Supplementary information for

"Gas-particle partitioning of polyol tracers in the western Yangtze River Delta, China: Absorptive or Henry's law partitioning?"

Chao Qin[a], Yafeng Gou[b], Yuhang Wang[c], Yuhao Mao[b], Hong Liao[b], Qin'geng Wang[d], Mingjie Xie[b,*]

[a] Colleges of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

[b] Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, 219 Ningliu Road, Nanjing 210044, China

[c] School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332

[d] State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Nanjing 210023, China

*Corresponding to:

Mingjie Xie (mingjie.xie@nuist.edu.cn; mingjie.xie@colorado.edu);

Tel: +86-18851903788l; Fax: +86-25-58731051;

Mailing address: 219 Ningliu Road, Nanjing, Jiangsu, 210044, China

Text S1. Sample extraction and instrumental analysis

One eighth (25 cm^2) of each filter sample was spiked with 40 μL of internal standards solution (10 ng uL^{-1} of naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d10, and perylene-d12), followed by sonication in a mixture of methanol and methylene chloride (1:1, v/v) twice for 15 min each. All extracts were filtered through a prebaked glass fiber filter to a 100 mL pear shaped flask and rotary evaporated to ~0.5 mL. After that, the extract was transferred to a 2 mL glass vial and combined with 3 rinses of the flask using methanol and methylene chloride at a mixing ratio of 1:2. A gentle flow of N_2 was deployed to blow the concentrated extracts to dryness, and then 50 μL of N, O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and 10 μL of pyridine were added to react with the dried extracts at 70 ^{o}C for 3 h. Prior to the analysis using gas chromatography (GC, Agilent 7890) – mass spectrometry (MS, Agilent 5977B), the cooled BSTFA:TMCS/pyridine solution was diluted to a final volume of 400 μL using pure *n*-hexane. Polyurethane foam (PUF) samples were pre-spiked using the same internal standard solution as that for filter samples, and were Soxhlet extracted using a mixture of methylene chloride (225 mL) and methanol (25 mL) for 24 h. The following pretreatment procedures were visualized in Figure S1, mostly the same as those for filter samples except that 50 μL of pure water was added to the derivatized and diluted extracts prior to GC-MS analysis. This additional step was supposed to separate PUF residues from polyol derivatives in the supernatant and avoid changing GC inlet liners too frequently.

An aliquot of 2 μL of each sample was analyzed using GC-MS under electron ionization mode (EI, 70 eV), and target polyols were separated with a HP-5ms capillary column (30 m × 0.25 mm × 0.25 μm). The GC oven temperature was initially held at 50 ^{o}C for 2 min, and then programmed to 120 ^{o}C at 3 ^{o}C min^{-1} (hold for 0 min) and 300 at 6 °C min^{-1} (final temperature, hold for 10 min). A six-point calibration curve (0.05 – 5 ng μl^{-1}) was generated using an internal standard method. The final concentrations of polyol tracers in each sample were derived from their total amount in sample extract and the sample volume. Due to the limited availability of authentic standards, secondary products of isoprene including C5-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, and trans-2-methyl-1,3,4-trihydroxy-1-butene; abbreviated as C5-alkene 1, 2, and 3) and 2-methyltetrols (2-methylthreitol and 2-methylerythritol) were quantified as meso-erythritol; sugars and sugar alcohols were quantified using authentic standards; other acid tracers (e.g., diacids, polyacids) were all quantified as ketopinic acid, but were not reported here.

Text S2. Calculations of absorptive partitioning coefficients

In this study, absorptive gas-particle partitioning coefficients ($K_{\text{p,OM}}$, $\text{m}^3\ \text{ug}^{-1}$) were calculated empirically from measurements ($K^{\text{m}}_{\text{p,OM}}$; eq 1) and predicted theoretically ($K^{\text{t}}_{\text{p,OM}}$; eq 2)

$$K^{\text{m}}_{\text{p,OM}} = \frac{F/M_{\text{OM}}}{A} \qquad (1)$$

$$K^{\text{t}}_{\text{p,OM}} = \frac{RT}{10^6\,\overline{\text{MW}}_{\text{OM}}\zeta_{\text{OM}}p^{\text{o}}{}_{\text{L}}} \qquad (2)$$

