Electronic Supplementary Material

Experimentally Validated Mathematical Model of Analyte Uptake by Permeation Passive Samplers

F. Salim,[a] M. Ioannidis[b] and T. Górecki*[a]

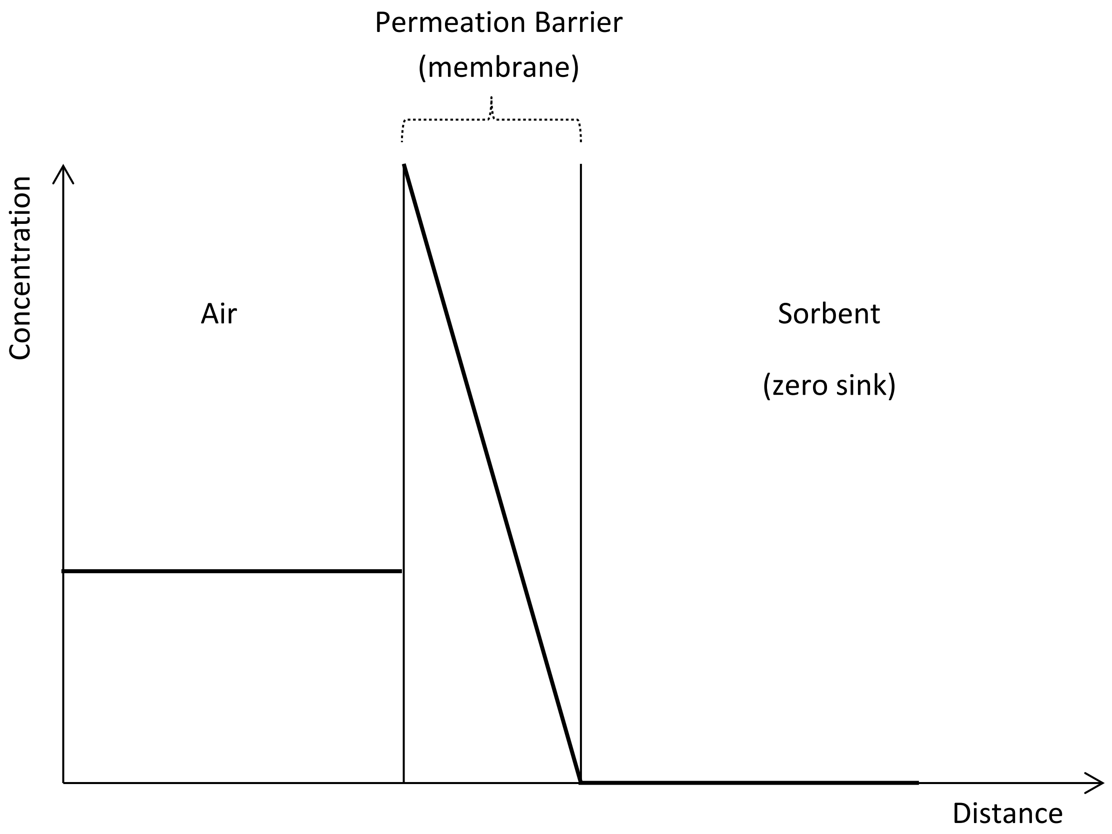

Figure S1: An ideal concentration profile in a permeation-based passive sampler

Evaluation of Mass Transfer Efficiency Using the WMS

Experimental Setup

The Waterloo Membrane sampler, WMS, was exposed to an atmosphere of nitrogen with vapors of 52 VOC using the setup presented in Figure S2. In this setup, the standard gas mixture in nitrogen was delivered from a pressurized cylinder at a flow rate of 10 mL/min and diluted with a nitrogen flow of 500 mL/min. The flow of the standard gas mixture and the diluting nitrogen were controlled using mass flow controllers (MKS, Andover, MA, 0-100 mL/min and 0-5000 mL/min respectively) connected to an MKS 4-channel readout system (Andover, MA, Type 247). The diluted standard gas mixture then entered the exposure chamber. This chamber consisted of a cylindrical glass jar of about 10-liter volume, equipped with a circulation fan inserted through the lid. The samplers were inserted through a hole drilled in the lid and kept closed during the exposure. The glass jar was wrapped with an insulated jacket connected to a water circulation thermostat (TOMSON, NESLAB Instrument, Inc.). The concentrations inside the chamber were evaluated using active sampling by pumping the exposure mixture from the chamber through sorption tubes packed with Anasorb 747 at flow rates ranging between 24 to 26 mL/min and times between one and two hours.

