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Exposure Science
Kick-off Meeting

Virginia Tech
Invent the Future

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Rapid methods to estimate exposure to SVOCs in indoor environments

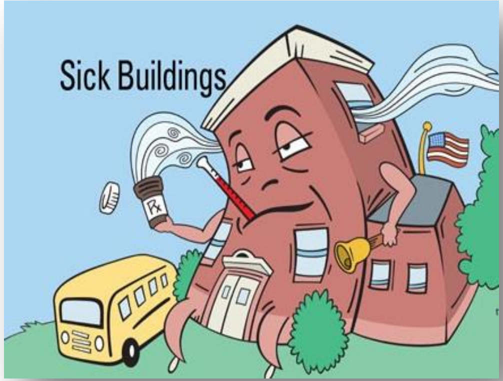
John Little and Linsey Marr

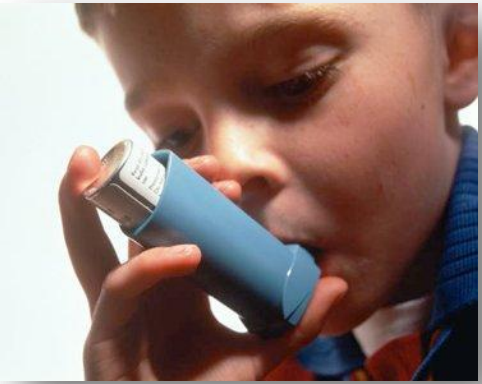
Yaoxing Wu, Mingjie Xie and Steven Cox

Department of Civil and Environmental Engineering

Virginia Tech

1. Introduction
2. Chamber studies
3. Estimating exposure to SVOCs
4. Measurement of key model parameters





VOCs & SVOCs – important indoor pollutants

- **Volatile organic compounds (VOCs)**
  - Vapor pressure ≥ 10 Pa at 20 ºC
  - Examples: formaldehyde, benzene, butanol, etc.
  - Sources: paints, adhesives, carpets, pressed-wood products, floorings, etc.

- **Semivolatile organic compounds (SVOCs)**
  - Vapor pressure in range of 10^{-9} to 10 Pa
  - Examples: phthalate plasticizers, brominated flame retardants, and organophosphate pesticides
  - Sources: polyvinyl chloride (PVC) products, lotions, nail polish, cling film, shampoo, computers, televisions, foams, shower curtains, etc.

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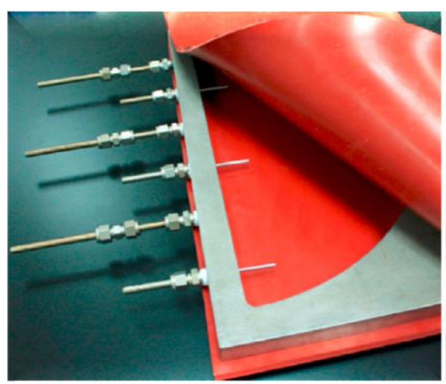
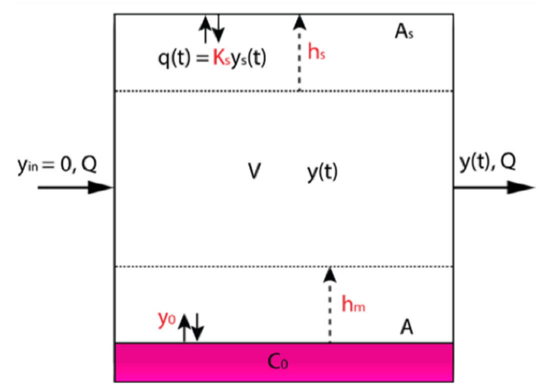




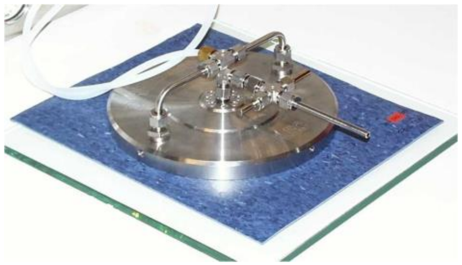
Chamber studies

- Determining emission rates of SVOCs in small chambers is much more difficult than for VOCs

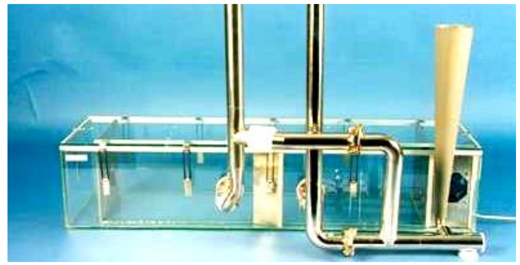
Compound	P_{vap} (Pa)	C_0 (g/m^3)
n-tetradecane	1.0	40
DEHP	4×10^{-5}	260,000

- Emission rates are controlled by external gas-phase resistance and exterior sinks
  - Slow emission rates
  - Very strong sorption to any surfaces (including sampling train)
  - Low gas-phase concentrations
  - Laboratory contamination is ubiquitous

Chamber studies

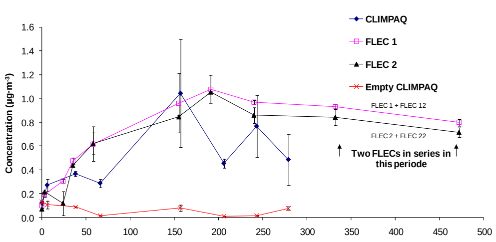


FLEC
(field and laboratory emission cell)

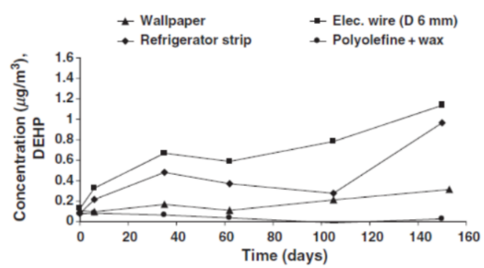


CLIMPAQ
(chamber for laboratory investigations of materials, pollution, and air quality)

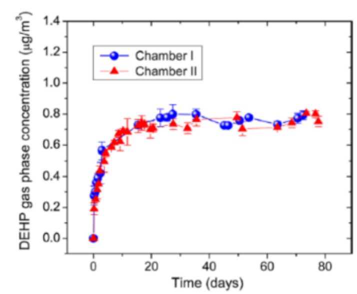
Specially designed chamber



Clausen et al. (2004)

