Determination of Uptake Rates of VOC Passive Sampler for the Canadian National Residential Indoor Air Survey

Jiping Zhu[1], Cecilia C. Chan[2], Qi-ming Xian[1], Yong-lai Feng[1] and Soheil Rastan[3]
1: Health Canada
2: CASSEN Testing Laboratories, Canada
3: Statistics Canada
Email: Jiping_Zhu@hc-sc.gc.ca
Phone: 1-613-946-0305; Fax: 1-613-946-3573

Health Canada Santé Canada

Indoor air is an important exposure route

Indoor Environments
Homes, schools, daycares, offices, hospitals, transportation ...

Indoor air
living room, bedroom, family room, Kitchen

Indoor dust
Floor dust, Floor dust, Surface dust

VOCs

SVOCs

National Indoor Air Survey (NIAS)

- Canadian government funded project
  - Approved in April 2008 for a total of $1.4 M (CAD)
- Representative Canadian data
  - Homes selected under Canadian Health Measures Survey (www.statcan.gc.ca/survey-enquete/household-menages/measures-mesures/intro-eng.htm)
  - Ca. 4000 homes across Canada
  - Sampling Sept 2009 – August 2011
  - Sample collection: Perkin-Elmer diffusive tube (Carbopack B)
- Selected VOCs
  - Government CEPA/CMP
  - Risk assessment, risk management, guideline for indoor air quality, biomonitoring
- Analytical method: Perkin-Elmer TD GC/MS

Thermal desorption is connected to GC/MS

Selection of Target Analytes

- Suitable for TD/MS/MS analysis
  - Volatile organic compounds (50 – 250 °C)
- Priority for regulatory work at Health Canada
  - Batch x: CMP Batch chemcials (Batch 1 to 12)
  - Mod: CEPA moderate priority chemicals with great potential for human exposure or with Persistence/bioaccumulation potential
  - DSL pilot: Chemicals designated for the pilot screening assessment from DSL under CEPA
  - AHED: Data needed for the development of indoor guideline by HC Air Health and Effects Division
  - Cosmetics: Chemicals that are being assessed by HC Products Safety Program
- Other considerations
  - BIO: Biomonitoring targets in CHMS
  - Major VOCs: Major VOCs detected inOttawa Residential Air Study (2002-2003) (*Environ. Sci. Technol.* (2005) 39, 3964 – 3971)

CMP batch chemicals

Target Chemicals	CEPA/CMP Category
Naphthalene	Batch 01, DSL pilot/Major VOC, BIO
Cyclotetrasiloxane, octamethyl- (D4)	Batch 02, Cosmetics/Major VOC
2-Methyl-1,3-butadiene	Batch 02/Major VOC
Ethanol, 2-(2-methoxyethoxy)-	Batch 03
Ethanol, 2-ethoxy-, acetate	Batch 03
Ethanol, 2-methoxy-, acetate	Batch 03
Hexane	Batch 04, BIO
1-Propene, 3-chloro-	Batch 06
Benzene, chloromethyl-	Batch 06
2-Cyclohexen-1-one, 3,5,5-trimethyl-	Batch 07
1,4-Dioxane	Batch 07, BIO
Toluene, 2-nitro-	Batch 08
2-Pyrrolidinone, 1-methyl-	Batch 09
Benzene, 1,2-dimethoxy-4-(2-propenyl)-	Batch 09
2-Furancarboxaldehyde	Batch 11

Chemicals related to CEPA

Pilot screening of DSL chemicals

Target Chemicals	CEPA/CMP Category
1,1'-Biphenyl	DSL pilot
1,2-Dibromo-ethane	DSL pilot
1,2-Dichloro-propane	DSL pilot
4-Chloro-3-methylphenol	DSL pilot
Camphene	DSL pilot
Quinoline	DSL pilot
Ethylbenzene	DSL pilot, BIO
Benzene, 1,2,4-trimethyl	DSL pilot, major VOC
1-Butanol	DSL pilot, Mod - GPE
2-Propanone=acetone	DSL pilot, Mod - GPE
Cyclohexane	DSL pilot, Major VOC
Decane	DSL pilot, Major VOC
2-Butanone	DSL pilot, Major VOC, Mod - GPE
2-Pentanone, 4-methyl-	DSL pilot, Mod - GPE,
2-Propanol	DSL pilot, Major VOC, Mod - GPE

