Supplemental Information

Novel field-portable high-pressure adsorbent tube sampler prototype for the direct *in situ* preconcentration of trace compounds in gases at their working pressures: application to biomethane

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Supplemental Information

Theoretical note on multibed adsorbent tubes

Multibed adsorbent tubes (MAT) are attractive preconcentration supports for complex gas samples with unknown composition such as biomethane in view of the large diversity of chemical TC families it can contain [1–6] with associated large boiling points- and polarity-ranges [5,7]. While not any adsorbent is universal enough to adsorb all TC [5,8], the working principle of a MAT precisely enables to preconcentrate a large range of TC in a wide volatility range in one single sampling run. In a MAT, different adsorbents are arranged in order of increasing sorption strength (increasing surface area, decreasing pore size) in the gas sampling direction [9,10]. As the gas matrix (CH_4 in the case of biomethane) passes through the tube without being retained due to its too high volatility, the weak front adsorbent (here Tenax®TA) traps relatively large, heavy, high-boiling TC (boiling point > ~80°C) but is not strong enough to retain small volatile nor very volatile TC (boiling point < ~50 – 80°C). Those hence move onwards to the next gradually stronger adsorbent beds (here Carbopack™X) whereon they eventually get adsorbed. Importantly, thermodesorption of MAT must occur in the reverse direction as compared to the gas sampling direction. Thermodesorbing a MAT in the same direction as sampling would result in the carrier gas of the TD to blow high-boiling compounds desorbed from the weak front bed towards the stronger back bed whereon they could (partly) re-adsorb and not enter the GC-column. The critical benefits of MAT are that (1) the gas matrix is not retained enabling preconcentration ('isolation') of TC, (2) high-boiling TC never meet strong adsorbents whereon they would irreversibly adsorb, impeding their desorption upon analysis, and (3) very volatile TC can be trapped on and desorbed from strong adsorbents. Therefore, MAT enable quantitative adsorption and desorption (which is analytically at least as important as adsorption) of TC over a wider volatility and polarity range than single adsorbent beds do.

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Supplemental Tables

*Table SI-1: Chromatographic retention times (min) of compounds identified from the TD-GC-MS analysis of the SGM sampled at different test-pressures and different volumes at 1 L_N·min^{-1} on the TA14-CpX29 MAT in the HPTS prototype. STDEV : standard deviation. * : absent. ◊ : co-elution of tetrachloromethane, acrylonitrile and benzene*

Sampling pressure (bar$_a$)	**100**		**40**					**5**	
Sampled volume (L_N)	**2**		**2**		**5**	**1**		**2**	
Replicates	n=3		n=2		n=1	n=2		n=3	
Compounds from the SGM	**Mean**	**STDEV**	**Mean**	**STDEV**	**Value**	**Mean**	**STDEV**	**Mean**	**STDEV**
Dichlorodifluoromethane	**1.217**	0.018	**1.227**	0.018	**1.217**	**1.250**	0.006	**1.245**	0.030
Chloromethane	*	*	*	*	*	*	*	*	*
Chloroethene	**1.270**	0.013	**1.282**	0.025	**1.267**	**1.300**	0.005	**1.294**	0.030
1,3-Butadiene	**1.275**	0.023	**1.283**	0.008	**1.28**	**1.311**	0.006	**1.306**	0.030
1,2-Dichloro-1,1,2,2-tetrafluoroethane	**1.244**	0.017	**1.254**	0.018	**1.245**	**1.277**	0.006	**1.271**	0.031
Bromomethane	**1.325**	0.017	**1.334**	0.017	**1.326**	**1.357**	0.006	**1.352**	0.030
Chloroethane	**1.345**	0.017	**1.354**	0.017	**1.348**	**1.377**	0.006	**1.371**	0.029
Trichloromonofluoromethane	**1.427**	0.016	**1.436**	0.017	**1.429**	**1.459**	0.006	**1.453**	0.029
1,1-Dichloroethene	**1.538**	0.015	**1.546**	0.016	**1.54**	**1.568**	0.006	**1.563**	0.028
Dichloromethane	**1.602**	0.015	**1.611**	0.016	**1.606**	**1.633**	0.006	**1.627**	0.027
1,1,2-Trichloro-1,2,2-trifluoroethane	**1.569**	0.015	**1.577**	0.016	**1.571**	**1.599**	0.006	**1.594**	0.028
1,1-Dichloroethane	**1.833**	0.014	**1.841**	0.016	**1.836**	**1.863**	0.006	**1.857**	0.027
cis-1,2-Dichloroethene	**2.070**	0.014	**2.079**	0.015	**2.073**	**2.101**	0.006	**2.093**	0.025
Trichloromethane	**2.157**	0.014	**2.164**	0.016	**2.159**	**2.185**	0.007	**2.178**	0.025
1,1,1-Trichlorethane	**2.451**	0.014	**2.457**	0.014	**2.452**	**2.479**	0.006	**2.471**	0.025
Tetrachloromethane ◊	**2.664**	0.013	**2.671**	0.013	**2.666**	**2.691**	0.007	**2.684**	0.025
Acrylonitrile ◊	**2.664**	0.013	**2.671**	0.013	**2.666**	**2.691**	0.007	**2.684**	0.025
Benzene ◊	**2.664**	0.013	**2.671**	0.013	**2.666**	**2.691**	0.007	**2.684**	0.025
1,2-Dichlorethane	**2.517**	0.015	**2.525**	0.015	**2.516**	**2.548**	0.007	**2.537**	0.024
Trichloroethene	**3.317**	0.013	**3.323**	0.014	**3.318**	**3.345**	0.008	**3.335**	0.024
1,2-Dichloropropane	*	*	*	*	*	*	*	*	*
cis-1,3-Dichloropropene	**4.401**	0.015	**4.413**	0.014	**4.389**	**4.447**	0.001	**4.416**	0.017
Toluene	**5.056**	0.011	**5.060**	0.011	**5.058**	**5.077**	0.006	**5.068**	0.018
trans-1,3-Dichloropropene	**5.139**	0.017	**5.159**	0.022	**5.119**	**5.270**	0.004	**5.149**	0.014
1,1,2-Trichlorethane	**5.242**	0.011	**5.251**	0.011	**5.233**	**5.201**	/	**5.250**	0.014
Tetrachloroethene	**6.145**	0.008	**6.148**	0.007	**6.15**	**6.159**	0.004	**6.153**	0.011
Chlorobenzene	**7.080**	0.009	**7.083**	0.008	**7.077**	**7.098**	0.001	**7.085**	0.010
1,2-Dibromoethane	**6.103**	0.015	**6.119**	0.007	**6.087**	**6.150**	0.008	**6.114**	0.009
Ethylbenzene	**7.452**	0.004	**7.456**	0.004	**7.452**	**7.463**	0.001	**7.458**	0.004
p-Xylene	**7.637**	0.006	**7.639**	0.005	**7.649**	**7.648**	0.002	**7.642**	0.007
m-Xylene	**7.637**	0.006	**7.639**	0.005	**7.649**	**7.648**	0.002	**7.642**	0.007
o-Xylene	**8.149**	0.010	**8.153**	0.005	**8.163**	**8.161**	0.001	**8.154**	0.010
Styrene	**8.127**	0.010	**8.128**	0.008	**8.13**	**8.139**	0.000	**8.130**	0.009
1,1,2,2-Tetrachlorethane	**8.663**	0.013	**8.676**	0.011	**8.638**	**8.694**	0.003	**8.661**	0.007
1,3,5-Trimethylbenzene	**9.724**	0.002	**9.727**	0.002	**9.727**	**9.730**	0.001	**9.727**	0.002
1,2,4-Trimethylbenzene	**10.200**	0.003	**10.204**	0.003	**10.2**	**10.207**	0.000	**10.202**	0.001
1,3-Dichlorobenzene	**10.423**	0.006	**10.425**	0.006	**10.422**	**10.436**	0.000	**10.424**	0.005
1,4-Dichlorobenzene	**10.546**	0.005	**10.548**	0.006	**10.547**	**10.556**	0.000	**10.548**	0.004
1,2-Dichlorobenzene	**10.960**	0.006	**10.963**	0.007	**10.959**	**10.974**	0.001	**10.962**	0.006
1,2,4-Trichlorobenzene	**13.323**	0.005	**13.324**	0.004	**13.324**	**13.333**	0.001	**13.324**	0.003
Hexachloro-1,3-Butadiene	**13.903**	0.001	**13.904**	0.001	**13.913**	**13.904**	0.001	**13.906**	0.002