where M_{OM} denotes the mass concentration of absorptive organic matter (OM = OC × 1.6; Turpin and Lim, 2001); F (ng m^{-3}) and A (ng m^{-3}) are particulate and gaseous concentrations of individual polyols, respectively. In eq 2, R (m^3 atm K^{-1} mol^{-1}) and T (K) are the ideal gas constant and ambient temperature; $\overline{\text{MW}}_{\text{OM}}$, average molecular weight of absorptive OM, was set at 200 g mol^{-1} for all samples (Barsanti and Pankow, 2004; Williams et al., 2010); ζ_{OM} denotes the mole fraction scale activity coefficient, and was presumed to be unity for all species in each sample; $p^{\text{o}}{}_{\text{L}}$ (atm) is the vapor pressure of each pure compound. The $p^{\text{o}}{}_{\text{L}}$ values of individual polyols for each sampling interval were adjusted using the average temperature

$$p_{\mathrm{L}}^{\mathrm{o}} = p_{\mathrm{L}}^{\mathrm{o},*} \exp\left[\frac{\Delta H_{\mathrm{vap}}^{*}}{\mathrm{R}}\left(\frac{1}{298.15} - \frac{1}{\mathrm{T}}\right)\right] \tag{3}$$

where $p^{\mathrm{o},*}_{\mathrm{L}}$ is the subcooled liquid vapor pressure and $\Delta H^{*}_{\mathrm{vap}}$ (kJ mol^{-1}) is the enthalpy of vaporization of the liquid at 298.15 K (Table S3). The $p^{\mathrm{o},*}_{\mathrm{L}}$ values of polyol tracers in this study were obtained from the Estimation Programs Interface (EPI) Suite developed by the US Environmental Protection Agency and Syracuse Research Corporation (US EPA, 2012). $\Delta H^{*}_{\mathrm{vap}}$ values were estimated empirically from the correlation between $\Delta H^{*}_{\mathrm{vap}}$ and ln $p^{\mathrm{o},*}_{\mathrm{L}}$ (Goss and Schwarzenbach, 1999)

$$\Delta H_{\mathrm{vap}}^{*} = -3.82 Inp_{\mathrm{L}}^{\mathrm{o},*} + 70.0 \tag{4}$$

Text S3. Prediction of Henry's law coefficient in pure water

The Henry's law coefficients of polyols tracers in pure water at 25 $^{\mathrm{o}}$C ($K^{*}_{\mathrm{H,w}}$, mol m^{-3} atm^{-1}) were obtained from the EPI suite (Table S3). Due to the variation in ambient temperature across air samples, $K_{\mathrm{H,w}}$ values of polyol tracers were adjusted for each sample using van 't Hoff equation

$$K_{\mathrm{H,w}} = K_{\mathrm{H,w}}^{*} \exp\left[\frac{\Delta H_{\mathrm{sol}}^{*}}{\mathrm{R}}\left(\frac{1}{298.15} - \frac{1}{\mathrm{T}}\right)\right] \tag{5}$$

where $\Delta H^{*}_{\mathrm{sol}}$ (kJ mol^{-1}) refers to the enthalpy of dissolution at 298.15 K. The $\Delta H^{*}_{\mathrm{sol}}$ values of meso-erythritol, xylitol, arabitol, and mannitol were obtained from Compernolle and Müller (2014), and were used as surrogates for other polyol compounds based on the number of hydroxyl groups. The $\Delta H^{*}_{\mathrm{sol}}$ of C5-alkene triols were substituted by that of glycerol (92.6 kJ mol^{-1}; Compernolle and Müller, 2014).

Table S1. Statistics of ambient temperature (°C), relative humidity (%), and $PM_{2.5}$ major species (µg m^{-3}) from Yang et al. (2021).

	Median	Mean ± stdev[a]	Range
Ambient temperature	18.2	17.9 ± 9.43	-4.18–36.1
Relative humidity	70.5	68.4 ± 17.6	24.5 – 99.5
$PM_{2.5}$	67.2	71.7 ± 34.5	18.9–165
NH_4^+	3.98	4.94 ± 3.31	1.08–21.7
NO_3^-	8.84	11.5 ± 10.4	0.12–53.2
SO_4^{2-}	7.54	8.70 ± 4.20	2.78–20.6
Ca^{2+}	1.35	1.85 ± 1.40	0.011–7.02
Mg^{2+}	0.10	0.13 ± 0.095	0.0088–0.43
K^+	0.77	1.00 ± 0.75	0.077–3.66
OC	6.82	7.61 ± 3.33	2.24–16.8
EC	2.83	2.93 ± 1.15	0.97–6.64
WSOC	3.93	4.35 ± 2.13	1.14–10.5
Aerosol liquid water[b]	12.2	21.3 ± 24.2	0.97–107

[a] Standard deviation; [b] predicted using ISORROPIA II model.