Chemicals related to CEPA

CEPA moderate priority chemicals (future risk assessment)

Target Chemicals	CEPA/CMP Category
1,2-Ethanediol, diacetate	Mod - GPE
1-Hexanol, 2-ethyl-	Mod - GPE
1-Nonanol	Mod - GPE
1-Octanol	Mod - GPE
1-Pentanol	Mod - GPE
1-Propanol	Mod - GPE
2-Hexanone, 5-methyl-	Mod - GPE
2-Pentanone	Mod - GPE
2-Pyrrolidinone, 1-ethenyl-	Mod - GPE
3-Penten-2-one, 4-methyl-	Mod - GPE
Benzaldehyde	Mod - GPE
Benzene, (1-methylethyl)-	Mod - GPE
Benzenepropanol	Mod - GPE
Benzoic acid, butyl ester	Mod - GPE
Benzoic acid, methyl ester	Mod - GPE
Cyclohexanol	Mod - GPE
Cyclohexanone	Mod - GPE
Ethanol, 2-(2-ethoxyethoxy)-	Mod - GPE
Furan, tetrahydro-	Mod - GPE
Octanal	Mod - GPE
2-Propanol, 2-methyl-	Mod - IPE w/PB
Benzoic acid, 2-methylpropyl ester	Mod - IPE w/PB
Benzoic acid, ethyl ester	Mod - IPE w/PB
Hexanoic acid, methyl ester	Mod - IPE w/PB
Methane, dimethoxy-	Mod - IPE w/PB
Toluene, 2,4-dichloro-	Mod - IPE w/PB

GPE:

Great potential for human exposure

IPE w/PB:

Intermediate potential for human exposure with persistency and bioaccumulation

Other needs are considered

Guideline development, Cosmetics, Biomonitoring etc.

Target Chemicals	CEPA/CMP Category
Cyclohexasiloxane, dodecamethyl- (D6)	Cosmetics/Major VOC
Cyclopentasiloxane, decamethyl- (D5)	Cosmetics/major VOC
Benzene	AHED/Major VOC, BIO
m-Xylene + P/XYLENE	AHED/Major VOC, BIO
o-Xylene	AHED/Major VOC, BIO
Toluene	AHED/Major VOC, BIO
Hexachloroethane	CEPA Risk management
Target Chemicals	**CEPA/CMP Category**
Benzene, 1,2-dichloro-	Biomonitoring
Benzene, 1,4-dichloro-	Biomonitoring
Bromodichloromethane	Biomonitoring
Bromoform	Biomonitoring
Carbon tetrachloride	Biomonitoring
Dibromochloromethane	Biomonitoring
Perchloroethylene	Biomonitoring
Styrene	Biomonitoring
Trichloroethylene	Biomonitoring

Major indoor air VOCs

Target Chemicals	CEPA/CMP Category
benzene, 1,2,3-trimethyl-	Major VOC
Decanal	Major VOC
Dodecane	Major VOC
ethanol, 2-butoxy-	Major VOC
Heptane	Major VOC
Hexanal	Major VOC
Limonene	Major VOC
Pentane	Major VOC
Undecane	Major VOC
α-pinene	Major VOC
Chloroform	Major VOC, BIO
Nonanal	Major VOC, Mod - GPE

Challenge: Uptake rates of most target chemicals were not available!

- VOC uptake rates are very limited for Perkin-Elmer tubes
  - Carbopack B adsorbent
  - Tenax adsorbent
- Non-occupational uptake rates are almost non-exist, except for BETX

Use air diffusion coefficient to predict uptake rate

- Hypothesis: Passive uptake rate is a function of air diffusion coefficient. There is a correlation between the two:
- UR (ml/min) = [A / Z] × 60 × D = K × D
  - A = Cross-sectional area of the tube (cm2)
  - Z = Path length of the air gap (cm)

Can we use VOC diffusion coefficients in air for estimating the uptake rate of passive VOC samplers for large scale indoor air surveys? J. Zhu, Q. Xian, S. Rastan, Y.-L. Feng and C.C. Chan. Proceedings of the Fifth International Workshop on Energy and Environment of Residential Buildings and The Third International Conference on Built Environment and Public Health (EERB-BEPH 2009), Guilin, China, May 25-31, 2009.