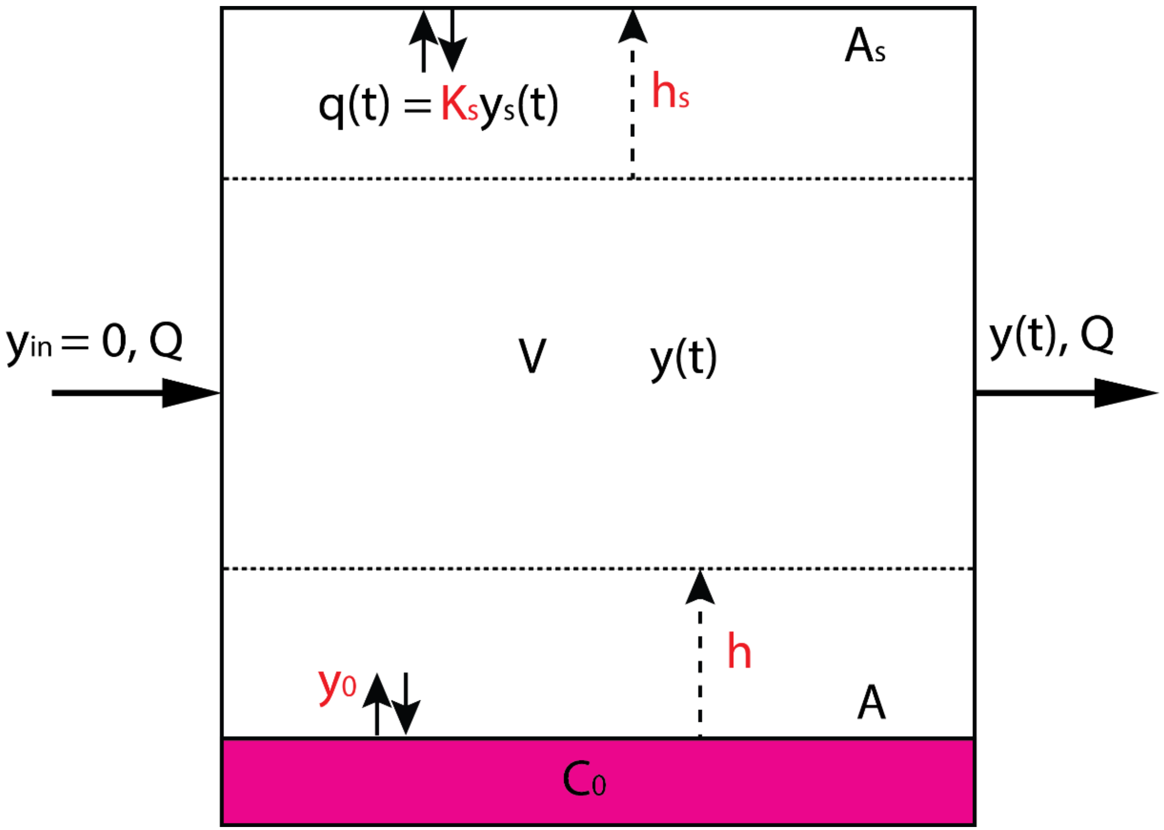


Afshari et al. (2004)

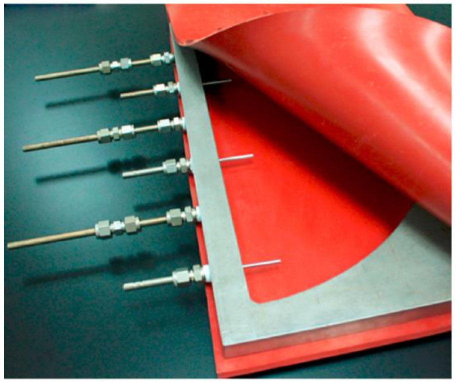


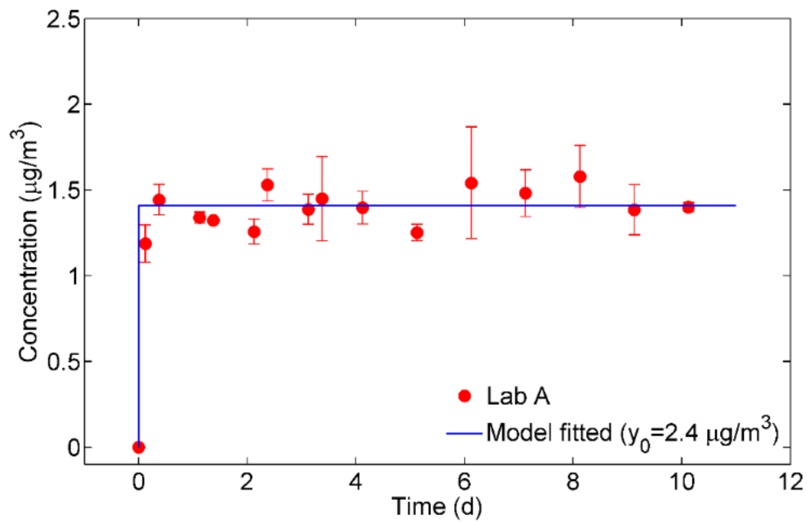
Xu et al. (2012)

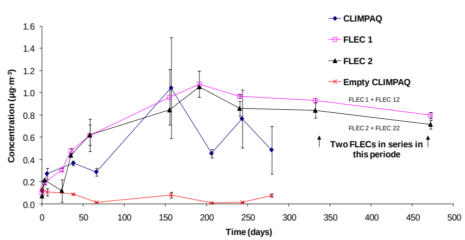
SVOC emission model (simplified)



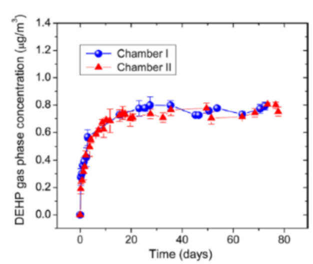
SVOC emission model – ILS study



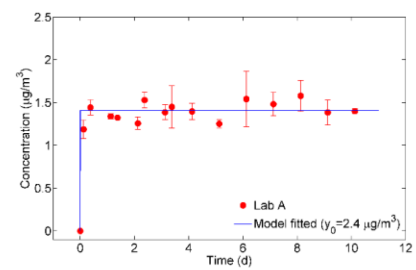




150 days
Clausen et al. (2004)



30 days
Xu et al. (2012)



2 days
Wu et al. (2014)