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Supplemental Figures

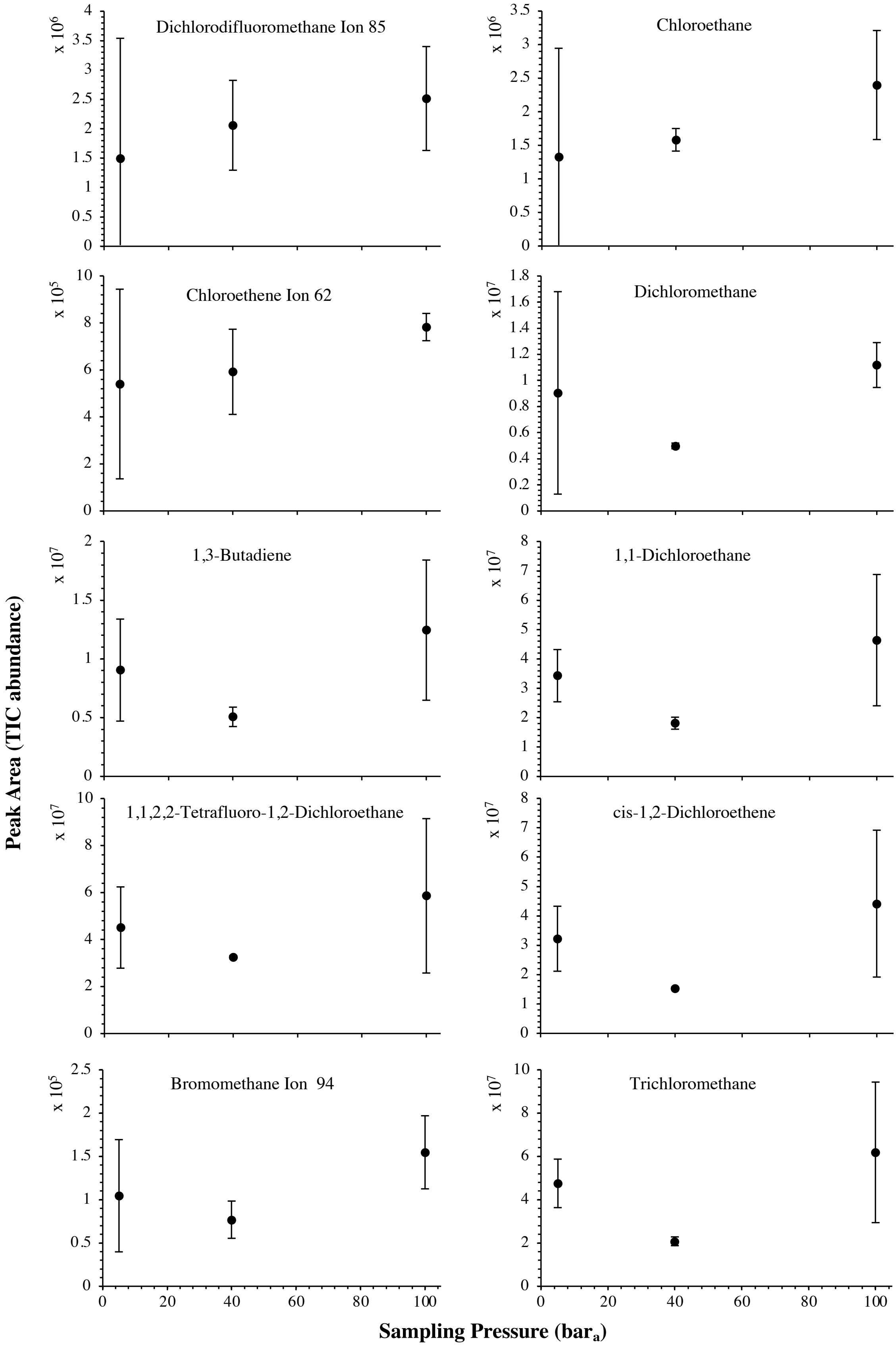
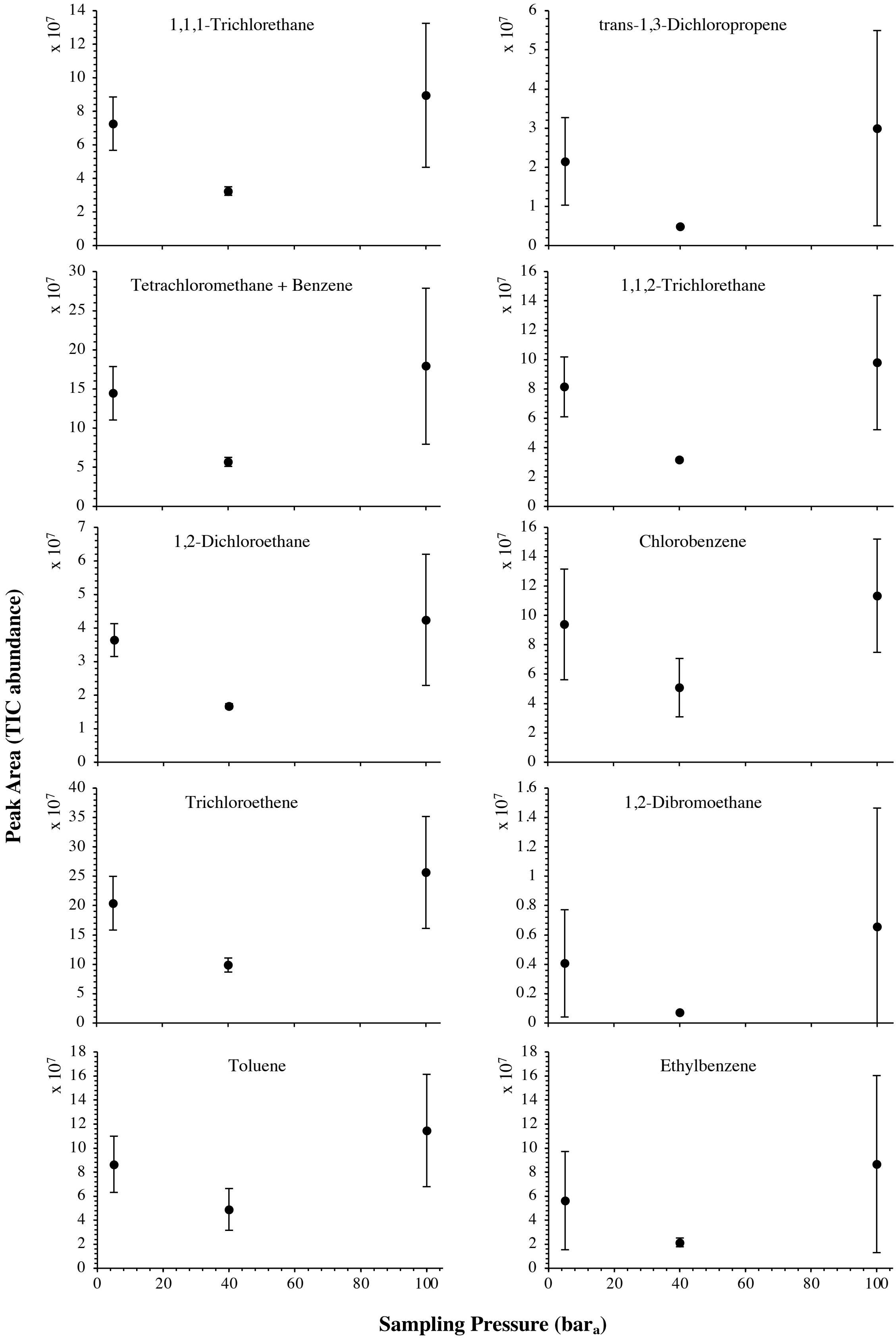