EPA Website provides an easy access to D values

D1 value

EPA On-line Tools for Site Assessment Calculation
(www.epa.gov/ATHENS/learn2model/part-two/onsite/estdiffusion-ext.htm)

Benzene (6 x H, 6 x C, 1 x 6-ring, 1 atm, 25 C)	D (cm^2/sec)
FSG Method	0.0822
FSG/LaBas Method	0.0923
WL Method	0.101
Average of WL, FSG and FSG/LaBas Methods	0.0919

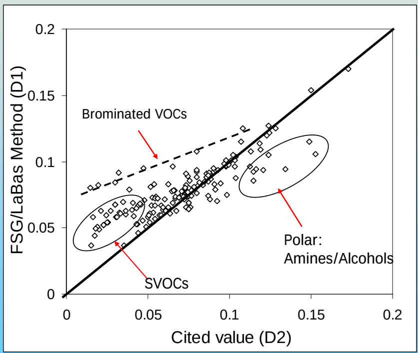
EPA Website (cont.)

D2 value

EPA Chemical and Physical Properties Database
(www.dep.state.pa.us/physicalproperties/Default.htm)

Benzene CAS number: 000071-43-2	D (cm^2/sec)
Perry and Chilton, Chemical Engineers' Handbook	0.077
EPA Soil Screening Guidance	0.088
EPA Region IX, PRG	0.088
EPA Physical Chemical Properties and Categorization of RCRA Wastes According to Volatility	0.0932
EPA Air Emissions Models for Waste and Wastewater	0.088
TPHCWG Volume 3: Fate and Transport	0.088
ORNL Risk Assessment Information System	0.088
D value taken	**0.088**

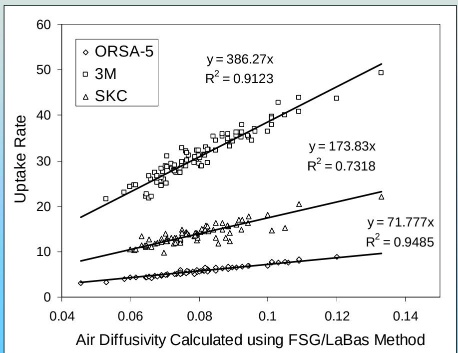
Correlation between D1 and D2



Current existing passive uptake rates – workplace application

- ORSA-5
- 3M
- SKC
- Evaluation levels:
  - A – full protocol (EN 838 or equivalent)
  - B – Partial range (EN838)
  - C – Theoretical or ideal calculation
- Level C uptake rate removed.

Relationship: D(1) vs. UR

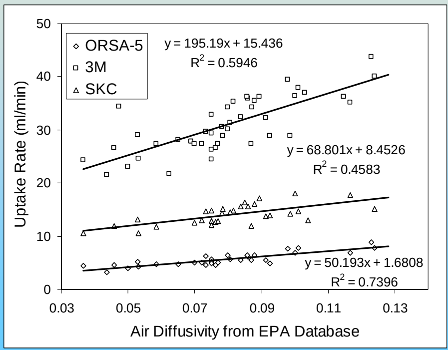


Deviation from prediction using regression curve

	ORSA-5	3M	SKC
Total VOC	66	100	74
Max	-15, 12	-14, 14	-21, 22
Diff (-10%)	2	3	7
Diff (+10%)	2	2	6
% of (>10%)	**6**	**5**	**18**

D values from FSG/LaBas method
Uptake rate from Level A and B

Relationship: D(2) vs. UR



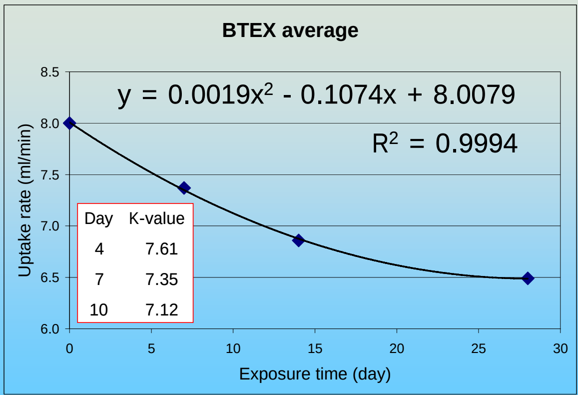
Perkin-Elmer Thermal Desorption tubes with passive diffusion caps