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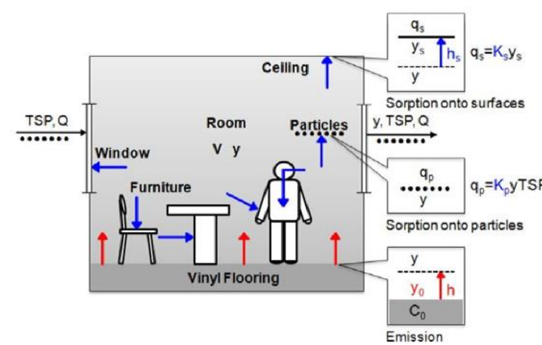
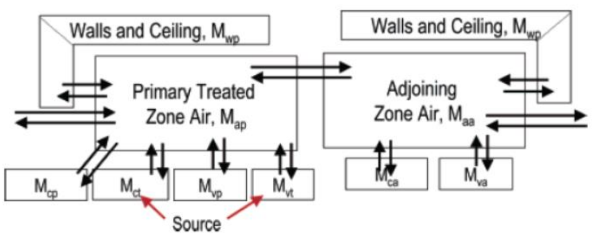
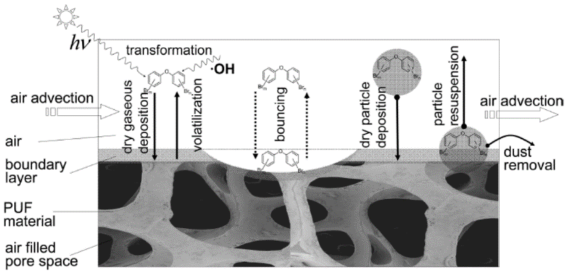


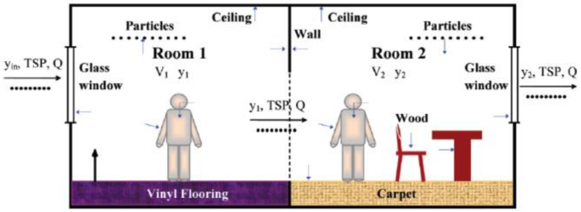
SVOC – fate and transport models



Indoor fugacity model
(Bennett and Furtaw, 2004)

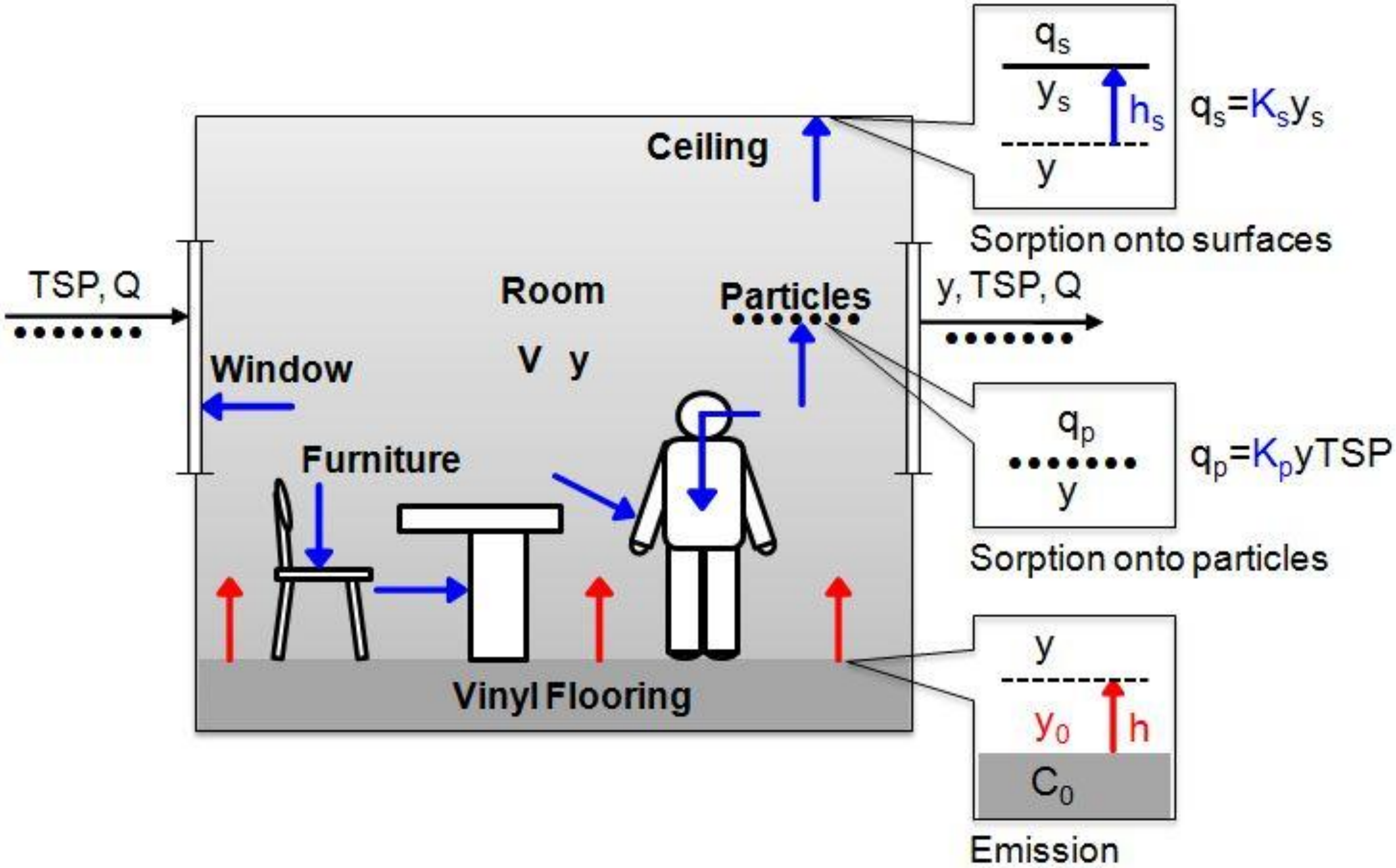


Multimedia model
(Zhang et al., 2009)



Two-room model
(Xu et al., 2009)

SVOC exposure model including particles



Little, Weschler, Nazaroff, Liu and Cohen Hubal (2012)

Estimating SVOC exposure

- Steady-state mass balance on SVOC in room

$$h \times (y_0 - y) \times A = Q \times y + Q \times (K_p \times TSP \times y)$$

- Gas-phase concentration is given by

$$y = \frac{h \times y_0 \times A}{h \times A + Q^*}$$

where

$$Q^* = (1 + K_p \times TSP) \times Q$$

Particle + dust partition coefficients + skin permeability

Parameter	Units	Equation
Particle/air partition coefficient (K_p)	$m^3/\mu g$	$K_p = f_{om\_part} \times K_{oa} / \rho_{part}$
Dust/air partition coefficient (K_{dust})	m^3/mg	$K_{dust} = f_{om\_dust} \times K_{oa} / \rho_{dust}$
Permeability through stratum corneum (k_{p_cw})	cm/s	$\log(k_{p\_cw}) = 0.7 \log(K_{ow}) - 0.0722\ MW^{2/3} - 5.252$
Ratio of stratum corneum to viable epidermis (B)	-	$B = [k_{p\_cw} \times (MW)^{0.5}]/2.6$
Permeability through stratum corneum/viable epidermis (k_{p_w})	cm/s	$k_{p\_w} = k_{p\_cw} / (1 + B)$
Permeability from skin surface to dermal capillaries (k_{p_b})	cm/s	$k_{p\_b} = k_{p\_w} \times K_{wa}$
Overall permeability from bulk air to dermal capillaries (k_{p_g})	m/d	$k_{p\_g} = [(1/v_d) + (1/k_{p\_b})]^{-1} \times 864$