Figure SI-1: High-pressure adsorption isotherms of the HVOC not shown in Fig.4 of the core paper for test-condition A (2 L_N of the SGM sampled at 5, 40 and 100 bar_a on TA14-CpX29 MAT). Average peak area with indication of the standard deviation.



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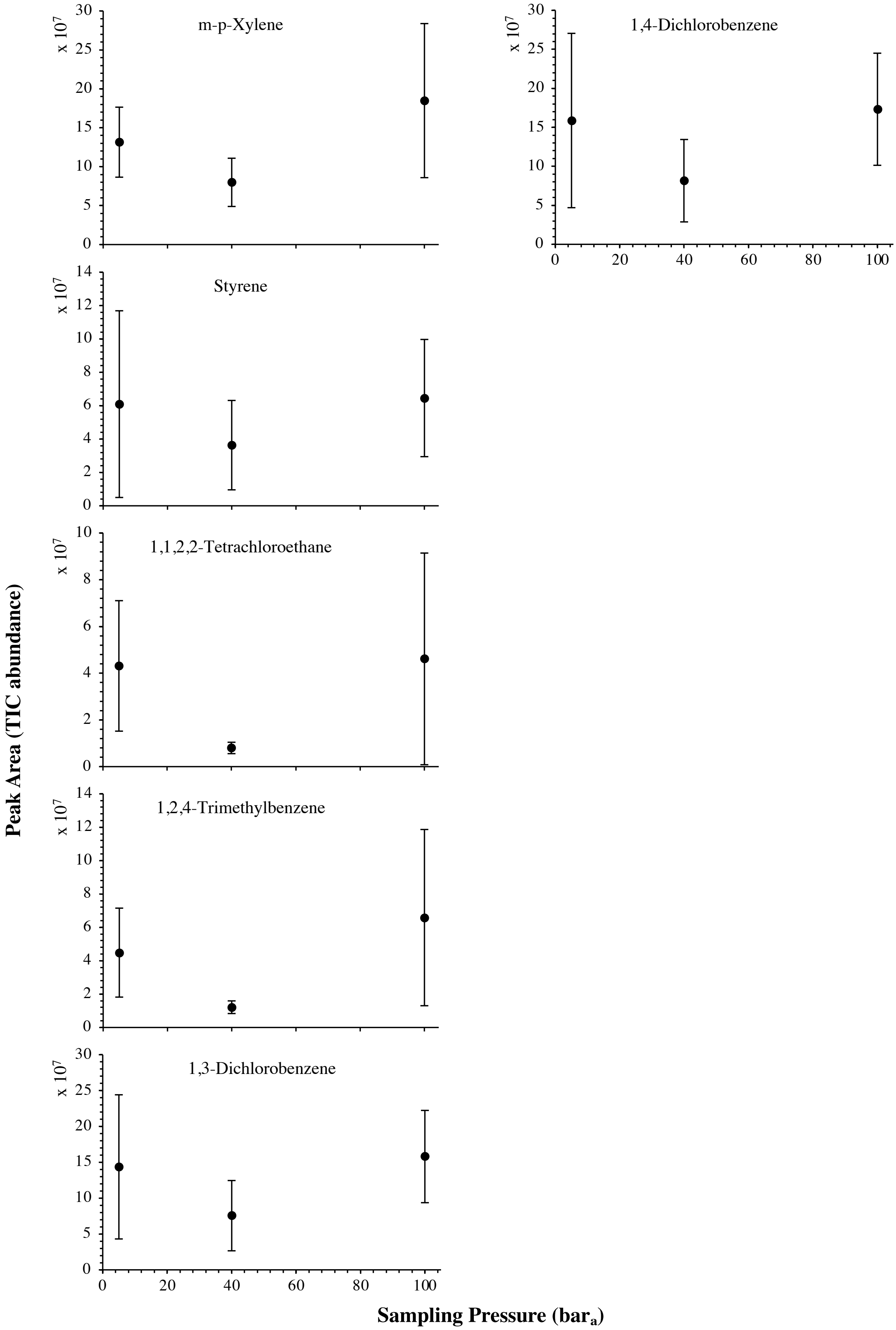