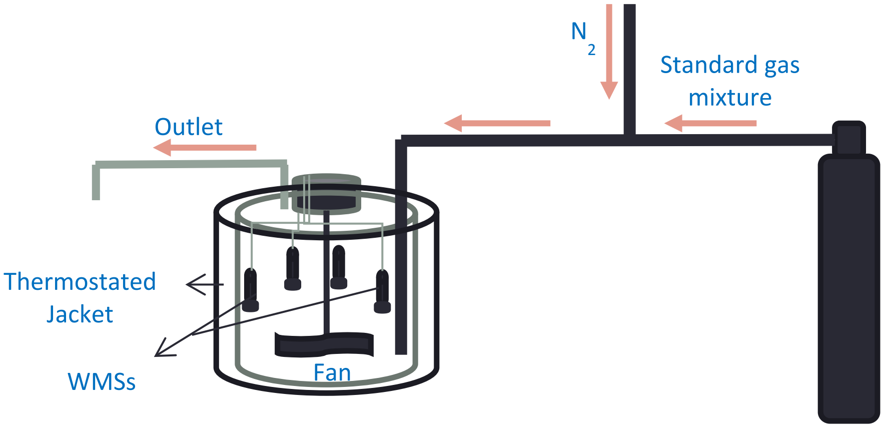

Figure S2: Experimental setup used to evaluate mass transfer efficiency using the microvial WMS

Waterloo Membrane Sampler (WMS)

The modified microvial WMS was prepared as described in the experimental section of the original paper except that the sampler was filled with ~165 mg of Anasorb 747® (SKC, PA, USA) as a sorbent. After each exposure, the sorbent was divided into two portions: Portion 1 included the layer of sorbent in contact with the sorbent (~ 45±5 mg) and Portion 2 included the rest of the sorbent deeper in the vial. The two portions were analyzed separately and for some samples Portion 2 was further sub-divided into two parts.

Desorption of Analytes

Anasorb 747® used in both sorption tubes and WMSs was transferred after sampling into 4 ml glass vials with PTFE/SIL screw caps. To each sample, one ml of CS_2 (purchased from Sigma-Aldrich, Canada) was added. The vials were subsequently sealed and left at ambient temperature for 40 min with intermittent shaking. For analysis, aliquots from the extract were drawn and transferred into 2 ml crimp top chromatographic vials with 100 µl glass inserts (Chromatographic Specialties Inc.).

GC-MS instrument

Agilent 6890 GC- 5973 MS system was used for the analysis. The system is equipped with a 7683 Agilent autosampler with a tray of a 100-sample capacity and a Hewlett Packard (HP) 3683 injector. An Rxi®-624Sil MS capillary column (60 m × 0.32 mm ID × 1.8 µm film thickness) was used with helium as the carrier gas. Chemstation software was used for data acquisition.

GC-MS method

The injection was performed in split mode at 2:1 split ratio and 250 °C inlet temperatures. The injection volume was 1 µl. The carrier gas flow rate was set at 2 ml/min. The oven temperature program was set as follows: 35 °C for 5 min, a ramp of 4 °C/min up to 220 °C, held for 3 min. External standards were used for multipoint calibration. Selected Ion Monitoring (SIM) mode was used with 2-3 ions for each compound. The list of analytes and target ions are presented in Table S1.