Exposure parameters for 3-year old child

Parameter	Value	Units
Inhalation rate (InhR)	0.64	$(m^3/kg)/d$
Dust ingestion rate (IngR)	4.3	(mg/kg)/d
Skin surface area (SA)	0.61	m^2
Fraction skin exposed (f_{SA})	1	(-)
Exposure duration (ED)	0.91	(-)
Body weight (BW)	13.8	kg

Estimating exposure to SVOCs (DEHP in vinyl flooring)

Exposure pathway	DEHP (µg/kg)/d	Equation
Inhalation (air)	0.12	$y \times InhR \times ED$
Inhalation (particles)	0.57	$y \times K_p \times TSP \times InhR \times ED$
Ingestion (dust)	18	$y \times K_{dust} \times IngR$
Dermal sorption (from air)	1.1	$(y \times k_{p\_g} \times SA \times f_{SA} \times ED)/BW$
Total	20	

Estimating exposure to SVOCs in various products

Exposure pathway	DEHP (µg/kg)/d	DnBP (µg/kg)/d	BDE-47 (µg/kg)/d	Chlorpyrifos (µg/kg)/d
Inhalation (air)	0.12	0.34	1.4×10^{-4}	0.32
Inhalation (particles)	0.57	0.02	3.5×10^{-5}	0.01
Ingestion (dust)	18	1.6	3.2×10^{-3}	0.59
Dermal sorption (from air)	1.1	2.7	1.0×10^{-5}	0.23
Total	20	4.6	3.5×10^{-3}	1.15

EPA project research objectives

1. Develop novel methods to measure model parameters (***C_0*** and ***y_0***) for representative sources that emit different SVOCs;
2. Develop novel methods to determine surface/air partition coefficients (***K_s***) for interior surfaces including airborne particles (***K_p***), dust (***K_{dust}***) and skin (***K_{skin}***) and develop correlations;
3. Conduct single-source **chamber tests** and validate the single-source model; and
4. Evaluate **assumptions** of rapid single-source and single-phase methods and characterize the uncertainty inherent in model predictions.

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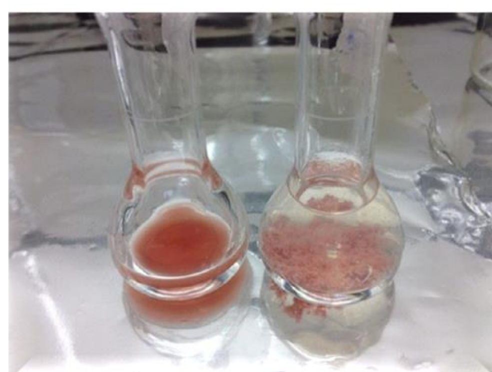
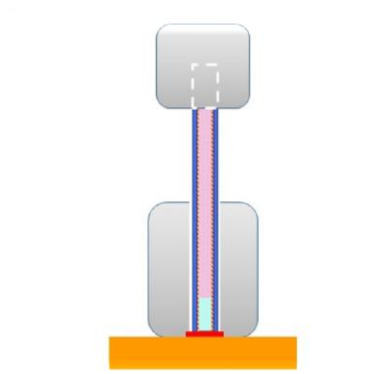




Measurement of C_0

Dissolve PVC using tetrahydrofuran (THF)

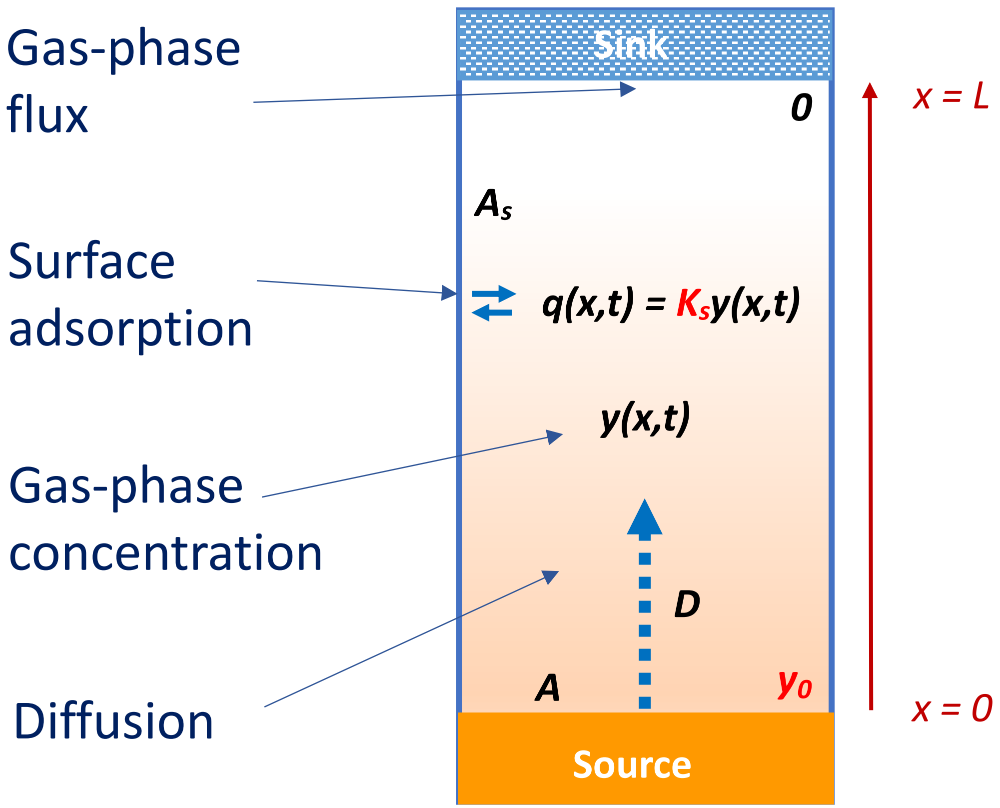
↓

Add methanol to precipitate PVC

↓

Analyze filtered liquid with GC-MS

Measurement of y_0 – diffusion tube



- Governing equation:

$$\frac{\partial y(x,t)}{\partial t} = \left(\frac{D}{R}\right)\frac{\partial^2 y(x,t)}{\partial x^2}$$

$$R = 1 + \frac{4}{d}K_s$$

- Initial condition:

