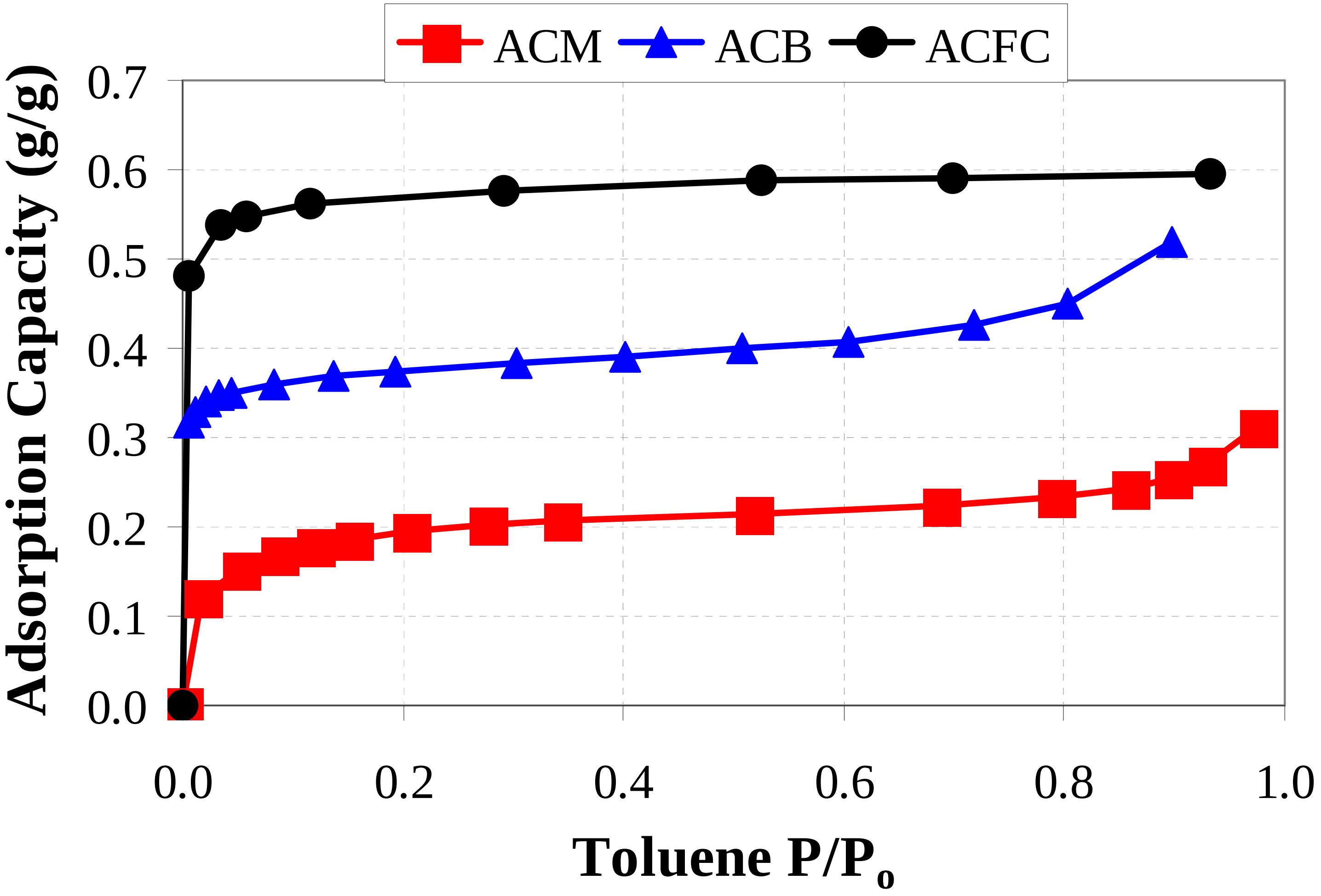
*This study

(Collins R.E., 1961)

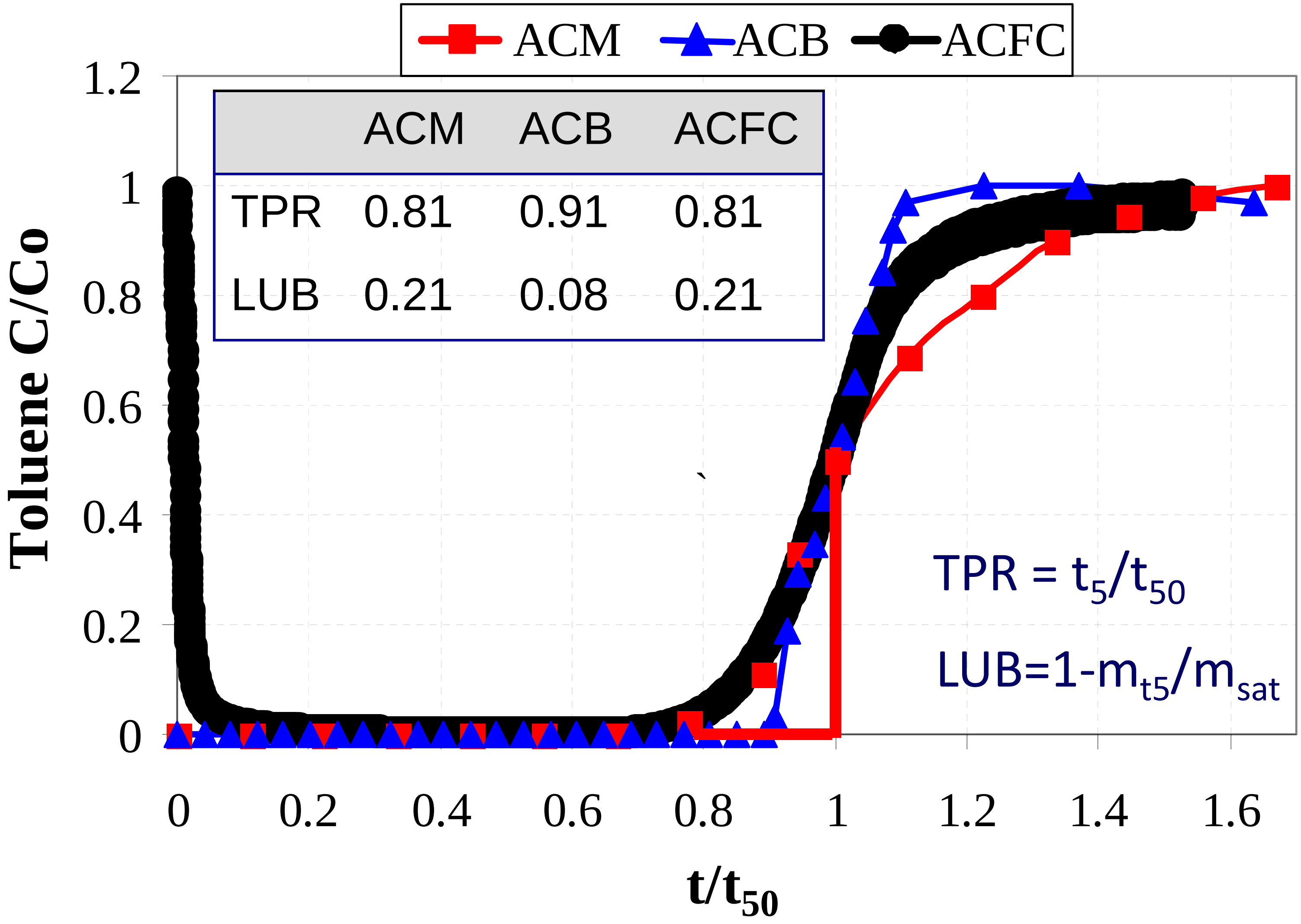
Dependence of Pressure Drop on Superficial Gas Velocity