Table S1: List of analytes and target ions used in the study

Analyte	Ions
1,1-Dichloroethylene	96, 61
Dichloromethane	49, 84
trans-1,2-Dichloroethylene	61, 96
1,1-Dichloroethane	63, 65
cis-1,2-Dichloroethylene	61, 96
2,2-Dichloropropane	77, 41
Bromochloromethane	49, 130
Chloroform	83, 85, 47
1,1,1-Trichloroethane	97, 99
1,1-Dichloro-1-propene	75
Carbon tetrachloride	117, 119
Benzene	78, 77
1,2-Dichloroethane	62, 64
Trichloroethylene	95, 130
1,2-Dichloropropane	63, 62, 41
Dibromomethane	93, 174
Bromodichloromethane	83, 85
Toluene	91, 92
1,1,2-Trichloroethane	97, 83
Tetrachloroethylene	166,164
1,3-Dichloropropane	76, 41
Dibromochloromethane	129, 127
1,2-Dibromoethane	109, 107
Chlorobenzene	112, 77
Ethylbenzene	91, 106
1,1,1,2-Tetrachloroethane	133, 131
p-Xylene + m-Xylene	91, 106
o-Xylene	91, 106
Styrene	104, 103, 78
Bromoform	173, 171
Isopropylbenzene	105, 120
Bromobenzene	77, 156
1,1,2,2-Tetrachloroethane	83, 85
1,2,3-Trichloropropane	75,77
Propylbenzene	91, 120
2-Chlorotoluene	91, 126
4-Chlorotoluene	91, 126
1,2,4-Trimethylbenzene	105, 120
tert-Butylbenzene	119, 91, 134
1,3,5-Trimethylbenzene	105, 120
sec-Butylbenzene	105,134, 91
p-Isopropyltoluene	119,134,91
1,2-Dichlorobenzene	146, 148
1,4-Dichlorobenzene	146, 148
1,3-Dichlorobenzene	146, 148
Butylbenzene	91, 92, 134
1,2-Dibromo-3-chloropropane	157, 75
1,2,4-Trichlorobenzene	180, 182
Hexachloro-1,3-butadiene	225, 227, 223
Naphthalene	128, 127, 129
1,2,3-Trichlorobenzene	180,182

Results

The results presented in Figure S3 demonstrated accumulation of analytes in the sorbent layer near the membrane surface, while the rest of the sorbent was found to be virtually analyte-free. Small analyte amounts were found in the second portion in some cases, but that could be attributed to imprecise separation of the second portion from the first portion of the sorbent.