  $y = 0$ for $t = 0$, $0 < x < L$

- Boundary condition:

  $y = y_0$ for $t \geq 0$, $x = 0$

  $y = 0$ for $t \geq 0$, $x = L$

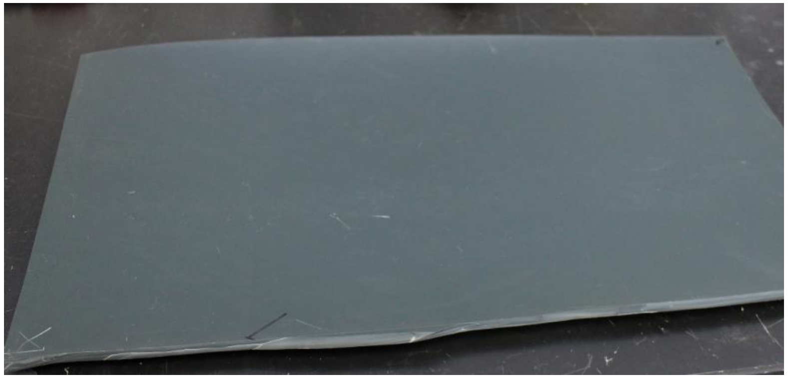
Diffusion tube – compounds and materials

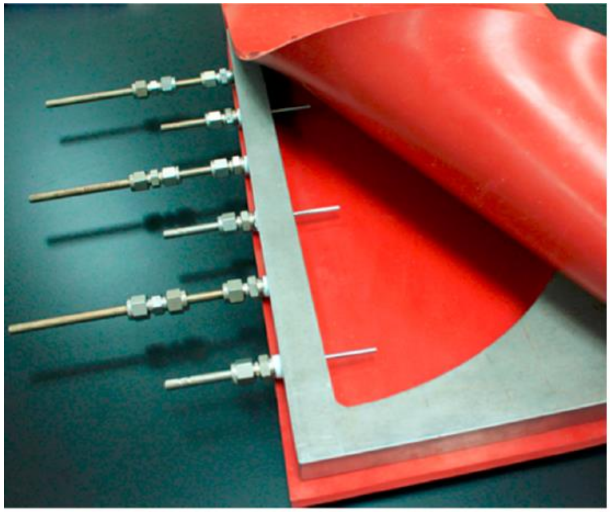
- DEHP ($\mathbf{P}_{\mathbf{vap}}$: 4×10^{-5} Pa)

  Green Vinyl Flooring ~ 15 wt %

- DiBP ($\mathbf{P}_{\mathbf{vap}}$: 6×10^{-3} Pa) & DnBP ($\mathbf{P}_{\mathbf{vap}}$: 4×10^{-3} Pa)