Toluene Adsorption Isotherms



Toluene Breakthrough Curves

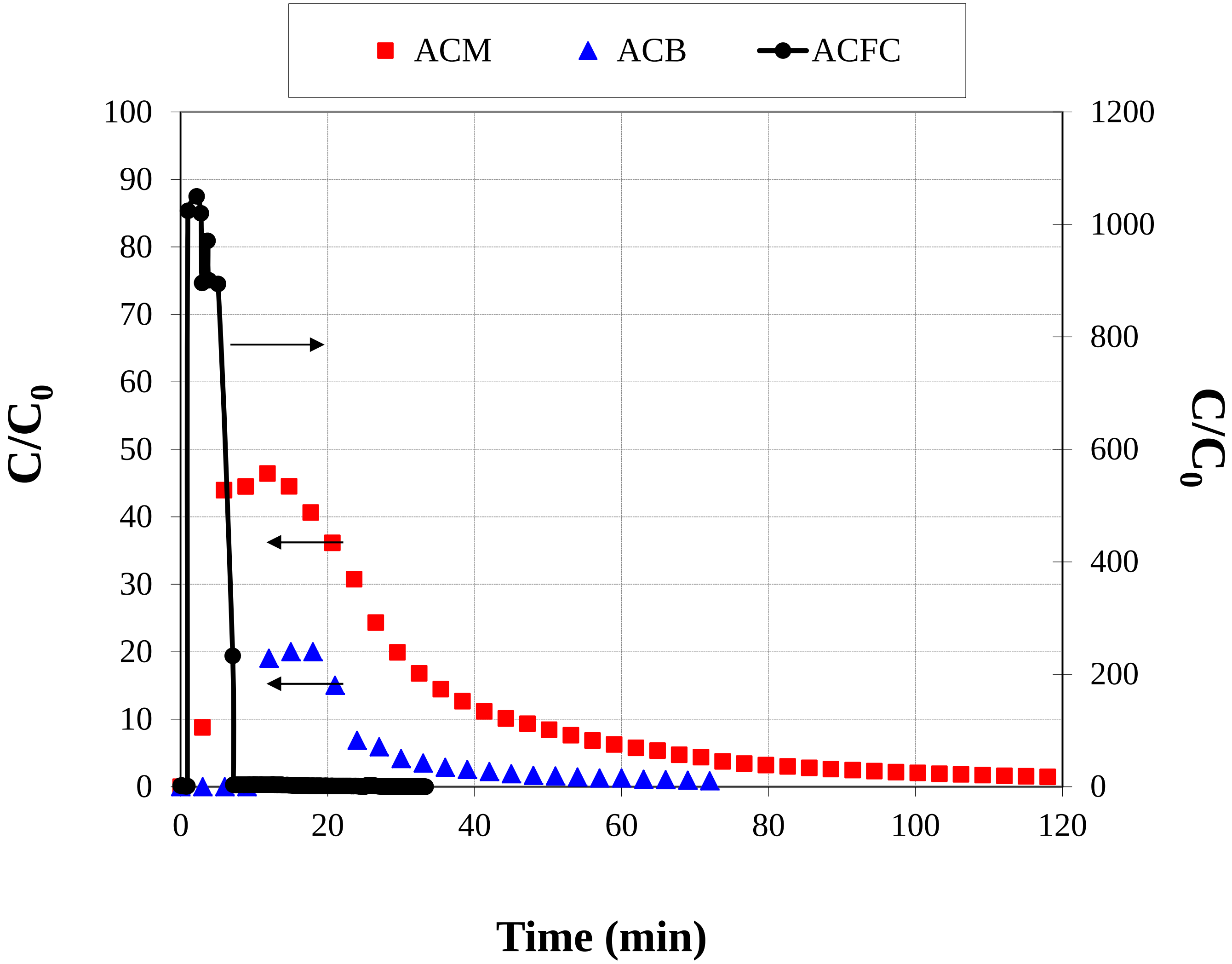


	ACM	ACB	ACFC
TPR	0.81	0.91	0.81
LUB	0.21	0.08	0.21

$TPR = t_5/t_{50}$

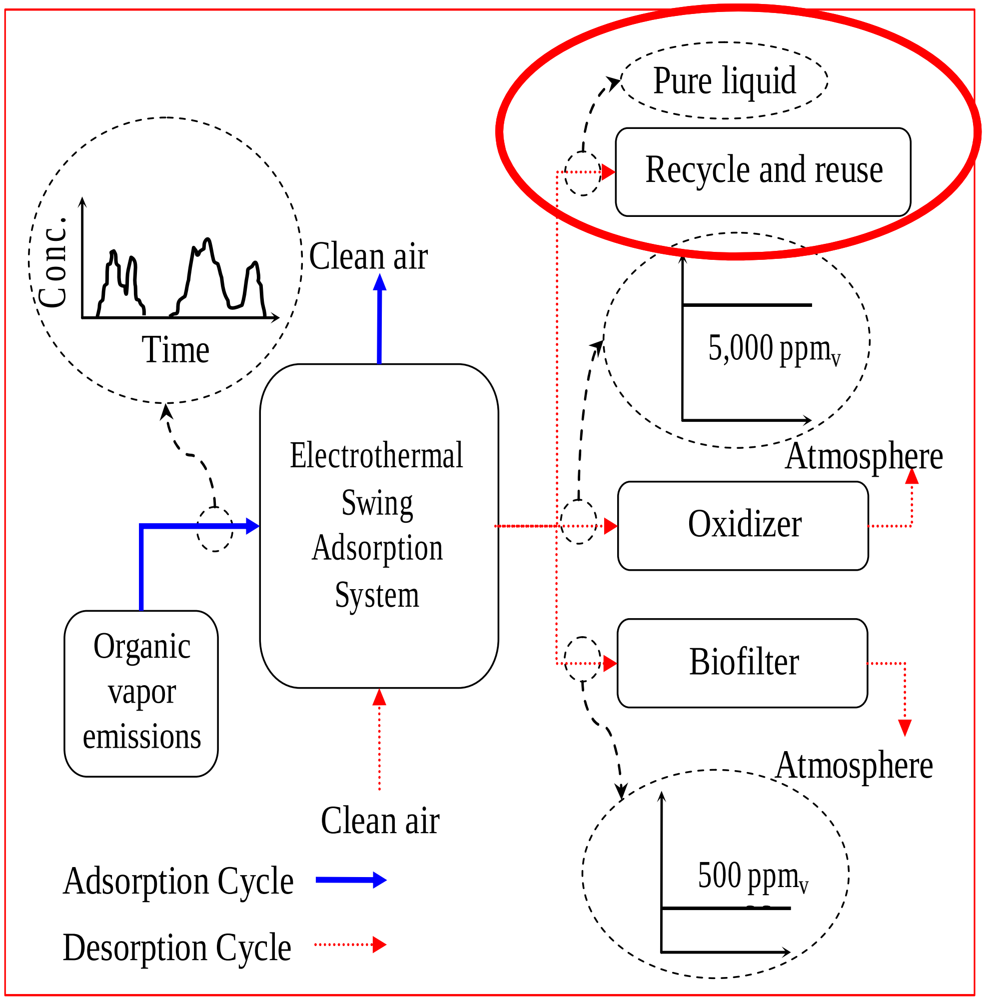
$LUB=1-m_{t5}/m_{sat}$

Adsorption with Pre-Concentration for Recovery and Reuse

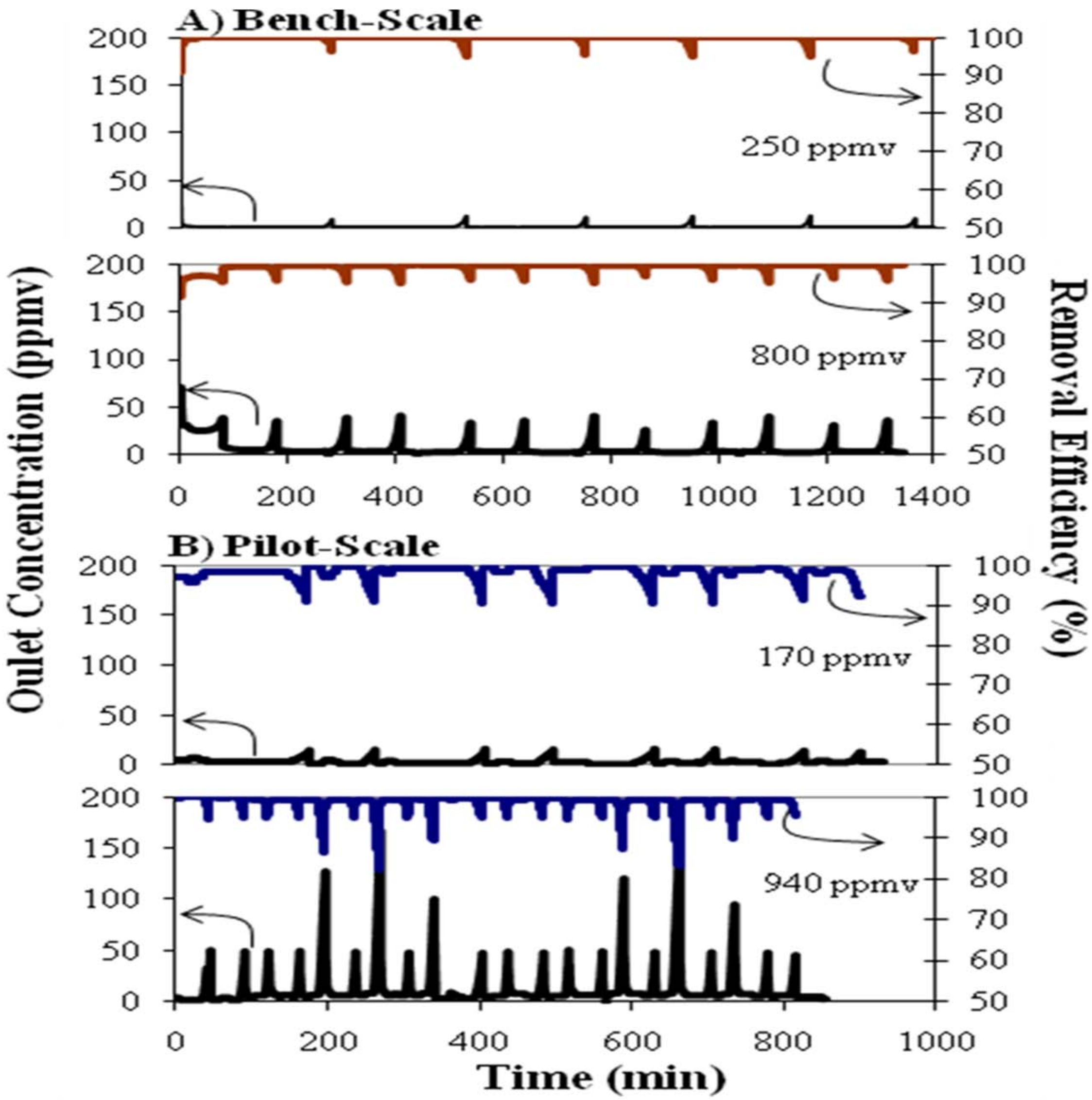


ESA: Vapor Phase Removal and Recovery System

- **Vapor Phase Removal and Recovery System (VaPRRS):**
  organic vapors are recovered as a liquid