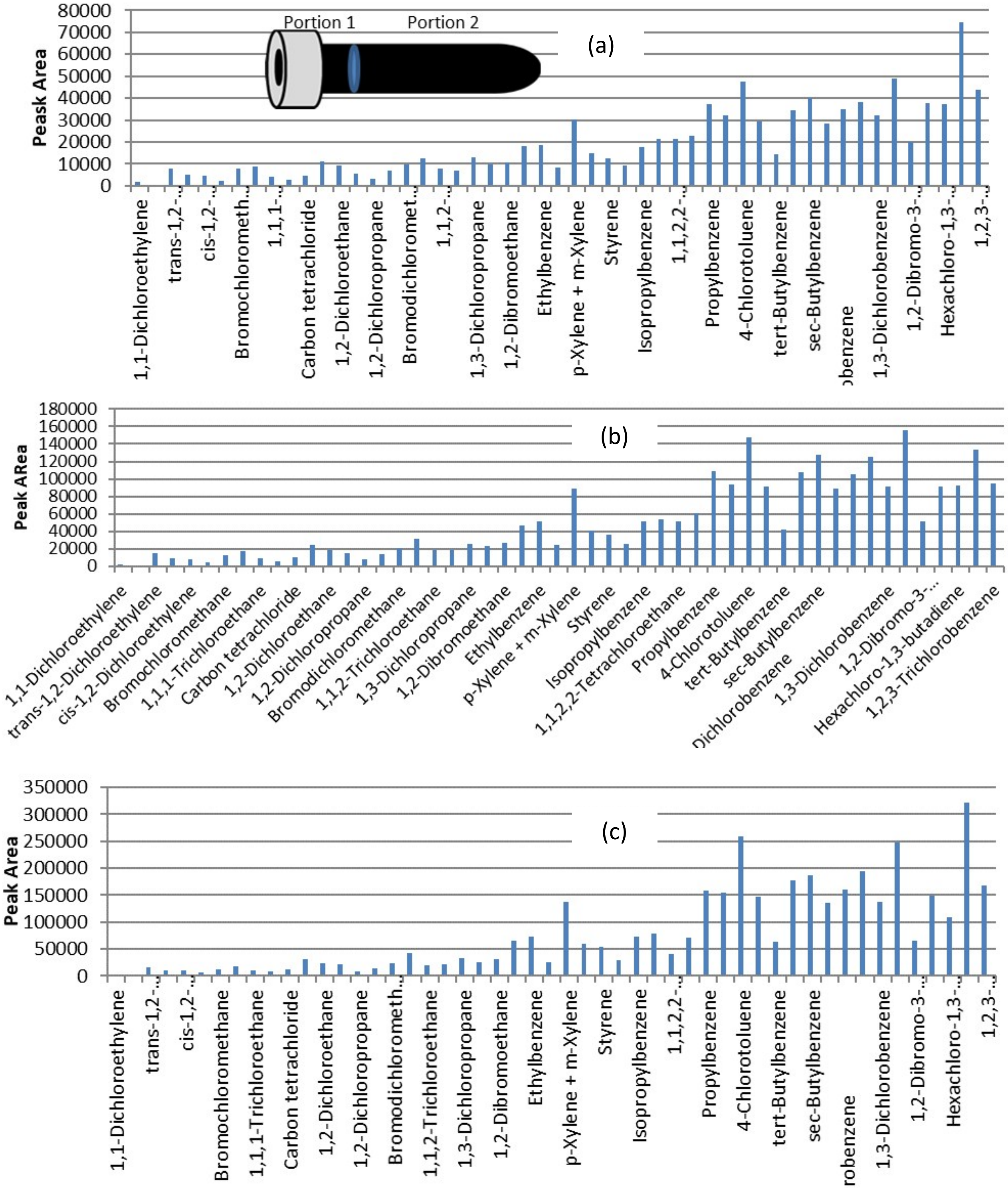

Figure S3: Distribution of analytes between the top portion (Portion 1) near the membrane surface, represented by the blue bars, and in Portion 2 deeper inside the vial, represented in red lines (which do not appear clearly in the figure due to the very negligible amounts found in this portion). The samplers were exposed for two days (a), five days (b) and seven days (c)