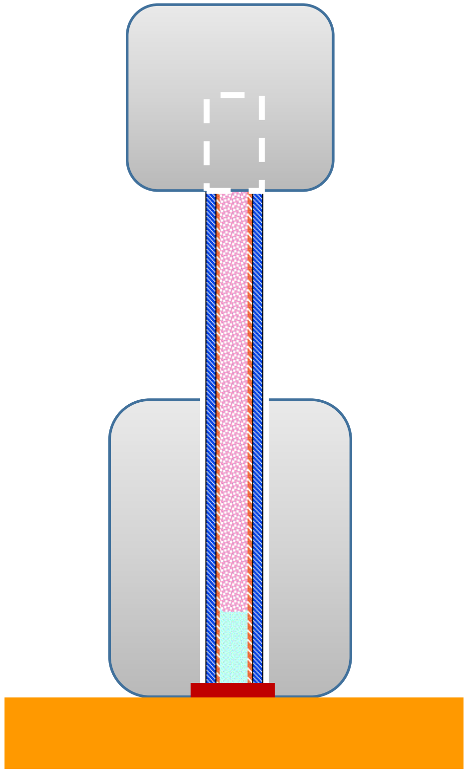
  Red Vinyl Flooring ~ 5 wt %

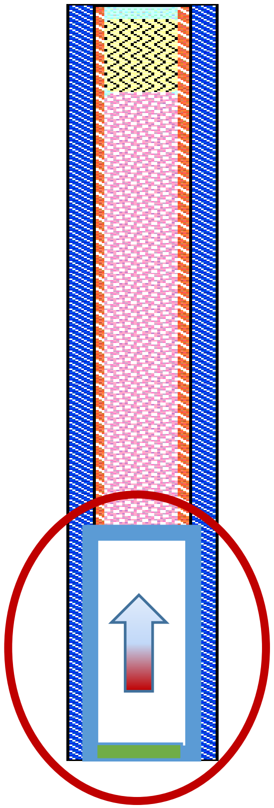




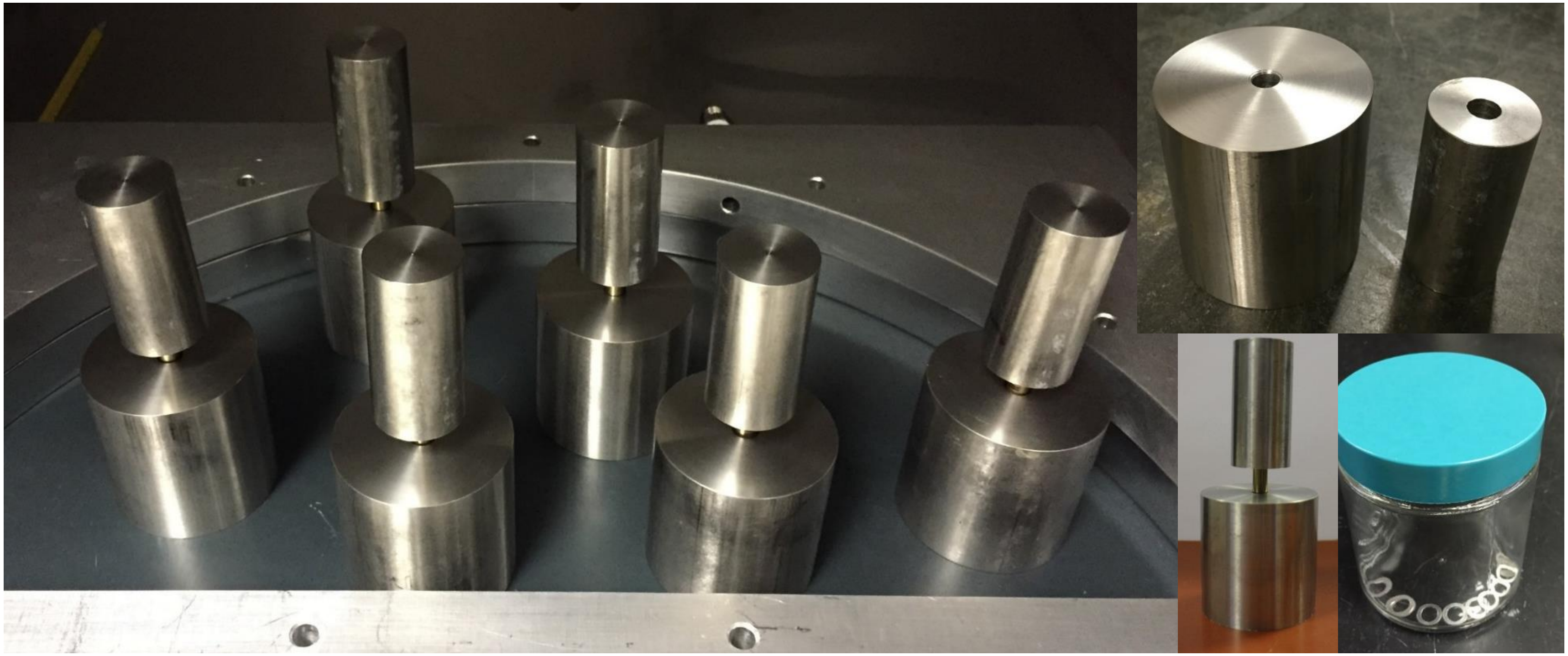
Diffusion tube – experimental setup

- **Diffusion tube**
  - Standard Tenax-TA sorbent tube
  - Stainless steel surface
- **Sampling**
  - Sorbent tube is inserted through cylinder and has a shim at bottom to prevent direct contact
  - Cap cylinder rests on the top of the tube, and holds the tube and shim firmly against material surface
- **TD-GC-FID for sample analysis**





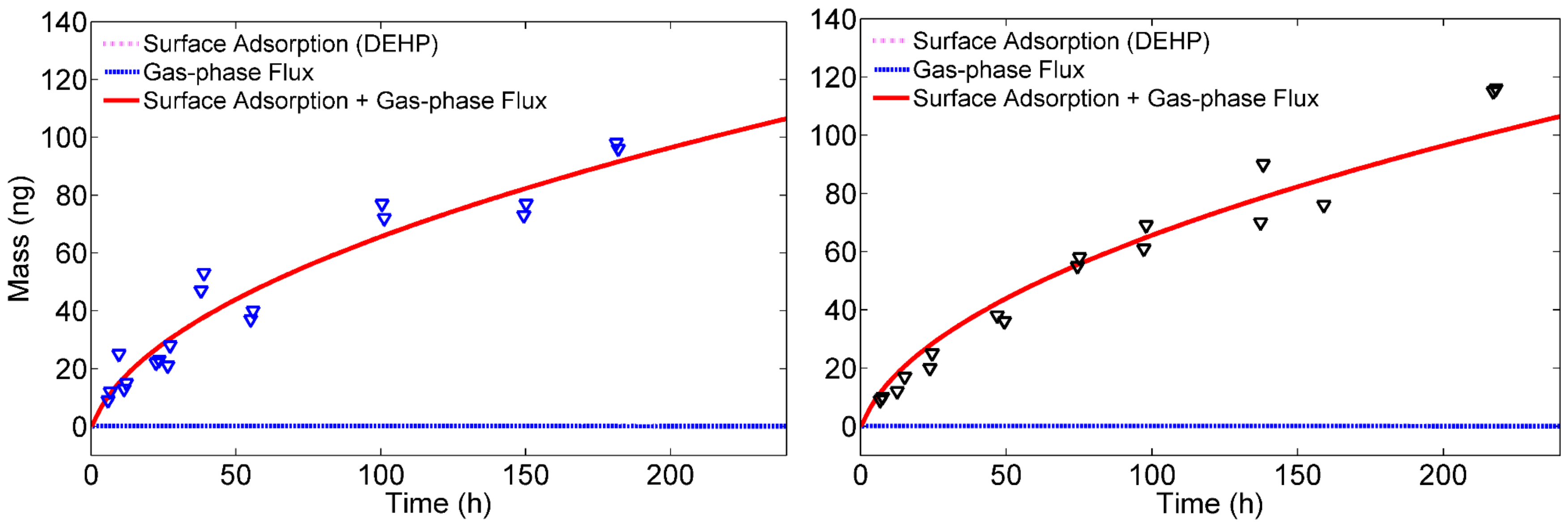
Diffusion tube – experimental setup



Diffusion tube – results (DEHP)

d = 0.005 m
$D = 3.8 \times 10^{-6}$ m²/s
L = 0.015 m
Li = 0.14 mm (shim thickness)

$y_0 = 2.4\ \mu g/m^3$
K_s = 1800 m



Diffusion tube – results (DiBP & DnBP)