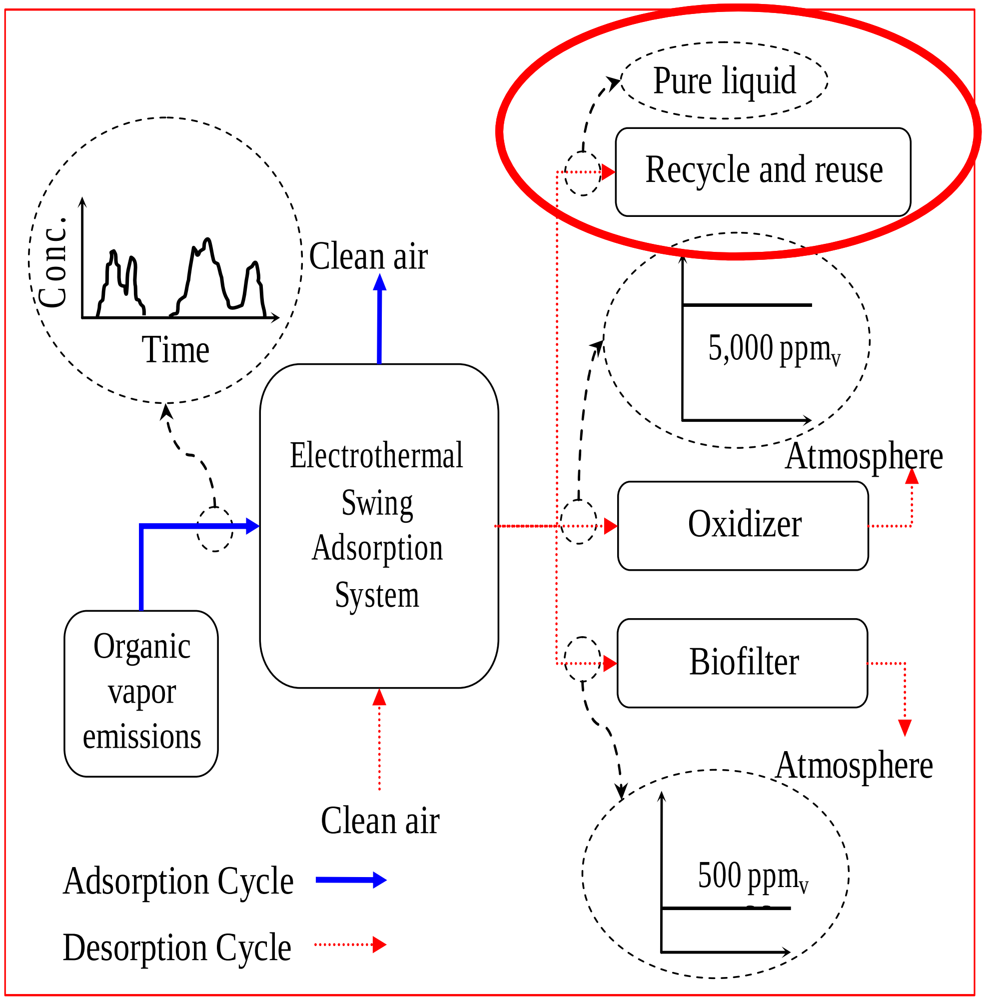


ESA: Automatic Cycling of the Bench-Scale and Pilot-Scale VaPRRS

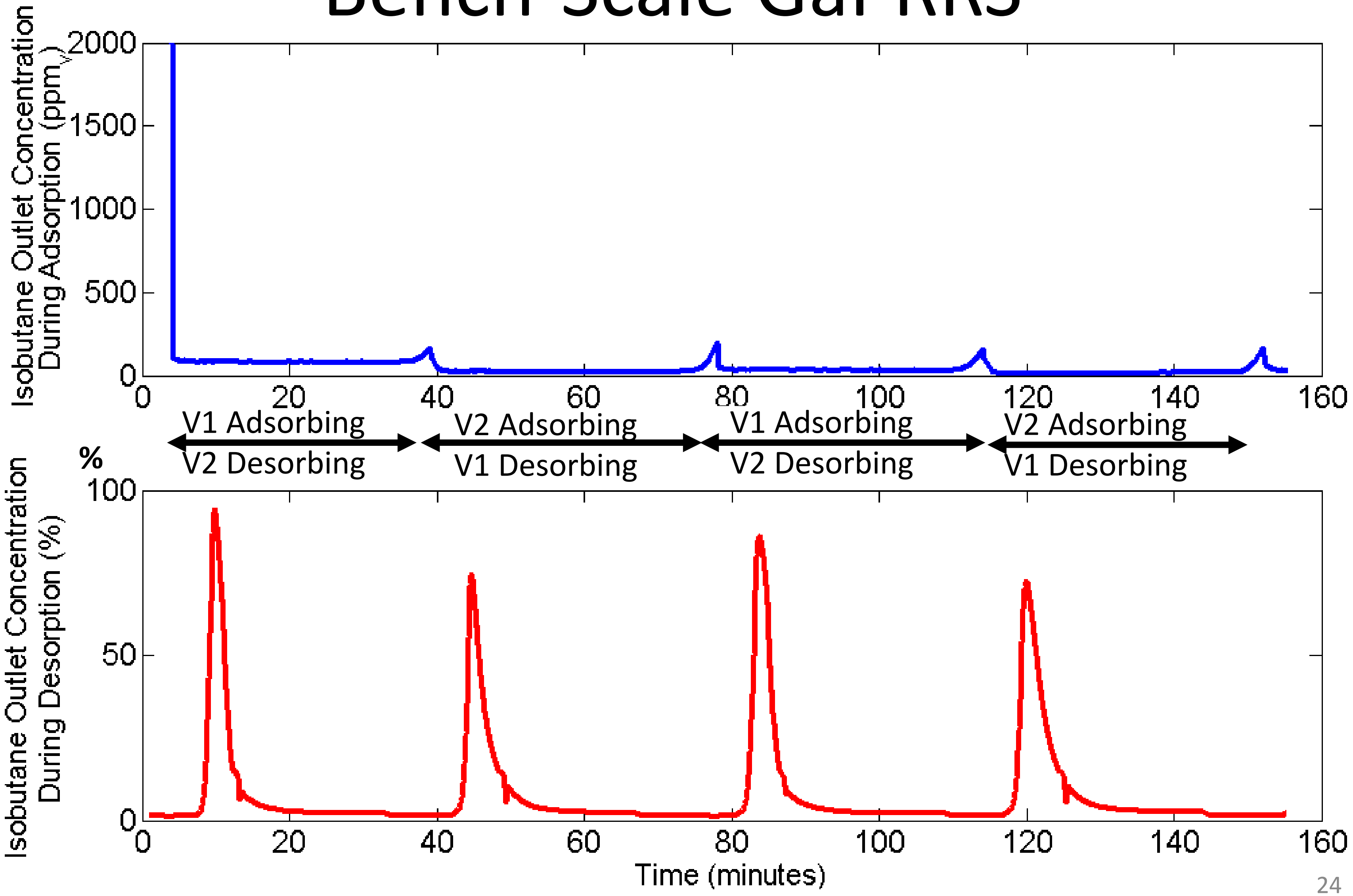


ESA: Gas Phase Removal and Recovery System

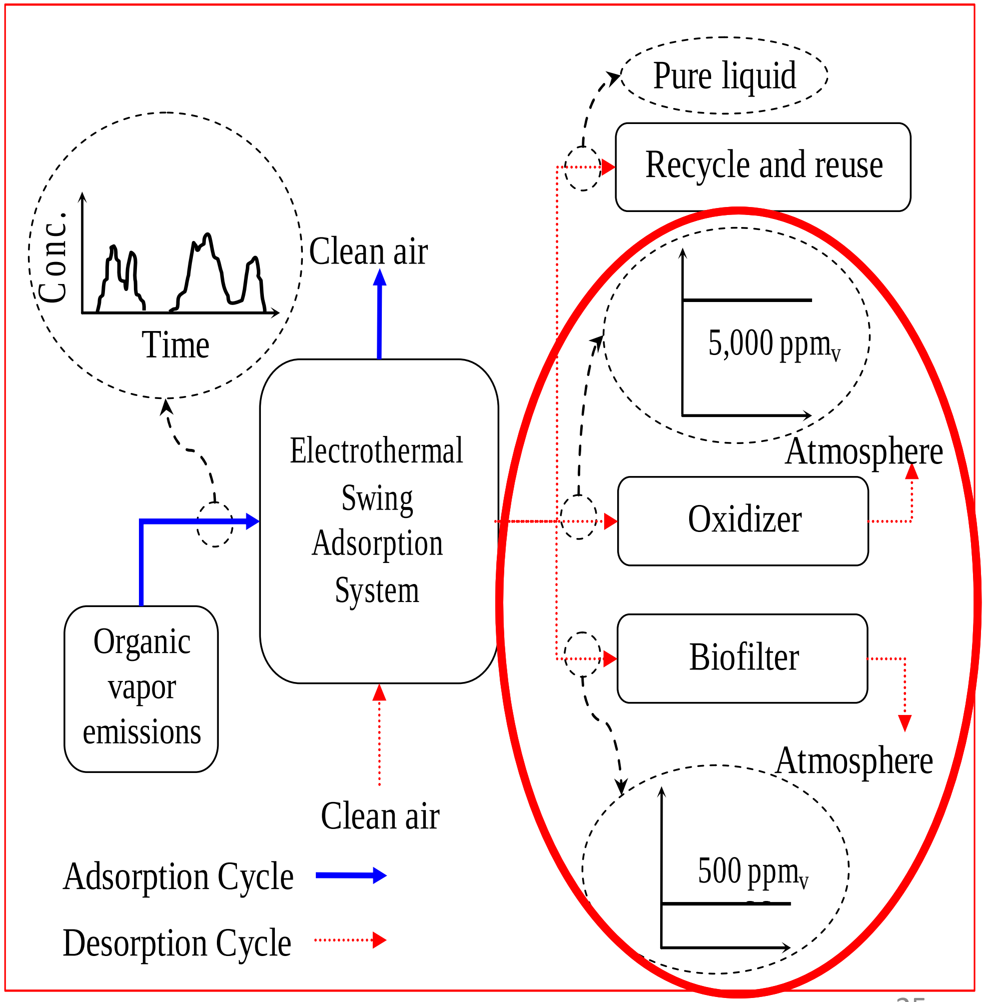
- **Gas Phase Removal and Recovery System (GaPRRS):**
  organic gases are recovered as a liquid