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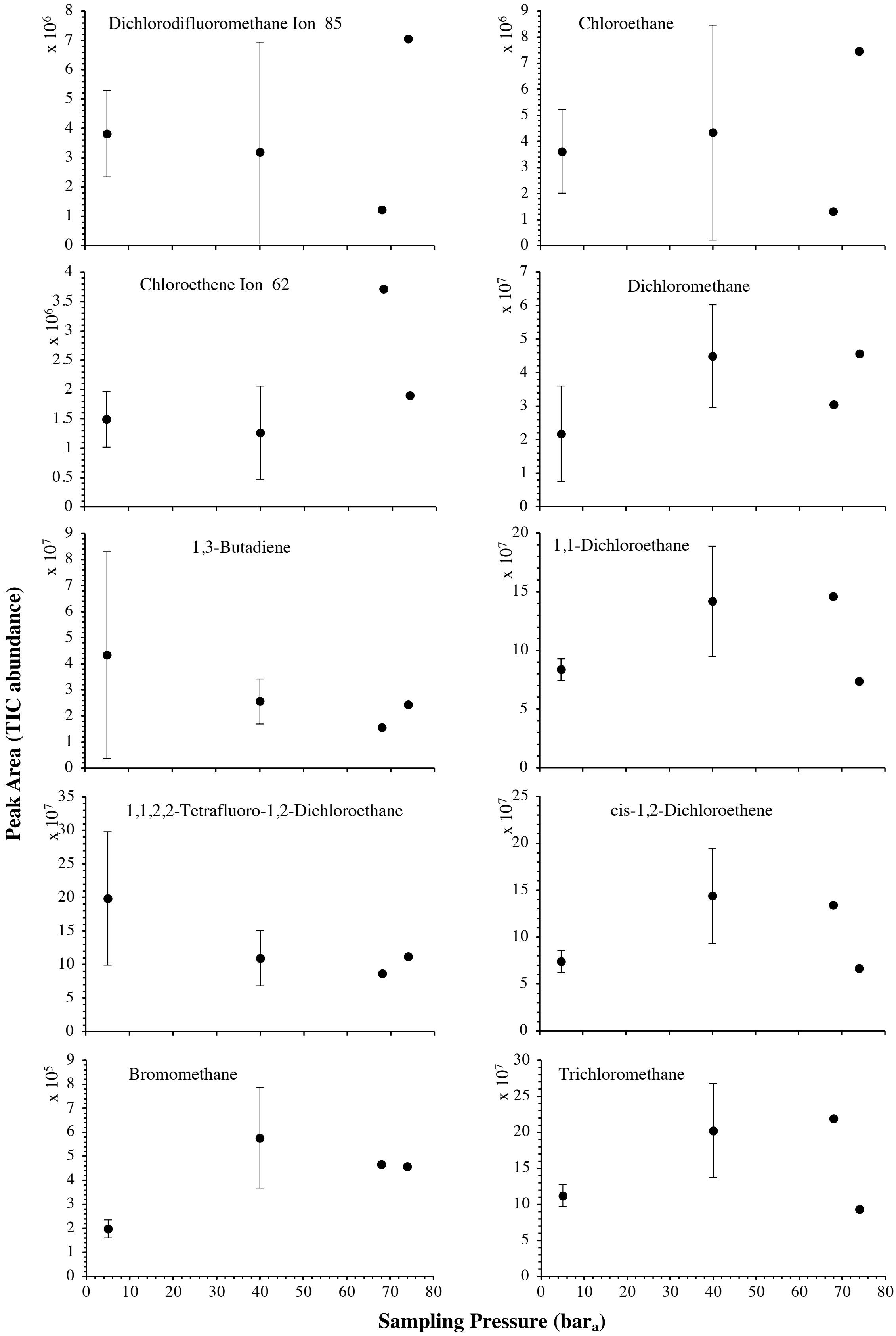
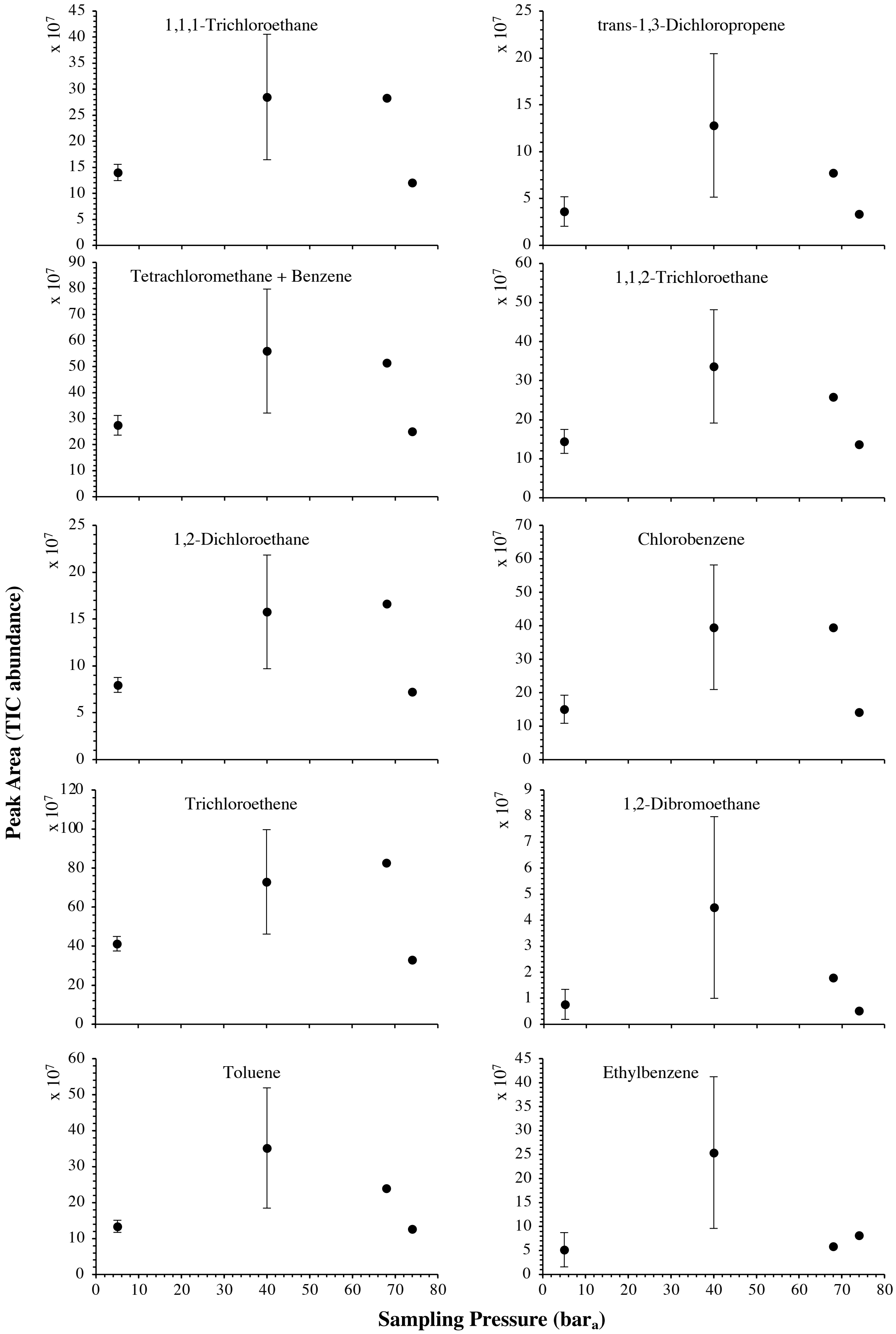


Figure SI-2: High-pressure adsorption isotherms of the HVOC not shown in Fig.5 of the core paper for test-condition B (5 L_N of the SGM sampled at 5, 40, 68 and 74 bar$_a$ on TA14-CpX29 MAT). Average peak area with indication of the standard deviation.