- Limited experimental data for UR values

	Diffusivity	1-week exposure		2-week exposure		4-week exposure	
VOC	cm^2/s	ml/min	K	ml/min	K	ml/min	K
Benzene	0.0887	0.67	7.55	0.63	7.10	0.58	6.54
Toluene	0.0797	0.57	7.15	0.56	7.03	0.55	6.90
Xylene	0.0728	0.54	7.42	0.47	6.46	0.44	6.04
Mean			7.37		6.86		6.49

U (ml min-1) = U (ng ppm-1 min-1) x 24.5/MW x T/298 x 101/P

References:Brown, R.H. J. Environ. Monit., 1999, 1, 115–116



Side-by-side exposure to determine the uptake rate

- Concept:
  - The active sampling rate should be close to the passive uptake rate (ca. 0.5 ml/min). No pump can deliver such low flow with accuracy, therefore, the accurate active sampling rate has to be determined in other ways;
  - Since BTEX uptake rate for Carbopack B Perkin-Elmer tubes were experimentally determined by others (ref.), we can use it to determine the active sampling rate by comparing the ratio of areas;
  - Once the active sampling rate was determined, we can use it to calculate the uptake rate (UR, ml/min) of other chemicals.

Side-by-side exposure to determine the uptake rate

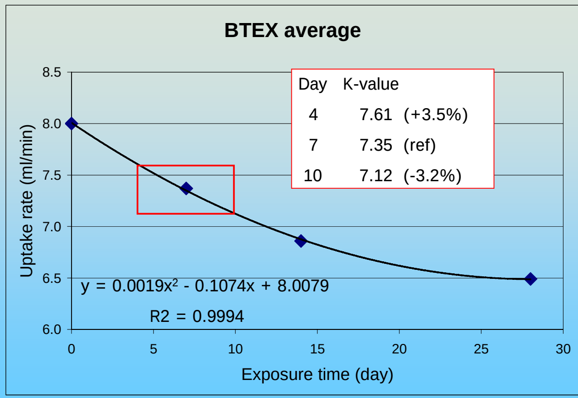
- Experiment design:
  - Active samplers (n=4) and passive samplers (n=3) were deployed side-by-side in each of the 5 homes
  - Exposure time: 4 days, 7 days, 10 days
  - Low flow pocket pumps (set nominal flow rate of 10 ml/min) through a manufolder to feed into 4 active sampling tubes (2.5 ml/min per tube

Side-by-side exposure to determine the uptake rate

- Instrument analysis and data process:
  - Thermal desorption GC/MS (full scan)
  - All peaks were integrated to give peak areas
  - Peaks in active and passive samples were paired
  - Peak areas were corrected with blank tubes
  - Blank corrected peak area ratios were calculated

Side-by-side exposure to determine the uptake rate

- Since BTEX uptake rate for Perkin-Elmer tubes were experimentally determined by others, we used BTEX uptake rates in passive samplers to determine the actual active sampling rate (SR)
  - SR (ml/min) = ($Area_{Active}/Area_{Passive}$) x UR
  - UR (ml/min) = K x Diff. Coeff.
  - K is exposure time dependent (7.61 (4 days), 7.35 (7 days) and 7.12 (10 days)



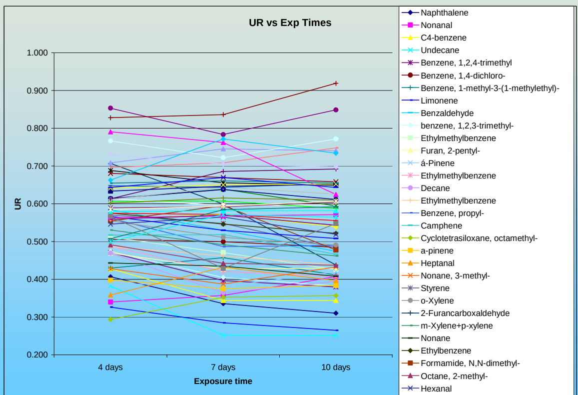
Side-by-side exposure to determine the uptake rate