ESA: Automatic Cycling of the Bench-Scale GaPRRS

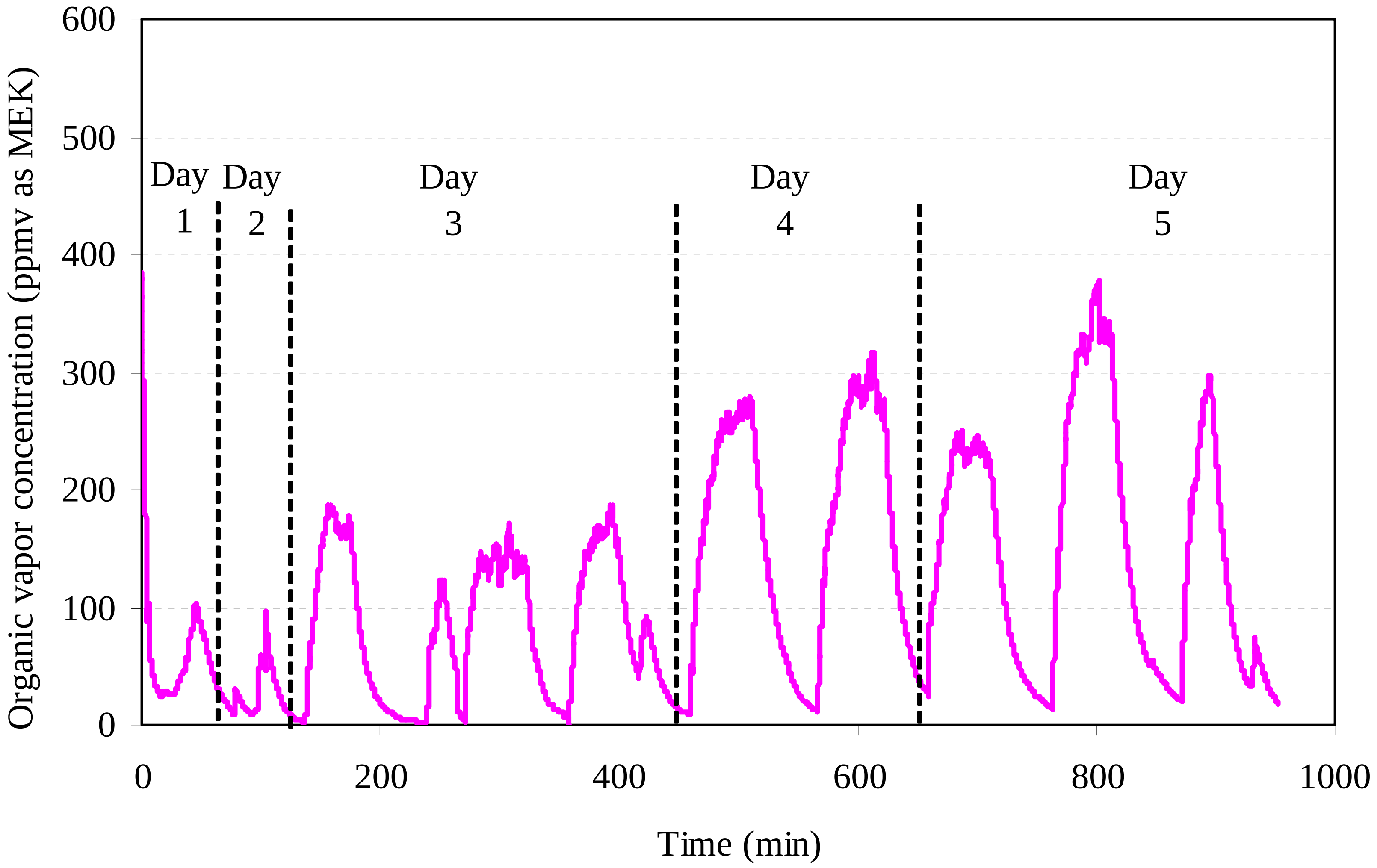


ESA: Steady State Tracking System

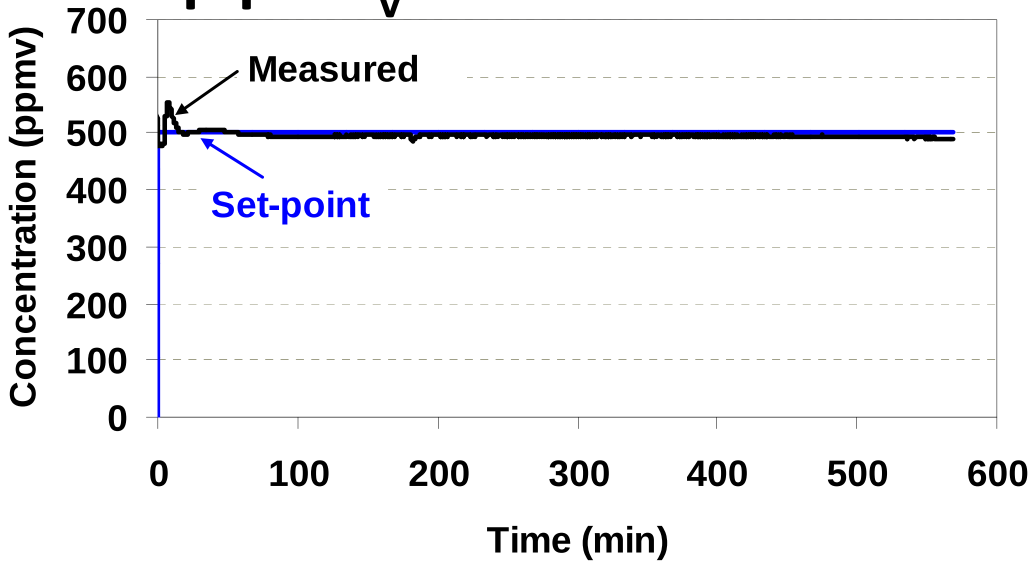


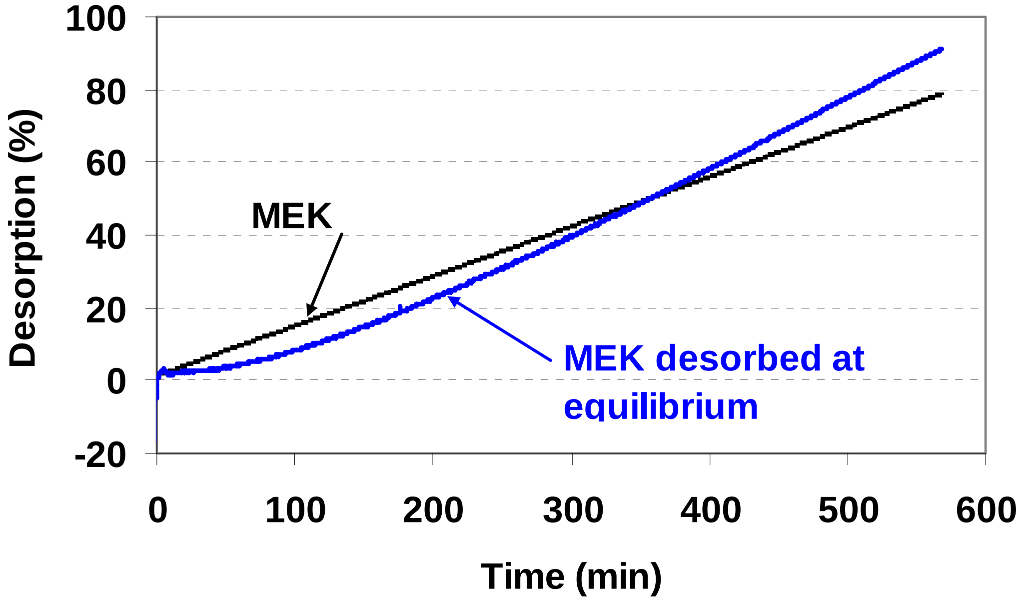
- **Steady State Tracking (SST) system:** organic vapors/gases are exhausted at