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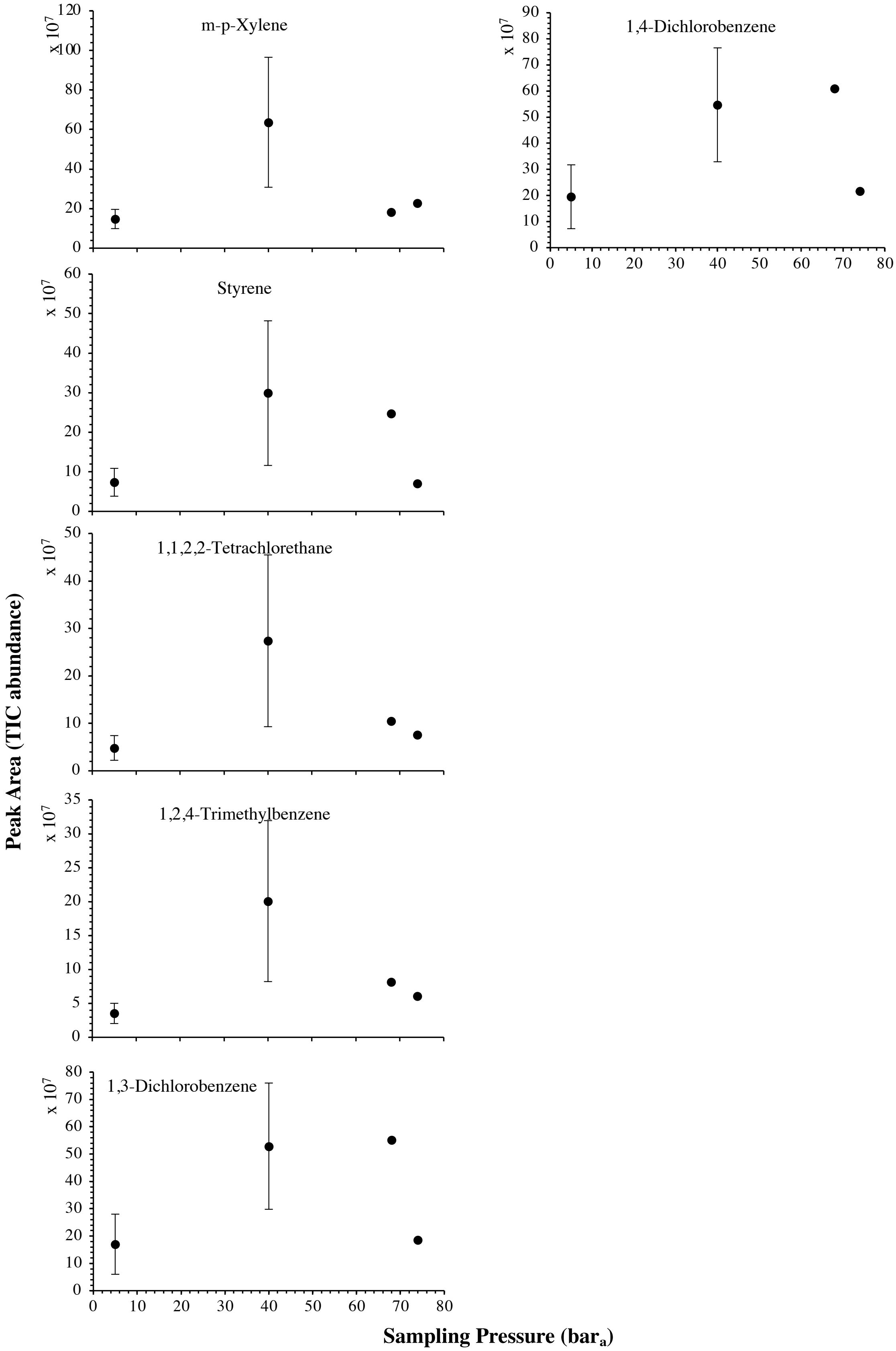