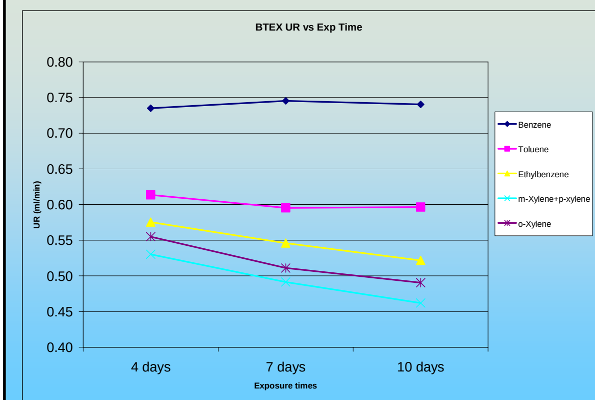
- Once the sampling rate of active samplers was determined (the rate of BETX applies to all chemicals), the uptake rates of the VOCs can be calculated:

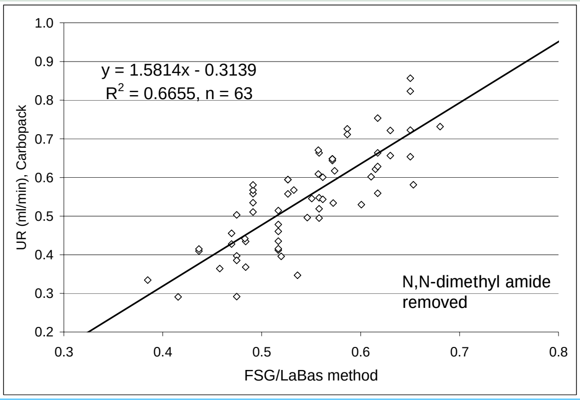
  UR (passive) = ($Area_{Pass}/Area_{Active}$) x Sampling rate

Side-by-side exposure to determine the uptake rate

- Data reduction:
  - If RSD>40 in the duplicates (n=3 or n=4), then the mean peak area was discarded;
  - UR of a particular exposure time (e.g. 7 days) in a particular house (e.g. House 6) was calculated;
  - The mean UR of a chemical was the average values of the five houses x three exposure times;
  - A UR was considered valid if RSD<20 and detection frequency >9/15.







Correlation of uptake rate of Perkin-Elmer Carbopack B tube and D value (n=63, found in indoor air)

Uptake rate (ml/min) = 1.5814 x 7.5 x D (cm^2/sec, FSG/LaBas method) - 0.3139

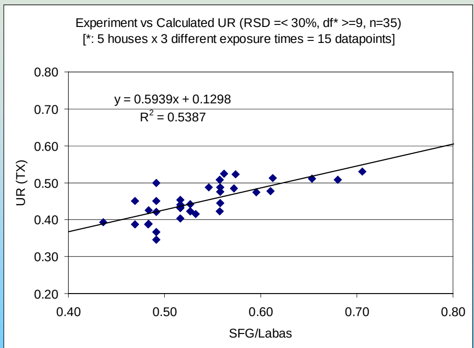
Side-by-side exposure to determine the uptake rate of NIAS targets