a specified steady-state concentration and flow rate for disposal by a much smaller oxidizer or biofilter

Emissions from a Painting Facility

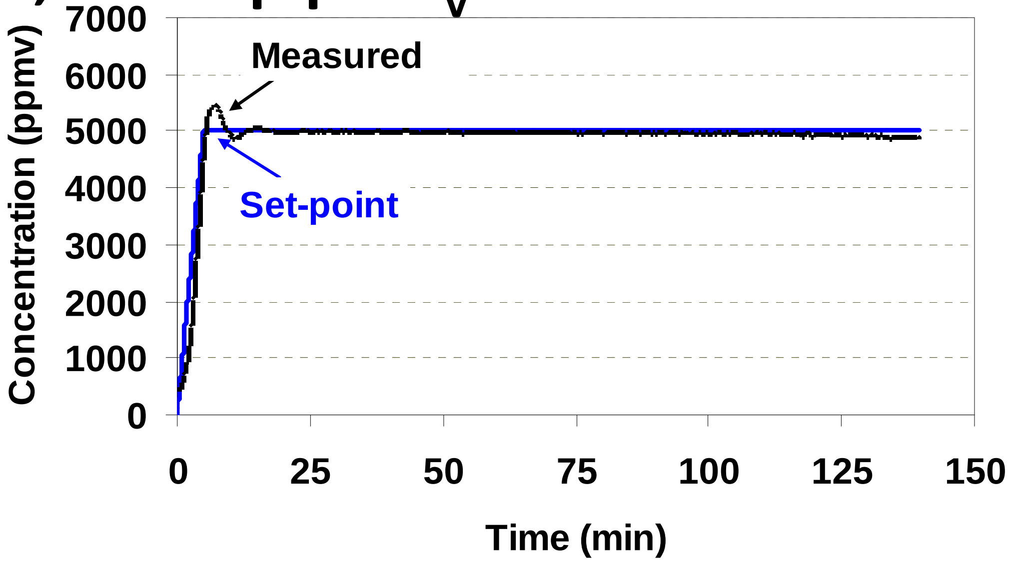


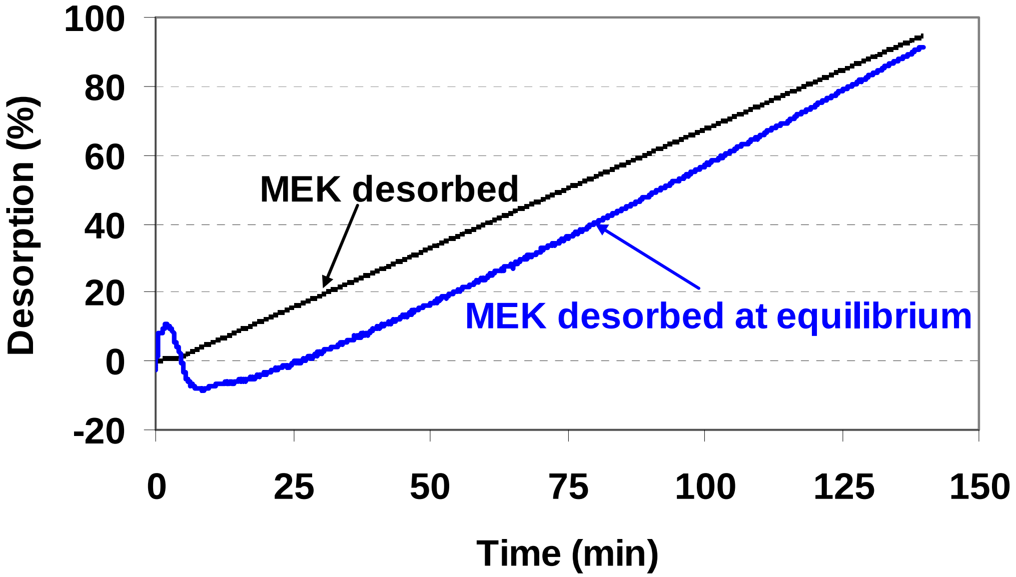
Steady-State Desorption Test at 500 ppm$_v$ for Biofiltration