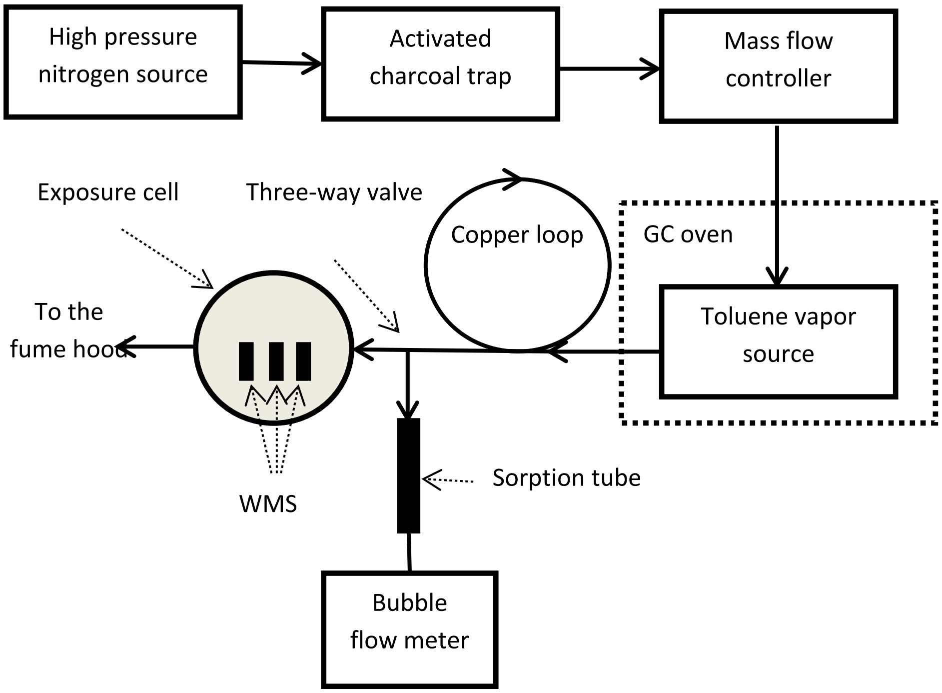

Figure S4: Setup used for the experimental evaluation of the model

Table S2: Summary of Parameters used in the model

Symbol	Description	Value	
		Regular 2-mL WMS	Microvial WMS
L_m	Membrane thickness (m)	1×10^{-4}	
L_b	Sorbent bed thickness (m)	1.4×10^{-2}	2.6×10^{-2}
A_m	Membrane sampling area (m^2)	34.476×10^{-6}	17.523×10^{-6}
D_m	Diffusion coefficient in the membrane (m^2/sec)	1.07×10^{-10}	
K	Partition coefficient between air and the membrane material (dimensionless)	843	
D_a	Diffusion coefficient in air (m^2/sec)	8.5×10^{-6}	
D_{eff}	Effective diffusion coefficient in the sorbent bed (m^2/sec)	2.11×10^{-6}	
ε	Sorbent bed porosity (dimensionless)	0.4	
τ	Tortuosity (dimensionless)	1.61	
α	Specific surface area (m^2/m^3)	$11226 \times 10^{+4}$	
k_c	Mass transfer coefficient (m/sec)	0.0198	
d	Sorbent particle diameter (m)	2.135×10^{-4}	
a	Parameter for the isotherm $C^* = a \times q^b$	7.66647×10^{-6}	
b	Parameter for the isotherm $C^* = a \times q^b$	1.566	

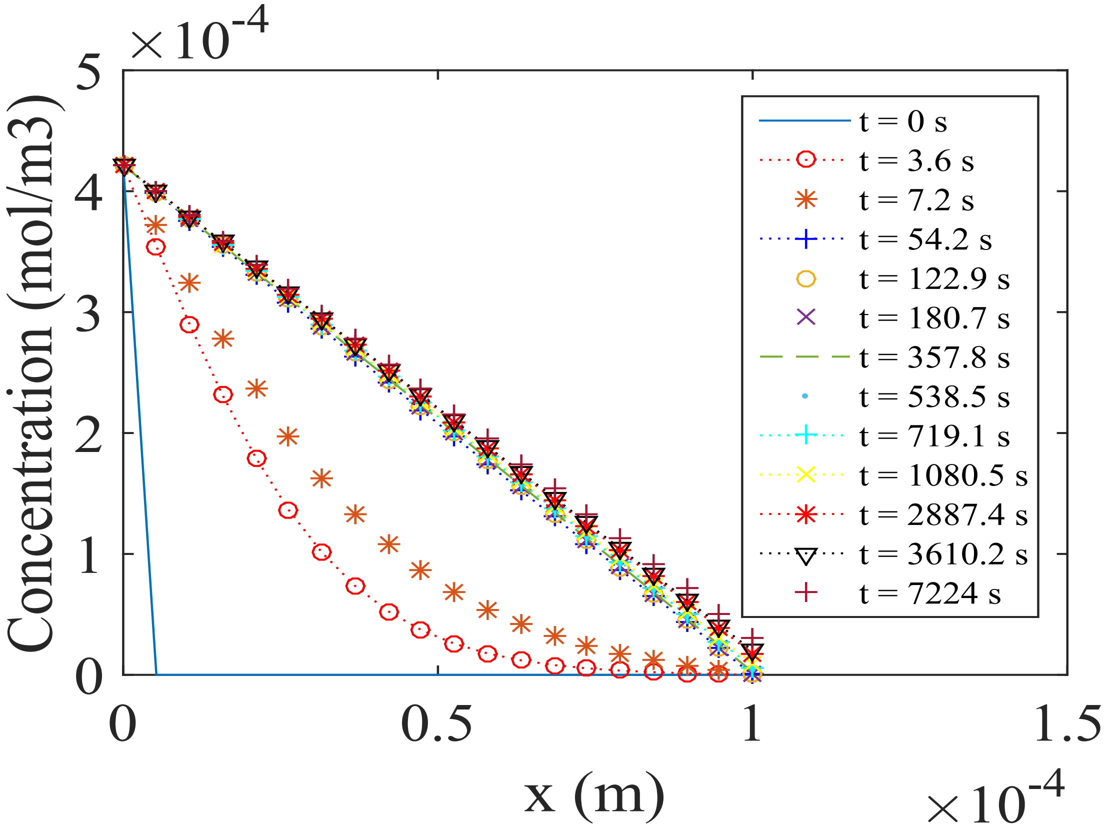

Figure S5: Concentration profiles in the membrane predicted by the model at selected time points within total exposure time of 2 hours at a toluene concentration of 0.01 ppmv in the air