Compound	UR	Compound	UR	Compound	UR
Pentane	0.656 *	Hexanal	0.543 *	Benzene, 1,4-dichloro-	0.496 *
2-Methyl-1,3-butadiene	0.749	3-Penten-2-one, 4-methyl-	0.597	benzene, 1,2,3-trimethyl-	0.415 *
2-Propanone (acetone)	0.931	Dibromochloromethane	0.661	1-Hexanol, 2-ethyl-	0.439
Methane, dimethoxy-	0.783	1,2-Dibromo-ethane	0.662	Benzene, chloromethyl-	0.557
2-Propanol	0.884	Ethanol, 2-methoxy-, acetate	0.523	Undecane	0.291 *
1-Propene, 3-chloro-	0.806	Ethylbenzene	0.548 *	Benzene, 1,2-dichloro-	0.550
2-Propanol, 2-methyl-	0.736	m-Xylene+p-xylene	0.495 *	Hexachloroethane	0.434
Hexane	0.648 *	2-Furancarboxaldehyde	0.581 *	1-Octanol	0.439
1-Propanol	0.884	2-Hexanone, 5-methyl-	0.508	Cyclopentasiloxane, decamethyl-	0.225
Nitromethane	1.050	o-Xylene	0.519 *	2-Pyrrolidinone, 1-methyl-	0.654
2-Butanone	0.773	Styrene	0.534 *	Nonanal	0.364 *
Furan, tetrahydro-	0.812	Ethanol, 2-ethoxy-, acetate	0.468	Benzoic acid, methyl ester	0.566
Chloroform	0.726	Cyclohexanol	0.662	Toluene, 2,4-dichloro-	0.489
Cyclohexane	0.662	Bromoform	0.641	Dodecane	0.322
Carbon tetrachloride	0.621	Hexanoic acid, methyl ester	0.475	2-Pyrrolidinone, 1-ethenyl-	0.595
Benzene	0.731 *	ethanol, 2-butoxy-	0.506	2-Cyclohexen-1-one, 3,5,5-trimethyl-	0.463
Heptane	0.558 *	a-pinene	0.386 *	Benzoic acid, ethyl ester	0.434
1-Butanol	0.736	Benzene, (1-methylethyl)-	0.503	1-Nonanol	0.397
Trichloroethylene	0.655	Cyclohexanone	0.638	Decanal	0.372
2-Pentanone	0.659	Cyclotetrasiloxane, octamethyl-	0.334 *	Toluene, 2-nitro-	0.496
1,2-Dichloro-propane	0.638	Camphene	0.503 *	Naphthalene	0.347 *
1,4-Dioxane	0.756	Decane	0.409 *	Cyclohexasiloxane, dodecamethyl-	0.175
Bromodichloromethane	0.688	Ethanol, 2-(2-methoxyethoxy)-	0.538	Benzenepropanol	0.450
Propane, 1-nitro-	0.716	Benzene, 1,2,4-trimethyl	0.412 *	Quinoline	0.541
propane, 2-nitro-	0.716	Benzaldehyde	0.529 *	Benzoic acid, 2-methylpropyl ester	0.413
2-Pentanone, 4-methyl	0.601 *	1,2-Ethanediol, diacetate	0.483	4-Chloro-3-methylphenol	0.528
Toluene	0.602 *	Octanal	0.453	Benzoic acid, butyl ester	0.375
1-Pentanol	0.631	Limonene	0.292 *	Benzene, 1,2-dimethoxy-4-(2-propenyl)-	0.386
Perchloroethylene	0.569	Ethanol, 2-(2-ethoxyethoxy)-	0.480	1,1'-Biphenyl	0.443

UR (ml/min) = 1.5814 x 7.5 x D (FSG/LaBas) - 0.3139 *: Experimentally determined UR

Carbopack B vs. Tenax?

- Tenax tubes were deployed and analyzed in the same way as Carbopack tubes
- Data were processed in the same way as well
- The uptake rates of both were compared

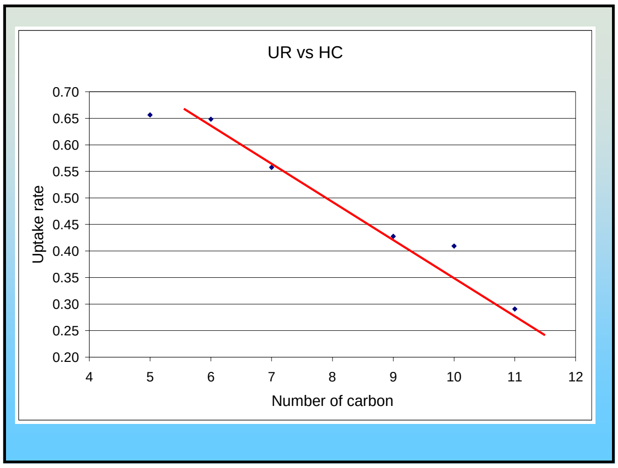


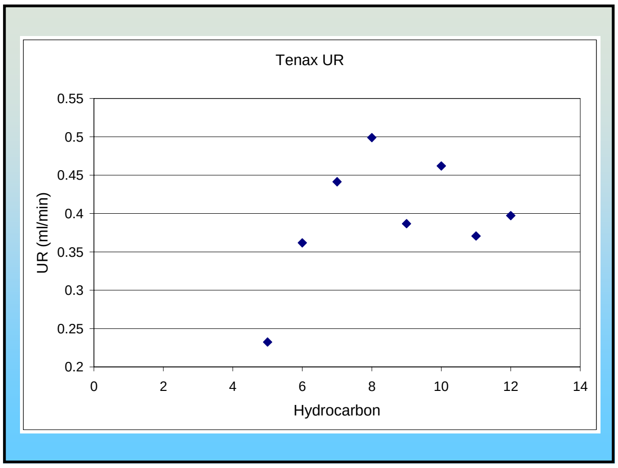
Excluding terpenes, and C7 HC and below.