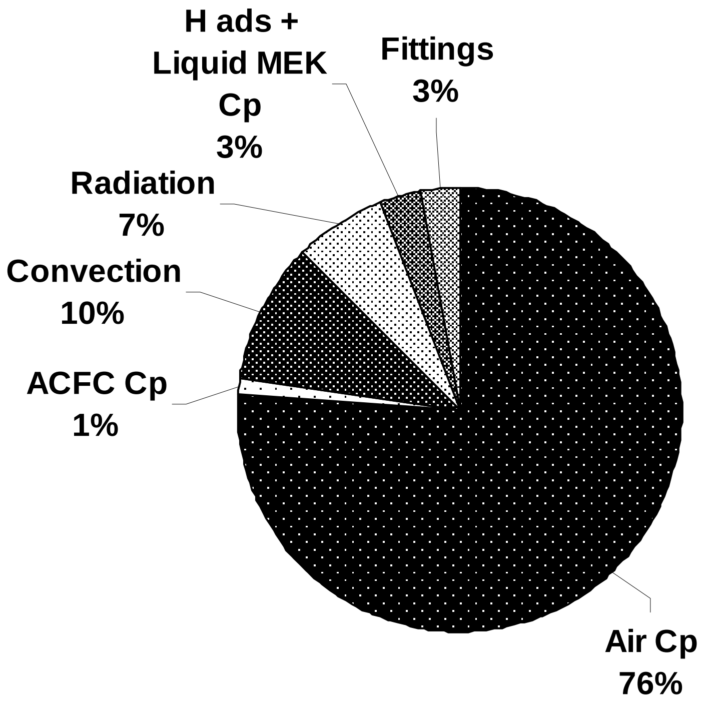


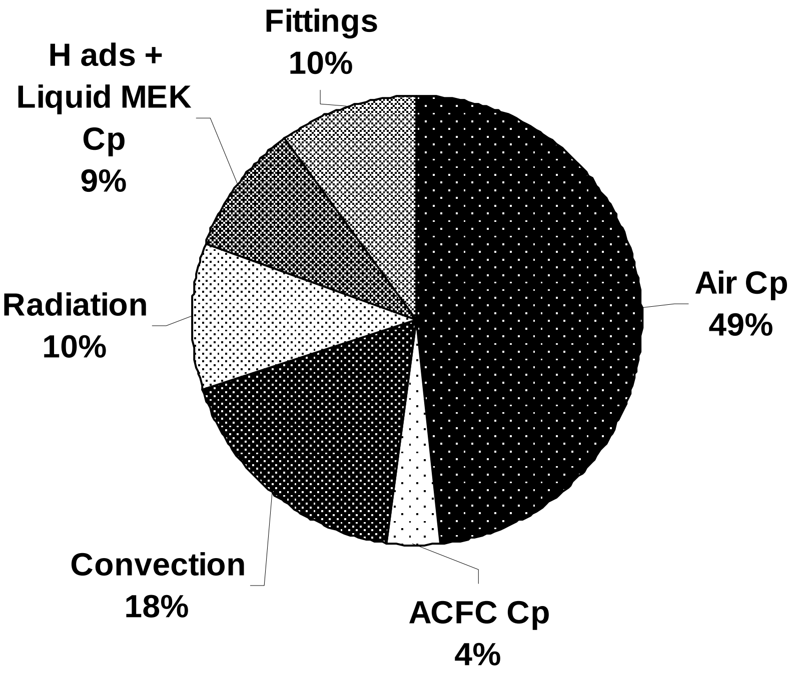
Steady-State Desorption Test at 5,000 ppm$_v$ for Oxidation





Energy Distributions during Regeneration Cycles



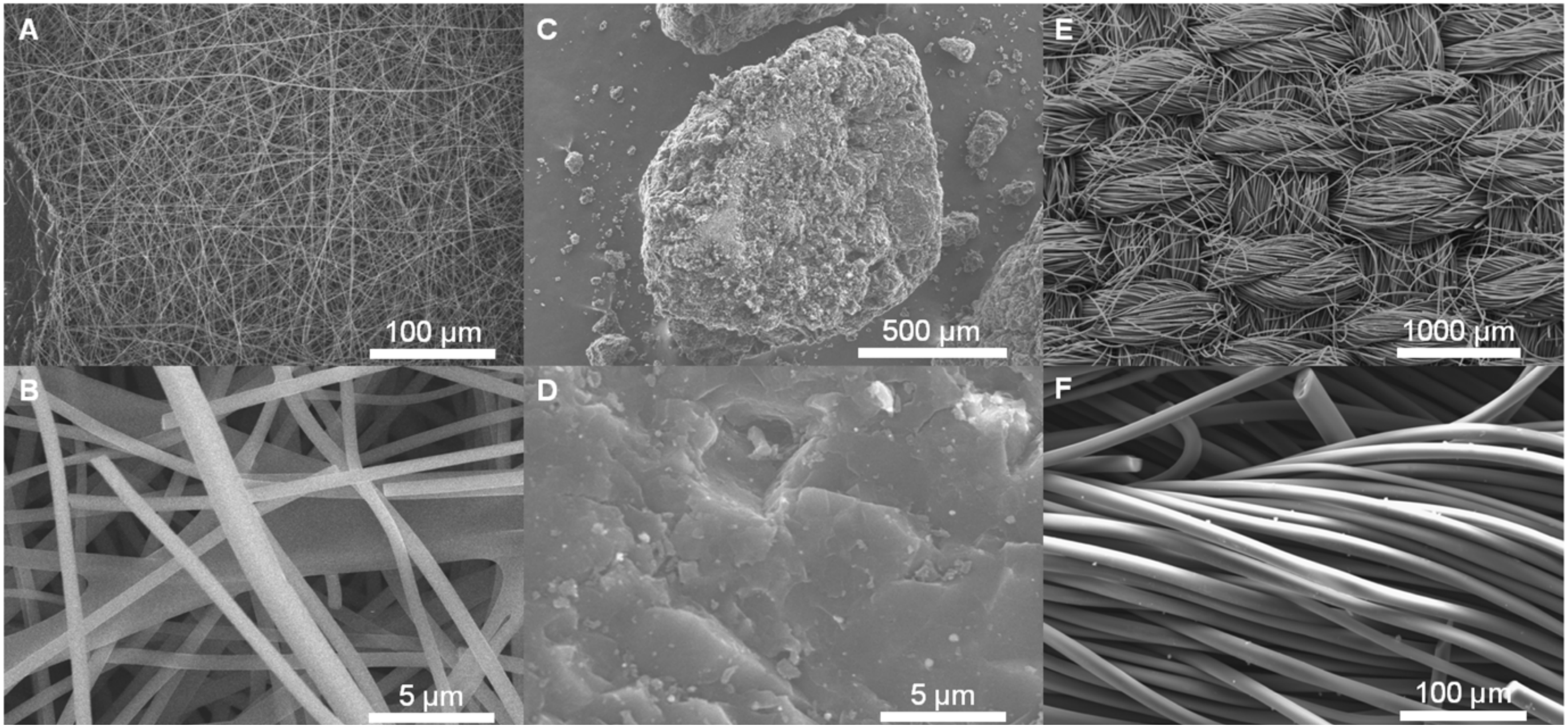


Steady-state desorption at 500 ppm_v

Steady-state desorption at 5,000 ppm_v

Adsorption of Toxic Industrial Chemicals with Novel Carbons

Scanning Electron Micrographs: e-Spin Nanofibers, GAC, Microfibers



Nanofibers
(e-Spin)

Granular Act. Carb.
(BPL)

Microfibers
(ACFC)

Physical and Chemical Properties Nanofibers, GAC, and Microfibers

Property	ACnF	BPL^{TM}	ACFC
Total Pore Volume (cm^3/g)	0.30	0.53	0.64
Micropore Volume (cm^3/g)	0.30	0.47	0.64
Microporosity (%)	100	89.0	99.8
Average Micropore Width (Å)	7.2	8.7	7.7
BET Surface Area (m^2/g)	693	942	1,262