DiBP

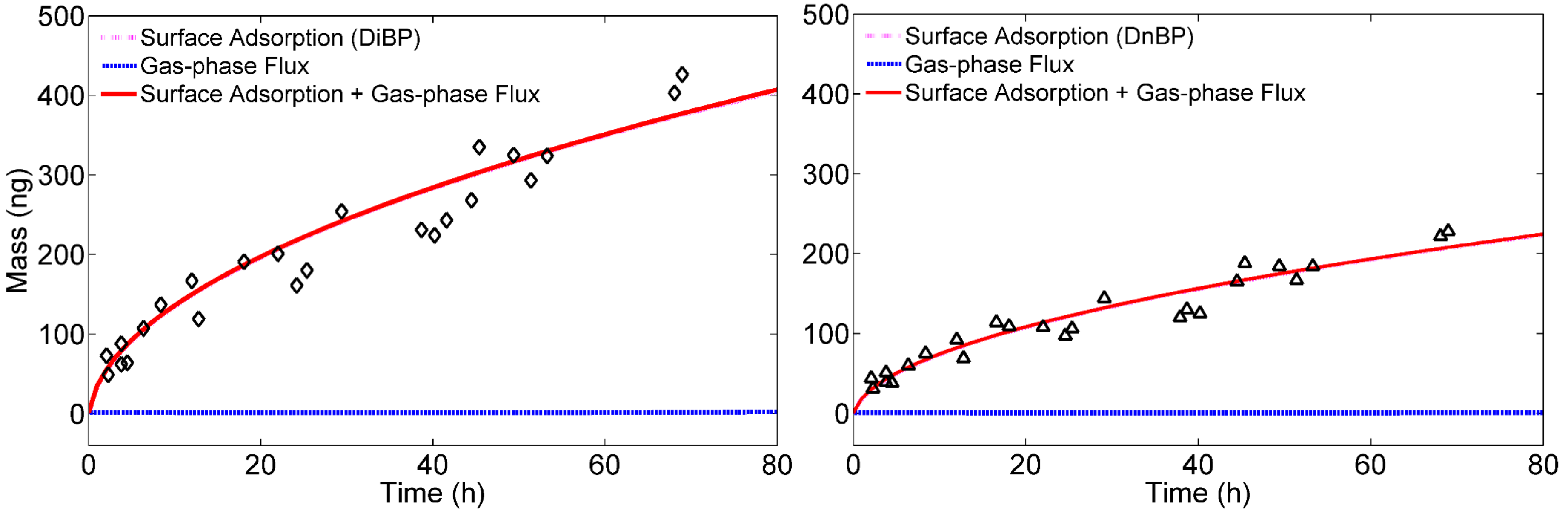
y_0 = 50 µg/m^3

K_s = 130 m

DnBP

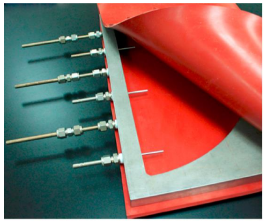
y_0 = 27 µg/m^3

K_s = 150 m



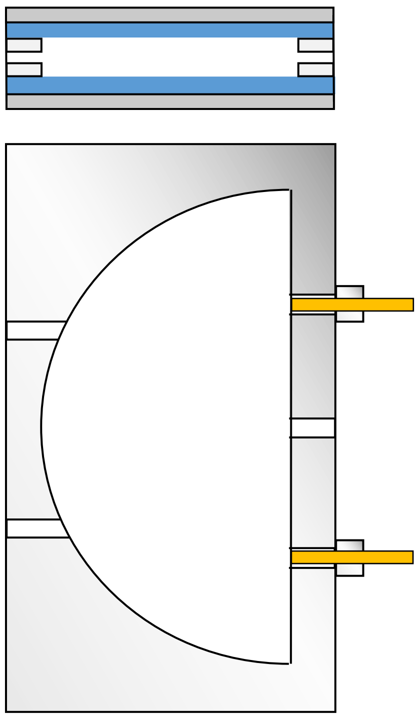
Diffusion tube – compare results

	This study (Diffusion tube)	Xu et al. (Chamber test)
DEHP	2.4 μg/m^3 1800 m	2.4 μg/m^3 1500 m
DnBP	27 μg/m^3 150 m	25 μg/m^3 80 m
DiBP	50 μg/m^3 130 m	

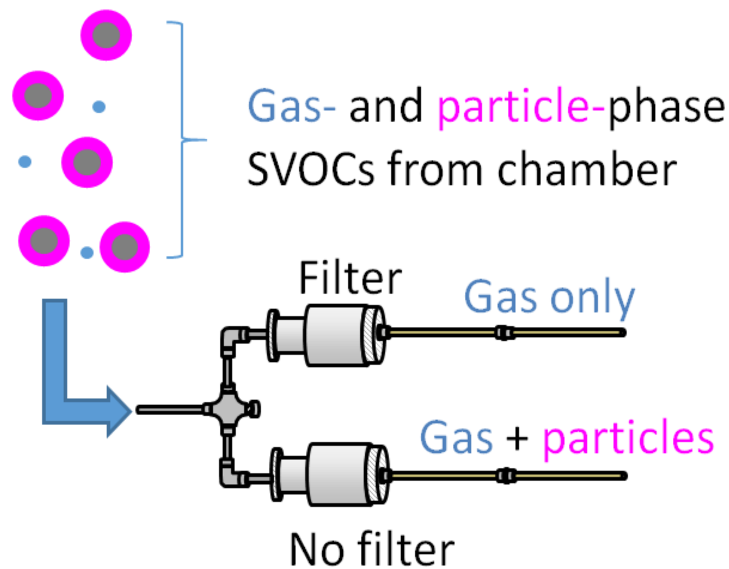


Liang and Xu (2014)