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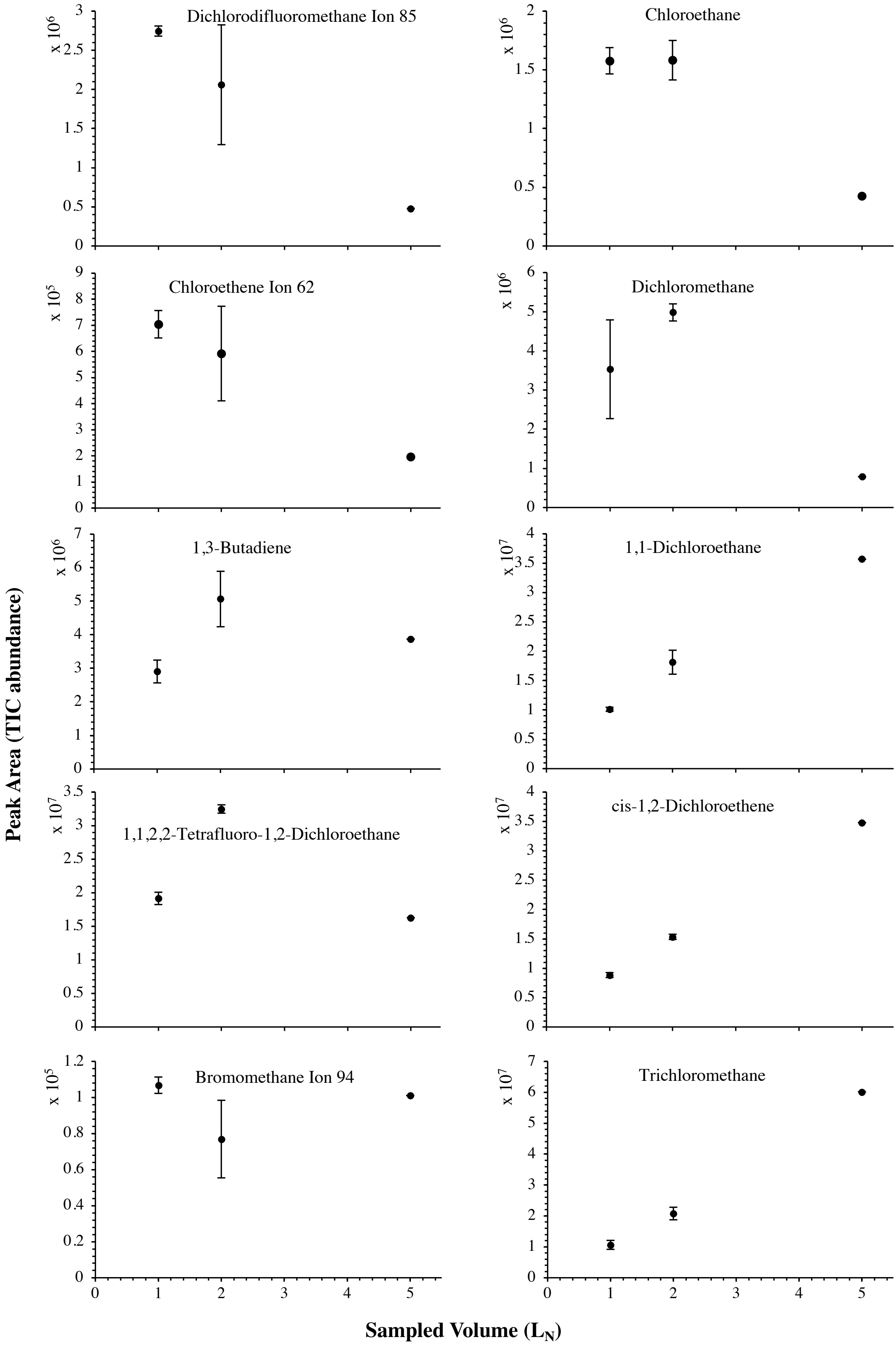
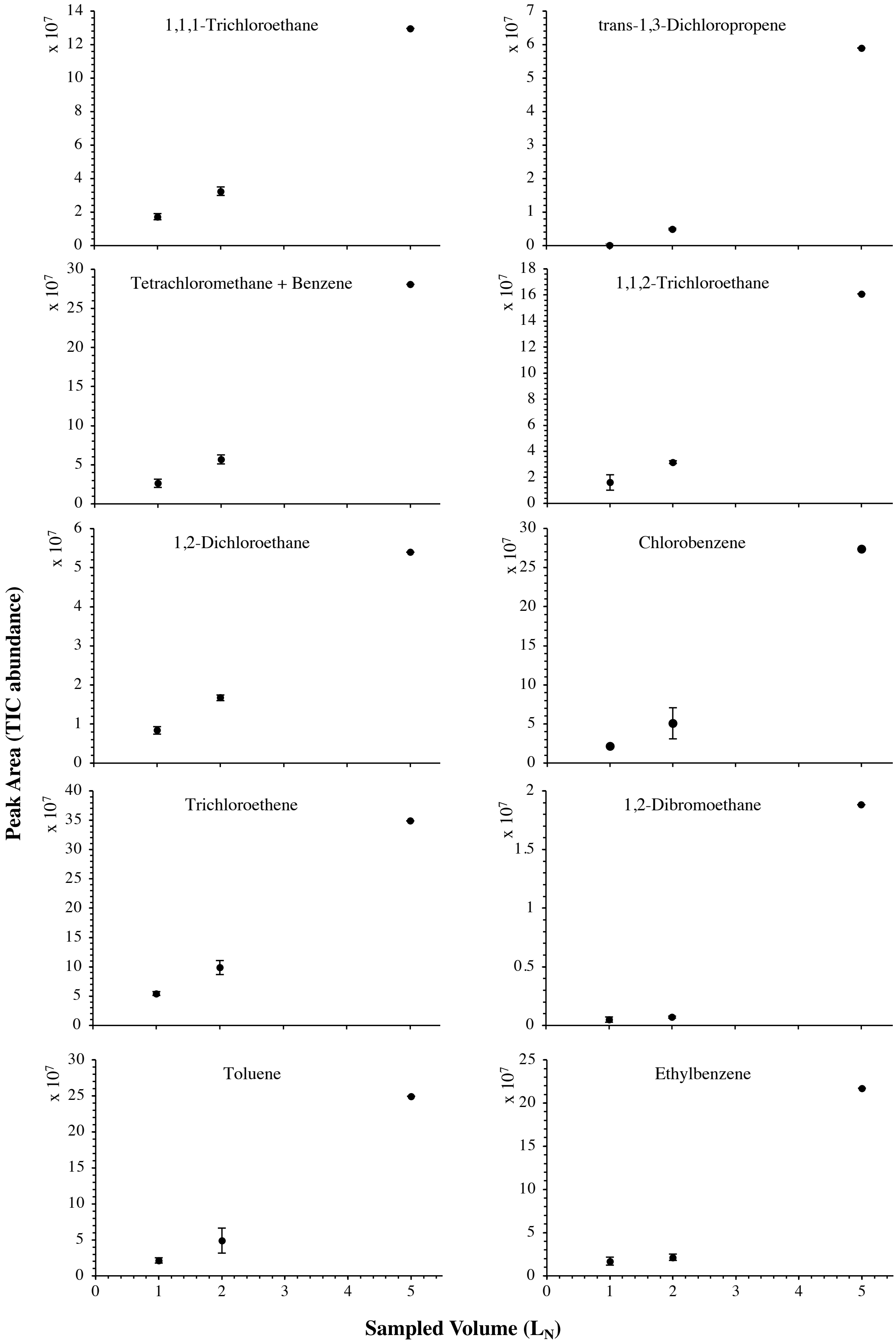


Figure SI-3: Partial breakthrough curves for the HVOC not shown in Fig.6 of the core paper for test-condition C (1, 2 and 5 L_N of the SGM sampled at 40 bar_a on TA14-CpX29 MAT). Average peak area with indication of the standard deviation.