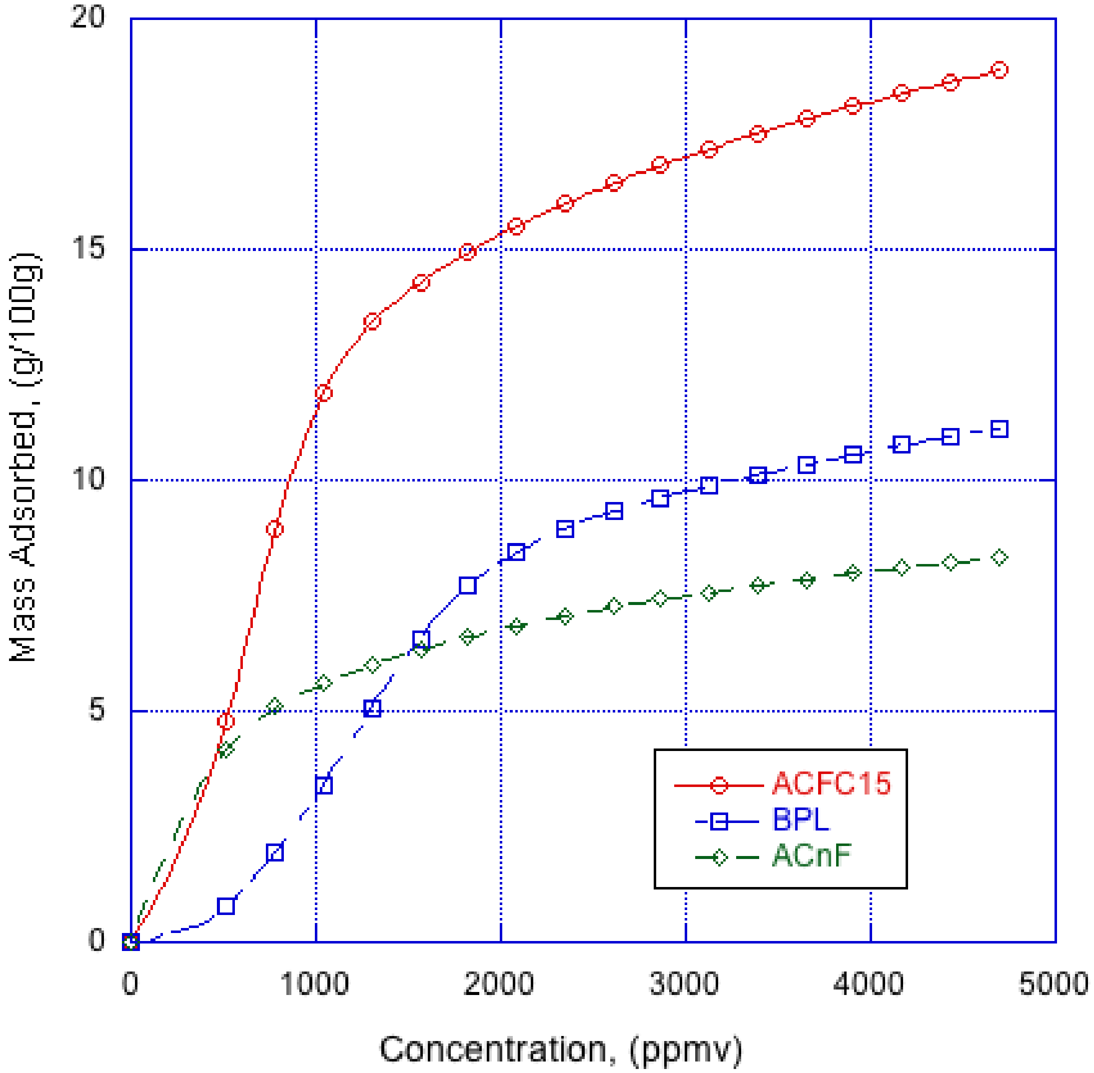
Bulk Analysis (CHN)

Material	Carbon (%)	Nitrogen (%)	Hydrogen (%)	Oxygen (%)
ACnF	81.83	6.45	1.40	10.32
BPL™	89.2	0.8	0.07	9.9
ACFC	95.1	0.4	0.6	3.9

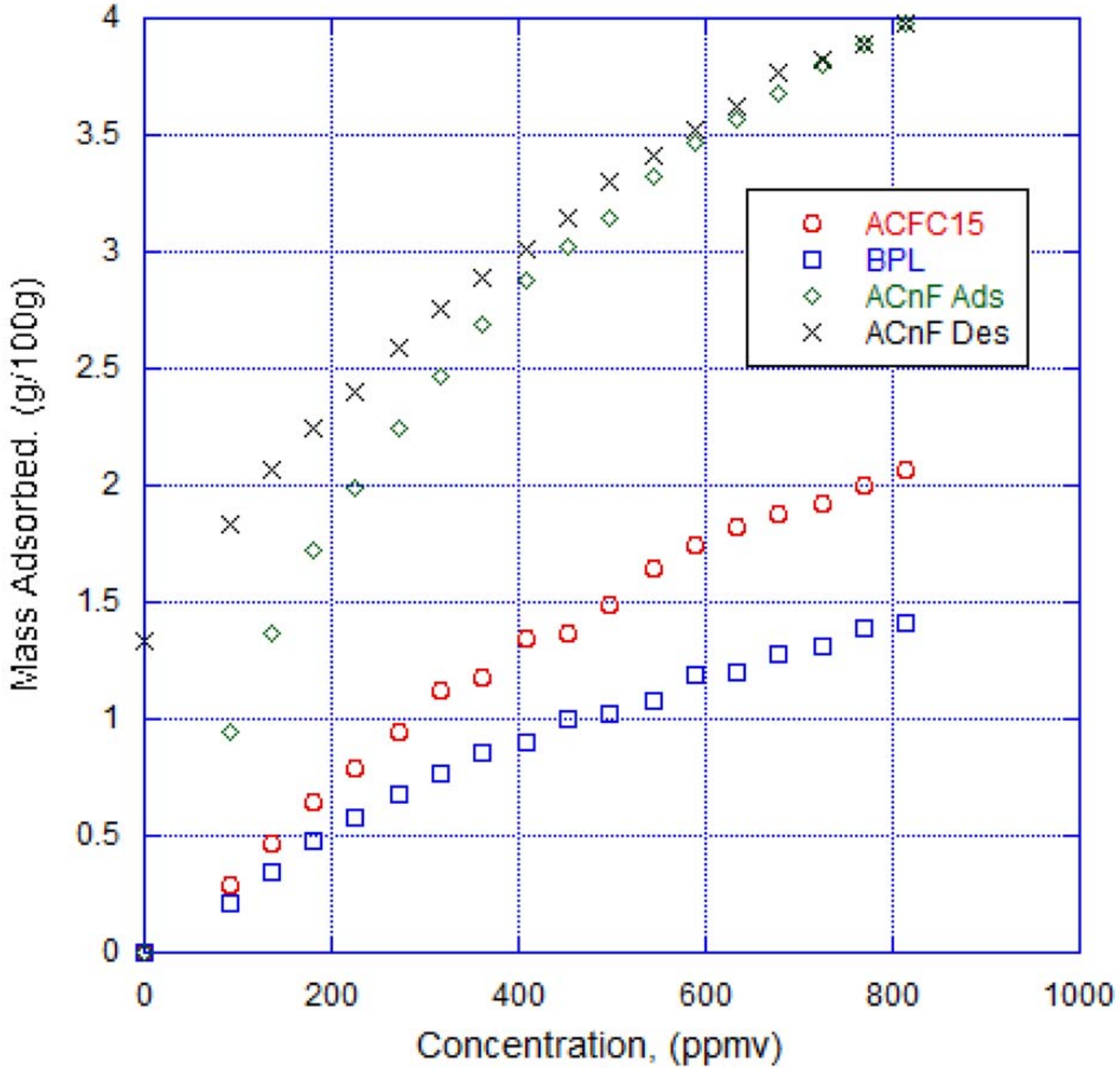
Surface Analysis (XPS^A)

Material	Carbon (%)	Nitrogen (%)	Hydrogen^B (%)	Oxygen (%)
ACnF	85.8 (84.7)	6.9 (9.6)	ND	7.3 (5.0)
BPL™	93.3	0.4	ND	6.3
ACFC	95.4 (94.6)	0 (1.4)	ND	4.5 (3.9)

n-Butane Adsorption Isotherms



SO_2 Adsorption Isotherms



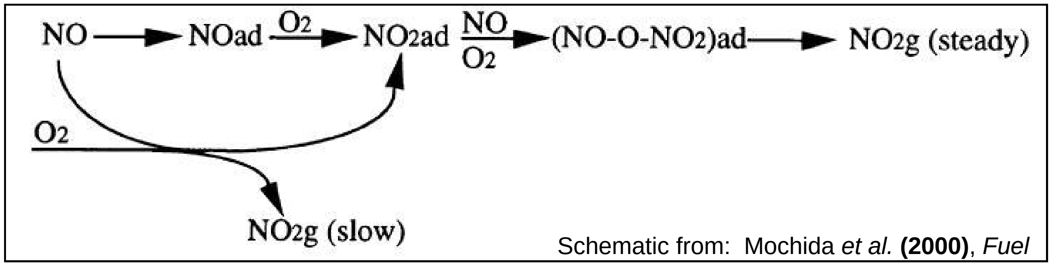
HCN Adsorption Isotherms

Trace Multipollutant Capture

Collaborative research with National Central University and National Taipei University of Technology, Taiwan