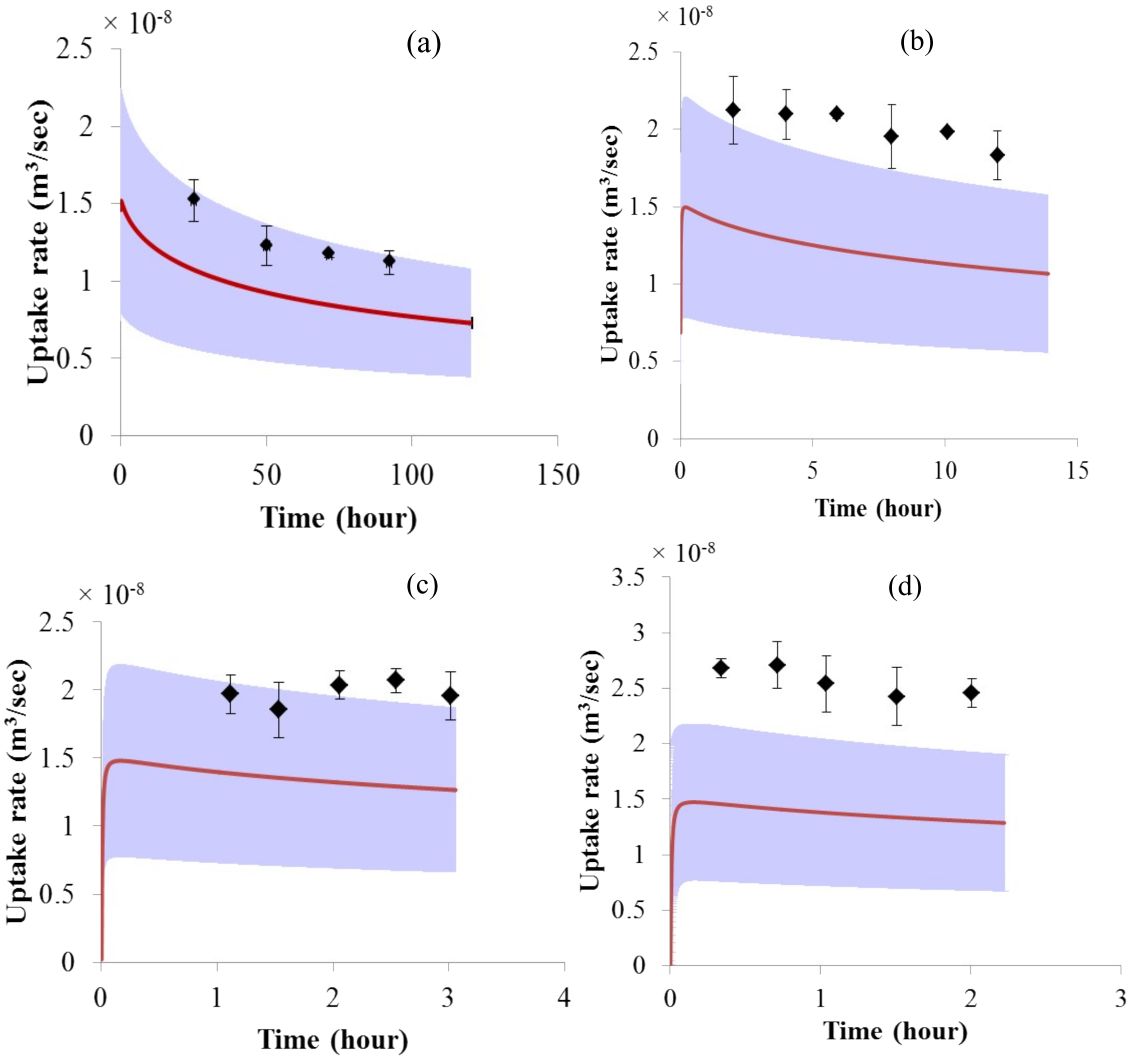

Figure S6: Experimental uptake rate profiles of the microvial WMS at the concentrations of 1.6 mg/m^3 (a), 9.2 mg/m^3 (b) , 26.8 mg/m^3 (c), and 43.0 mg/m^3 (d) compared to the model results, which are presented with an estimated uncertainty band based on the uncertainty in the parameter values. (⍰ Experimental data, - Model results)