Measurement of K_p – chamber test



$$K_p = \frac{q_p}{y \cdot TSP}$$

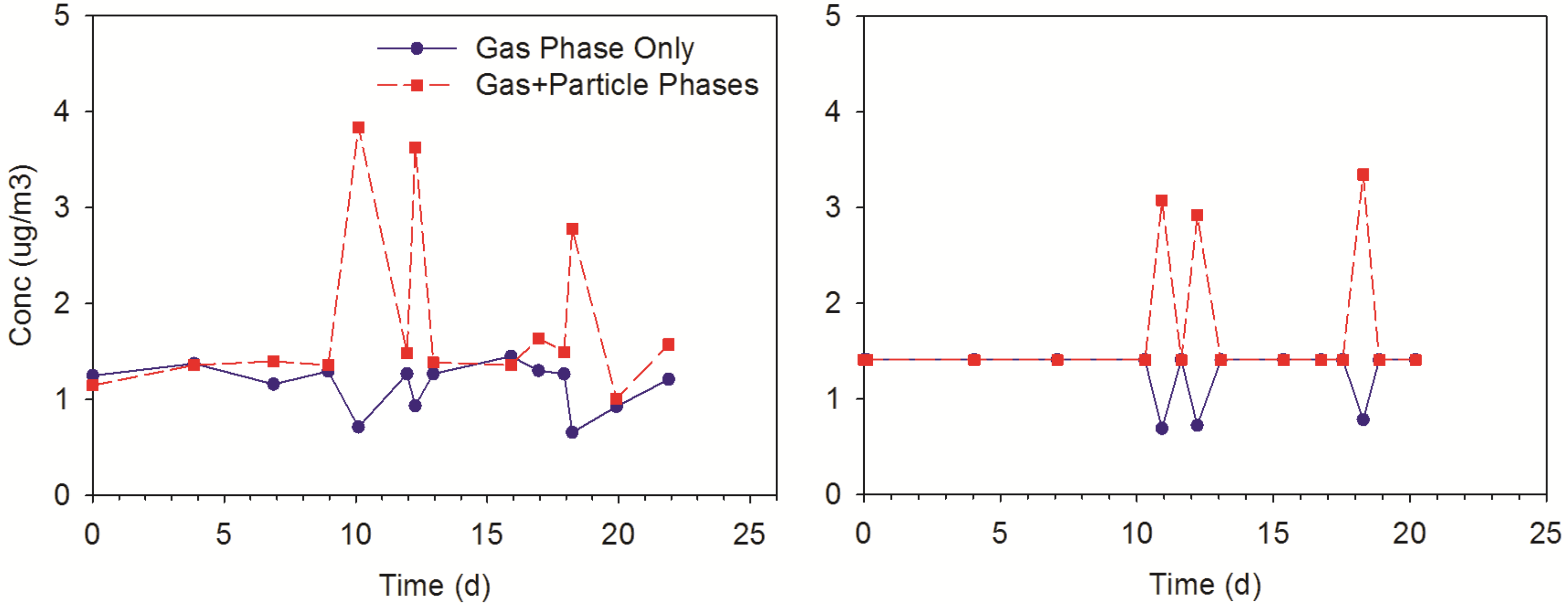


Particle capturing
PTFE filter 0.2 μm

Tenax tube

Measurement of K_P – results and model

$K_p = 0.034 \pm 0.006\ m^3/\mu g$, $n = 3$



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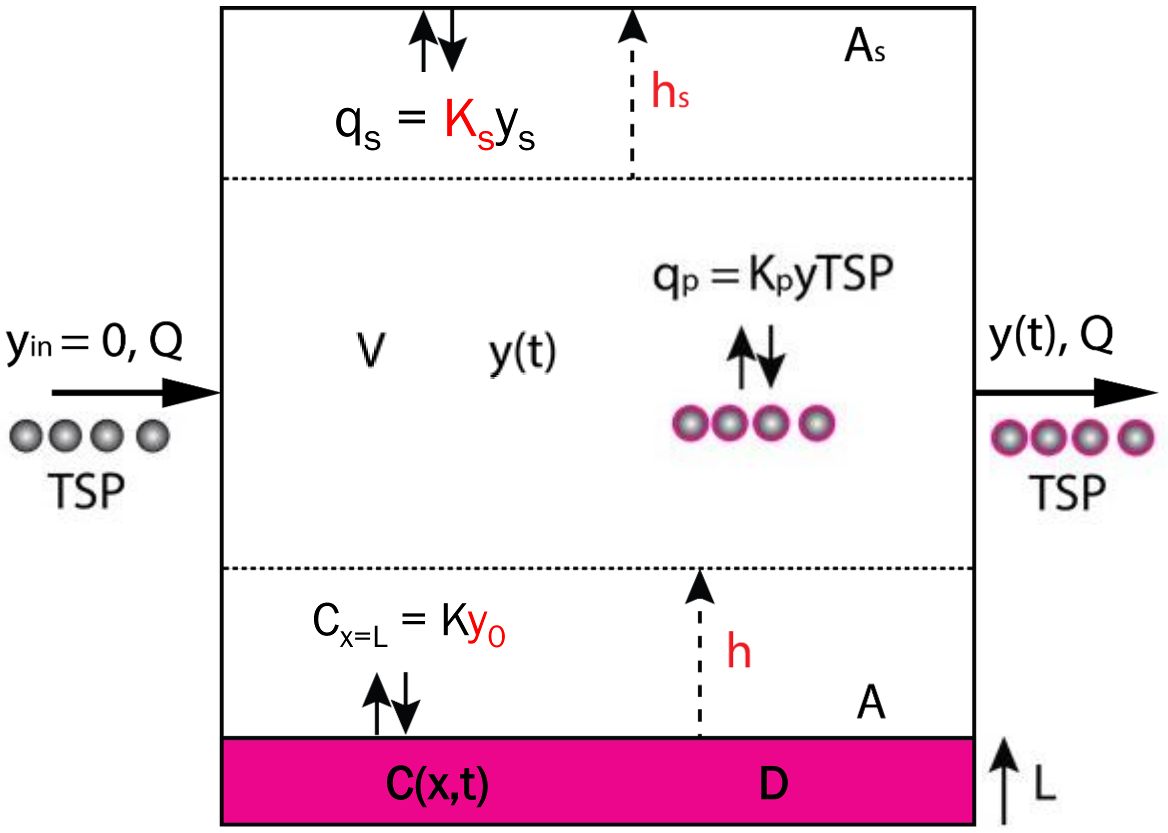
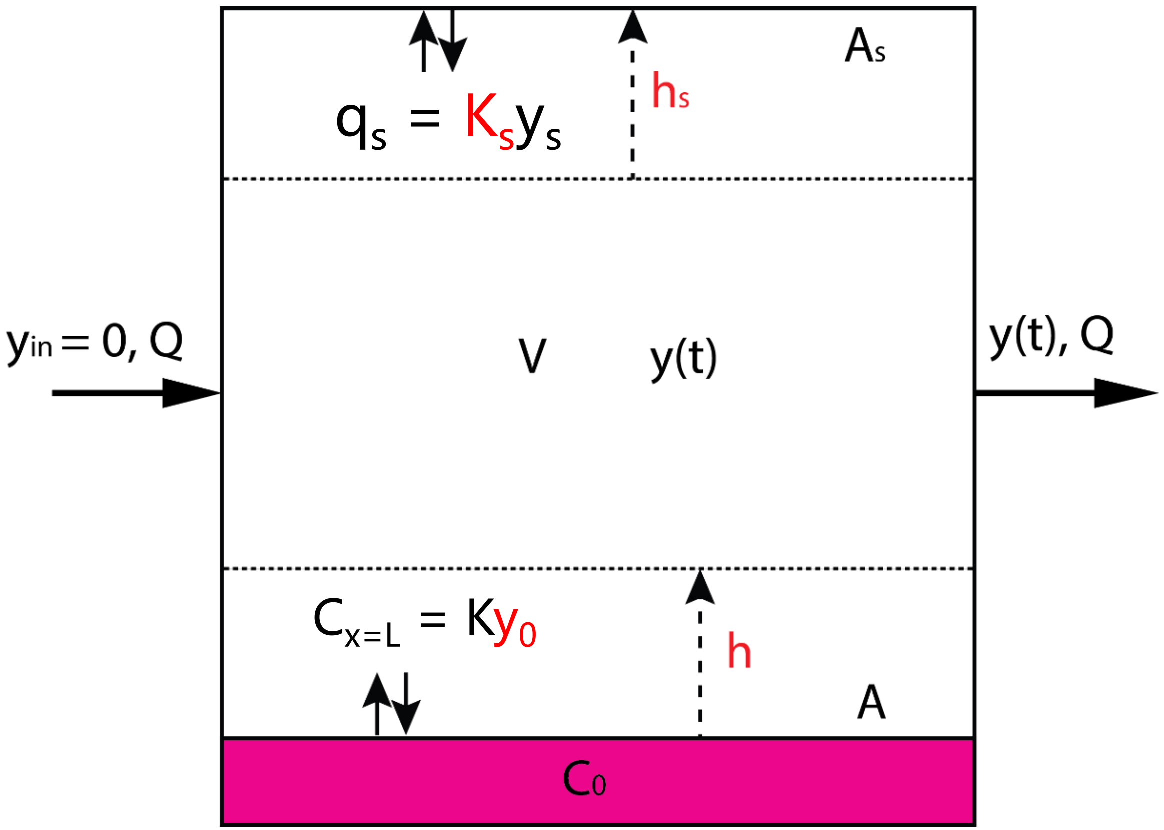
SVOC emission model



SVOC emission model (simplified)



SVOC emission model