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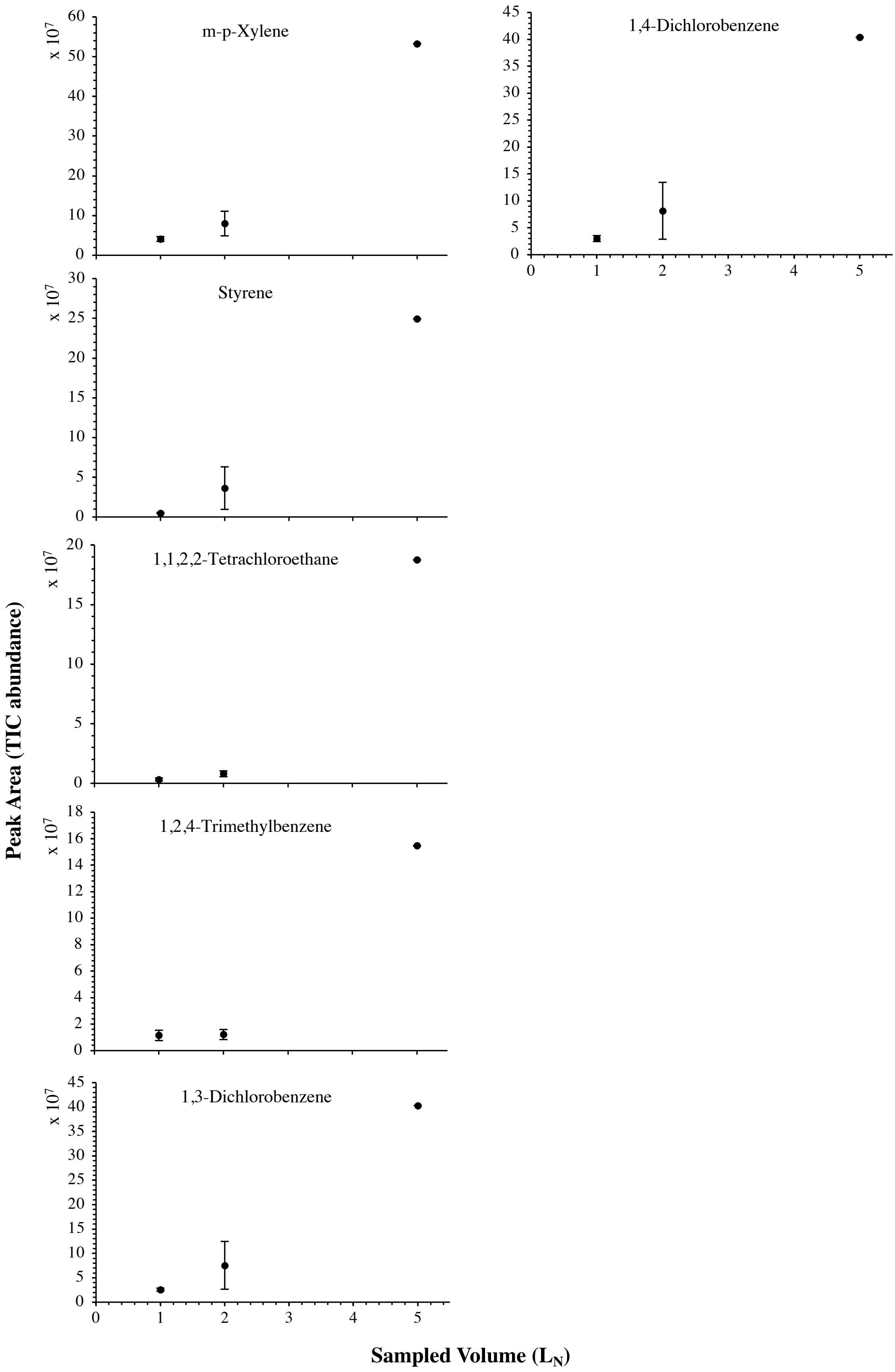

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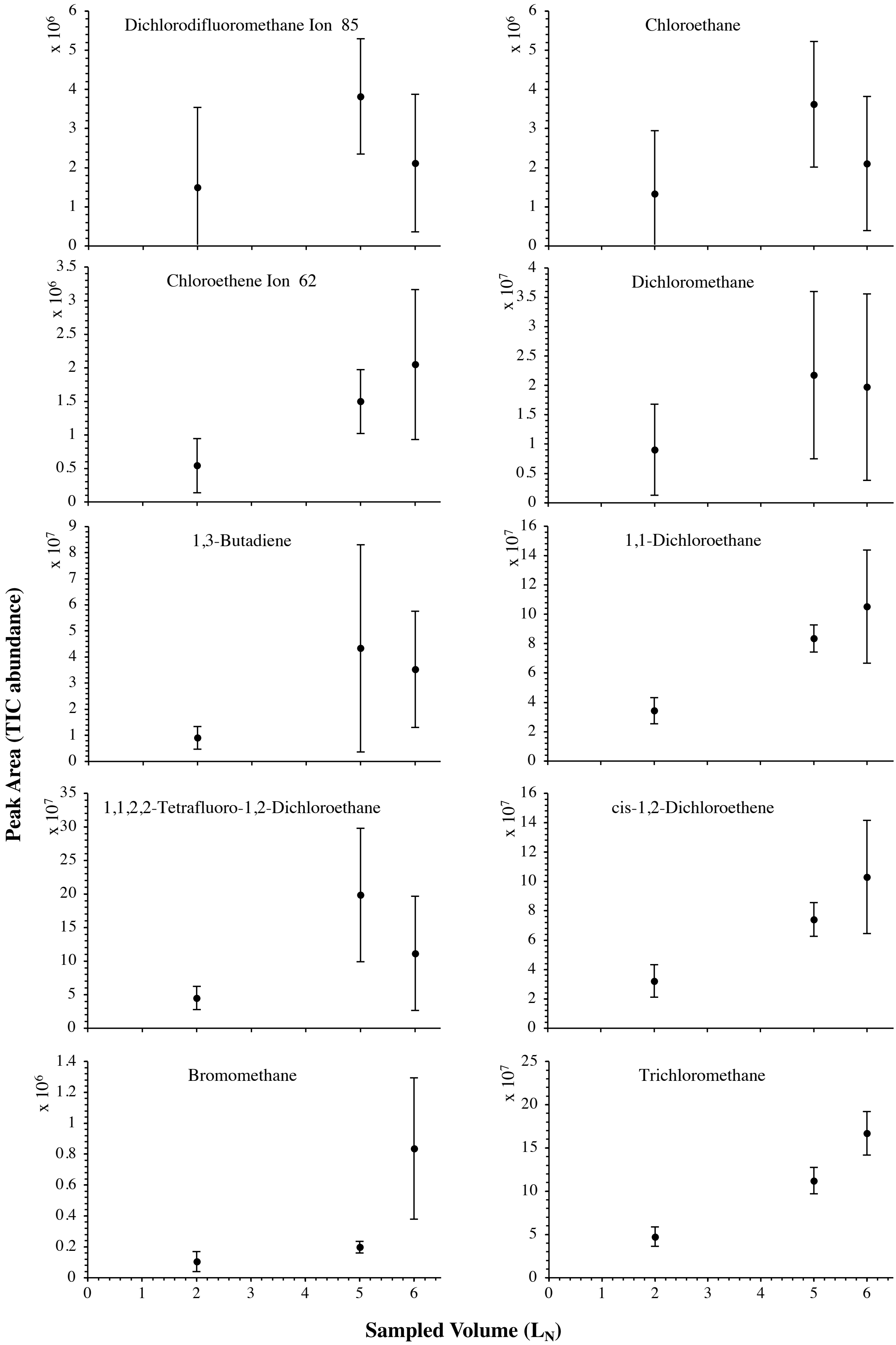
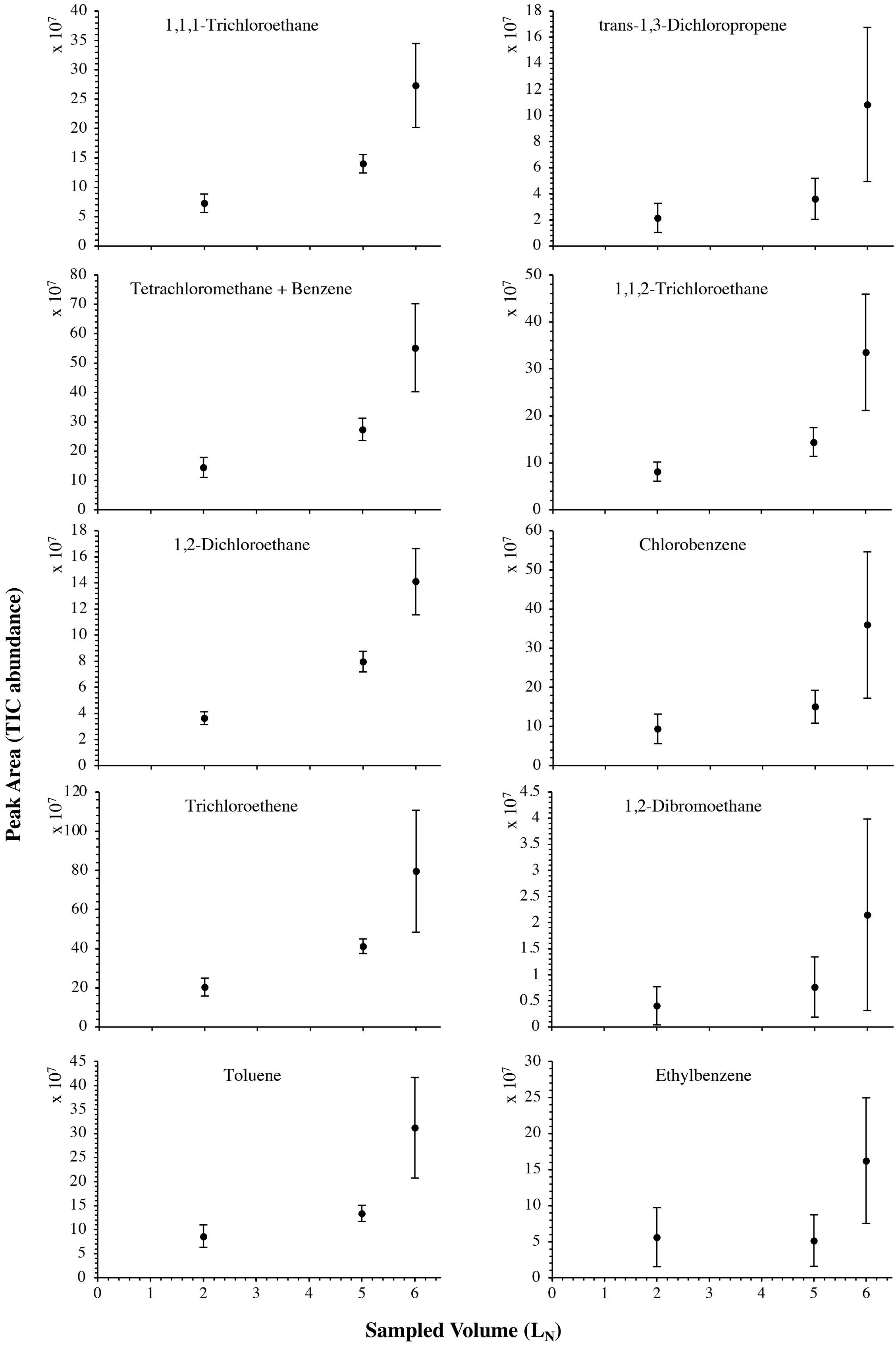