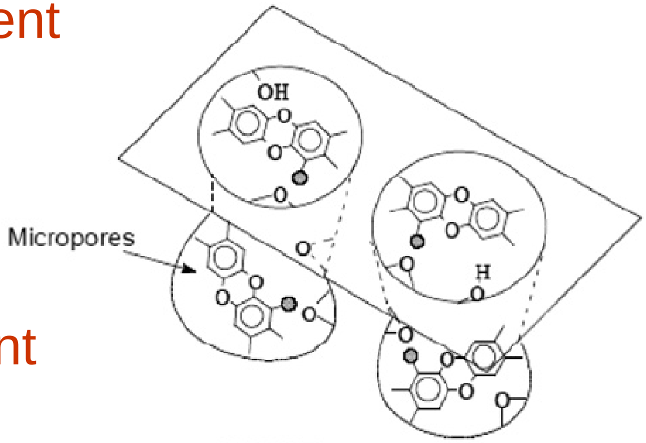
Multi-Pollutant Control Using Carbon-Based Materials

- NO Oxidation
  - Physical Adsorbent
  - Catalyst

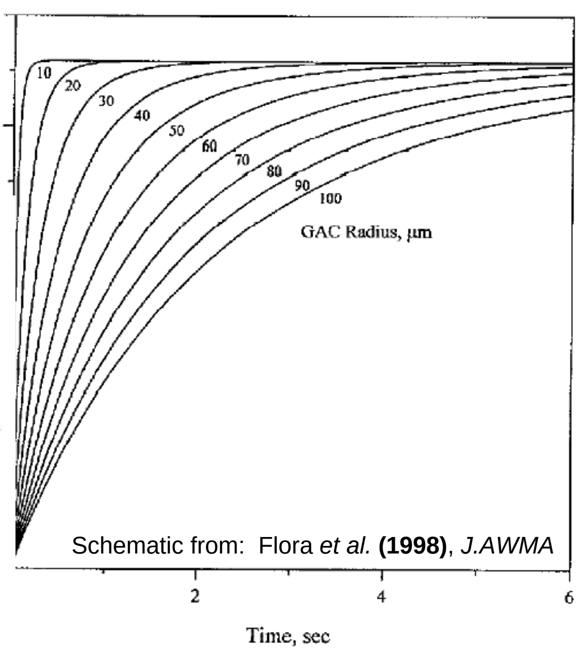


Schematic from: Mochida *et al.* **(2000)**, *Fuel*

- Hg Adsorption and/or Oxidation
  - Physical Adsorbent
  - Chemical Adsorbent
  - Catalyst Support
- PCDD/F Control
  - Physical Adsorbent
  - Catalyst Support



Schematic from: Ottaviani *et al.* **(2011)**, *Micropor Mespor Mat*



Schematic from: Flora *et al.* **(1998)**, *J.AWMA*

The versatility of carbon is clear,
but can these pollutants be controlled simultaneously…?

Multi-pollutant Control – Hg

- Carbon materials are the industry standard for reducing mercury emissions at power plants
  - Activated Carbon Injection (ACI) for removal
    - Physical adsorption – Carbon micropores
    - Chemical adsorption – Carbon surface functionalities

- International and Domestic Collaboration
  - Prof. Hsing-Cheng Hsi, National Taipei University of Technology (NTUT), Taipei, Taiwan
    - Expert on mercury control using carbon-based materials
    - Developed a mercury adsorption reactor at NTUT lab

Multi-Pollutant Control – PCDD/F

- Carbon materials have been used to aid the removal of PCDD/Fs
  - Adsorbent for removal
  - Support for metal nanoparticles to be used as catalysts

- International Collaboration
  - Prof. Moo-Been Chang, National Central University (NCU), Chungli City, Taiwan
    - Expert on PCDD/F measurement and control
    - Prepared a dioxin generation system for generating constant concentration PCDD/F gas streams
    - Prepared a catalytic / adsorption reactor to test PCDD/F destruction or removal from gas streams with a high resolution GC/MS detector

Anticipated Results

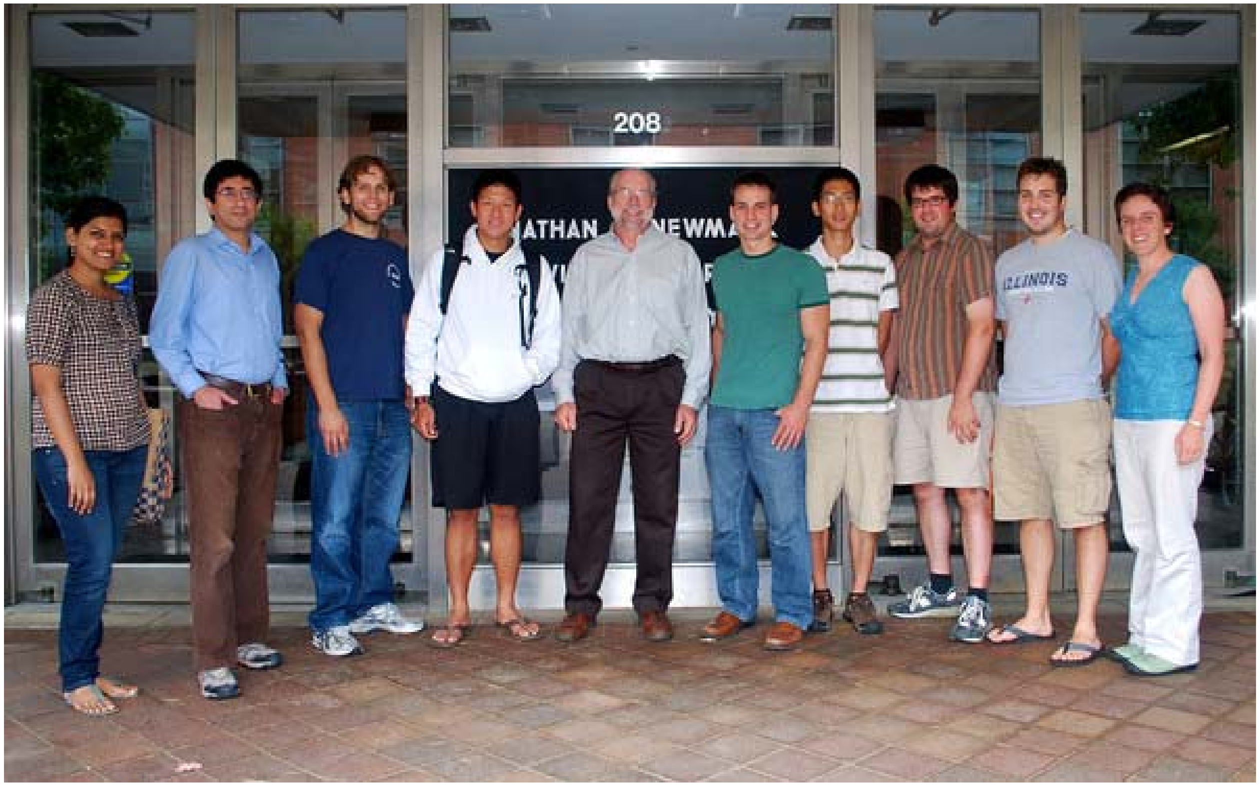
- Removal processes are different for three considered contaminants:
  - NO Oxidation – **Physical Adsorption with catalysis**
  - Mercury – **Chemical Adsorption**
  - PCDD/F – **Adsorption with catalysis**

- Proposed carbon that might be effective for this work:
  - **High microporosity and total pore volume**
    - Increased number of active sites allowing for rapid NO oxidation
  - **Removal of oxygen surface functionalities**
    - Increased adsorption of NO for oxidation
    - Decreased adsorption of H_2O
  - **Bromine surface functionalities**
    - Mercury chemisorption
  - **Iron nanoparticle impregnation**
    - Catalyst for PCDD/F destruction

Summary

- Commercially available activated carbons with novel morphologies have been shown to effectively remove toxic and valuable gases from gas streams: wide range of future applications
- Very important to consider engineering and economic properties
- Research future for combined physical/chemical adsorption with/without catalyst is bright to improve air quality

Comments and Questions?



Rood Research Group

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