Comparison of UR between CB and TX

(Tenax is not suitable for long term exposure for light VOCs due to weak adsorbent nature)

Compund	CB	TX	%Diff	Compund	CB	TX	%Diff
Naphthalene	0.347	0.422	9.7	cis-1,3-Dimethylcyclohexane	0.567	0.416	-15.4
C4-benzene	0.368	0.426	7.3	2-Pentanone, 4-methyl	0.601	0.524	-6.8
Benzene, 1,2,4-trimethyl	0.412	0.404	-1.0	Heptane, 3-methyl-	0.535	0.450	-8.6
Benzene, 1,4-dichloro-	0.496	0.487	-0.9	Heptane, 2-methyl-	0.558	0.421	-13.9
Benzene, 1-methyl-3-(1-methylethyl)-	0.434	0.389	-5.5	Pentane, 2,3,3-trimethyl-	0.567	0.346	-24.2
Limonene	0.292	0.278	-2.4	Pentane, 2,3,4-trimethyl-	0.581	0.366	-22.7
Benzaldehyde	0.529	0.704	14.1	Cyclopentane, ethyl-	0.670	0.508	-13.8
benzene, 1,2,3-trimethyl-	0.415	0.434	2.2	Pentanal	0.621	0.404	-21.2
Ethylmethylbenzene	0.478	0.441	-4.1	Cyclohexane, methyl-	0.609	0.423	-18.0
Furan, 2-pentyl-	0.442	0.388	-6.5	**Heptane**	0.558	0.441	-11.6
b-Pinene	0.397	0.277	-17.8	Dimethylcyclopentane	0.559	0.327	-26.3
Ethylmethylbenzene	0.435	0.431	-0.5	Dimethylcyclopentane	0.628	0.413	-20.7
Benzene, propyl-	0.514	0.453	-6.3	Ethane, hexamethyl-	0.511	0.264	-31.8
Camphene	0.503	0.290	-26.8	**Benzene**	0.731	0.508	-18.1
a-pinene	0.386	0.256	-20.1	Hexane, 3-methyl	0.594	0.423	-16.9
Heptanal	0.396	0.293	-14.9	Hexane, 2-methyl-	0.594	0.423	-16.8
Nonane, 3-methyl-	0.415	0.393	-2.7	Cyclopentene, 3-methyl-	0.753	0.326	-39.7
Styrene	0.534	0.484	-4.9	Cyclopentane, methyl-	0.664	0.394	-25.5
o-Xylene	0.519	0.475	-4.4	**Hexane**	0.648	0.362	-28.4
2-Furancarboxaldehyde	0.581	0.512	-6.4	1-Hexene	0.711	0.339	-35.5
m-Xylene+p-xylene	0.495	0.445	-5.3	Pentane, 3-methyl-	0.644	0.332	-31.9
Nonane	0.428	0.387	-5.0	Pentane, 2-methyl-	0.648	0.319	-34.0
Ethylbenzene	0.548	0.488	-5.8	Ethane, 1,1,2-trichloro-1,2,2-trifluoro	0.545	0.246	-37.8
Octane, 2-methyl-	0.455	0.451	-0.5	cis-2-Pentene	0.857	0.350	-42.0
Hexanal	0.543	0.352	-21.4	**Pentane**	0.656	0.232	-47.7
Perchloroethylene	0.664	0.540	-10.3	Butane, 2-methyl-	0.722	0.213	-54.4
Toluene	0.602	0.478	-11.5				





Conclusions

- Side-by-side experiment is a practical way to generate uptake rates for a large number of chemicals that are likely present in the indoor air.
- It is possible to use theoretical D value for estimating VOC uptake rate. A regression line was used to account for the real-world situation (UR (ml/min) = 1.5814 x 7.5 x D (FSG/LaBas) - 0.3139).
- Use of theoretical (calculated) D values is better than use of experimentally determined D values as latter has limited number of chemicals.
- The loss through back diffusion in long term exposure (7 days) is much server in Tenax (C8) than in Carbopack B (C5).