Figure SI-4: Partial breakthrough curves for the HVOC not shown in Fig.7 of the core paper for test-condition D (2, 5 and 6 L_N of the SGM sampled at 5 bar_a on TA14-CpX29 MAT). Average peak area with indication of the standard deviation.



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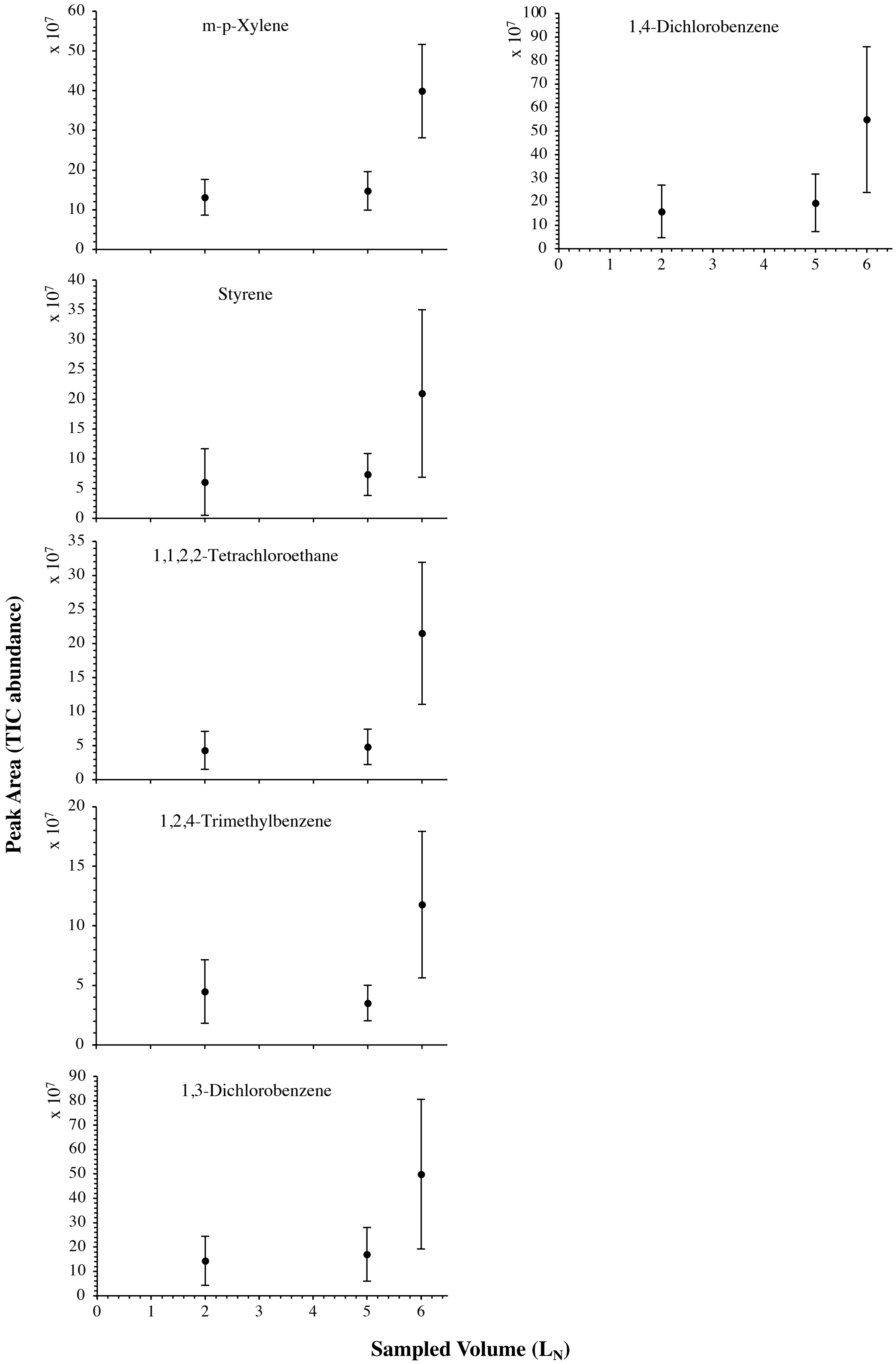

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