Table S2. Method detection limits (MDL, pg) and recoveries (%) of reference standards.

Polyol species	MDL	Filter (*N* = 6)		PUF (*N* = 6)	
		Average	Range	Average	Range
meso-erythritol	40.2	106 ± 1.90	102 – 108	50.7 ± 4.95	45.0 – 57.0
levoglucosan	43.8	99.3 ± 3.29	91.8 – 102	54.3 ± 5.92	46.5 – 63.9
fructose	54.9	79.3 ± 14.4	61.7 – 98.4	44.0 ± 13.2	30.4 – 57.9
mannose	46.4	79.9 ± 3.03	75.8 – 83.0	69.6 ± 10.5	57.2 – 84.5
glucose	88.3	100 ± 7.11	89.2 – 108	71.7 ± 22.3	53.8 – 109
xylitol	34.8	68.4 ± 5.68	61.6 – 75.8	44.9 ± 3.27	37.1 – 61.9
arabitol	42.6	75.8 ± 6.40	68.8 – 83.5	55.5 ± 8.21	45.1 – 67.7
mannitol	38.3	62.7 ± 9.02	48.5 – 74.9	55.3 ± 4.10	42.4 – 76.3

Table S3. Predicted physicochemical properties of target polyol tracers.

Polyol species	**Molecular formula**	**MW**	$p^{o,*}_{L}$ [a]	ΔH^{*}_{vap} [b]	ΔH^{*}_{sol} [c]	**Log** K_{OW} [d]	$K_{H,w}$ [e]
			atm	kJ mol^{-1}	kJ mol^{-1}		mol m^{-3} atm^{-1}
***Isoprene SOA* tracers**							
cis-2-methyl-1,3,4-trihydroxy-1-butene[f]	$C_5H_{10}O_3$	118	1.89×10^{-7}	84.3	-92.6	-0.90	1.28×10^{7}
3-methyl-2,3,4-trihydroxy-1-butene[f]	$C_5H_{10}O_3$	118	6.96×10^{-7}	79.0	-92.6	-0.86	1.51×10^{7}
trans-2-methyl-1,3,4-trihydroxy-1-butene[f]	$C_5H_{10}O_3$	118	1.89×10^{-7}	84.3	-92.6	-0.90	1.28×10^{7}
2-methylthreitol	$C_5H_{12}O_4$	136	2.28×10^{-8}	89.1	-133	-1.65	2.44×10^{9}
2-methylerythritol	$C_5H_{12}O_4$	136	2.28×10^{-8}	89.1	-133	-1.65	2.44×10^{9}
Biomass burning tracer							
levoglucosan	$C_6H_{10}O_5$	162	4.56×10^{-10}	100	-92.6	-1.25	7.04×10^{12}
Sugars and sugar alcohols							
meso-erythritol	$C_4H_{10}O_4$	122	6.91×10^{-10}	98.1	-133	-2.11	3.25×10^{9}
fructose	$C_6H_{12}O_6$	180	2.52×10^{-11}	110	-144	-1.55	1.03×10^{14}
mannose	$C_6H_{12}O_6$	180	2.13×10^{-11}	110	-144	-2.43	1.70×10^{10}
glucose	$C_6H_{12}O_6$	180	1.76×10^{-10}	112	-144	-2.89	1.03×10^{14}
xylitol	$C_5H_{12}O_5$	152	7.40×10^{-13} [g]	133	-140	-2.56	6.67×10^{10}
arabitol	$C_5H_{12}O_5$	152	2.07×10^{-13} [g]	138	-147	-2.56	6.67×10^{10}
manitol	$C_6H_{14}O_6$	182	1.73×10^{-12}	114	-184	-3.01	1.38×10^{12}

[a] Subcooled liquid vapor pressure at 298.15 K;
[b] enthalpy of vaporization;
[c] enthalpy of dissolution, obtained from Compernolle and Müller. (2014);
[d] logarithm of *n*-octanol/water partition coefficient;
[e] Henry's law constant in pure water at 298.15 K;
[f] abbreviated as C5-alkene triol1, 2, and 3, respectively;
[g] estimated as their solid-state vapor pressures from Compernolle and Müller. (2014).

Table S4. Concentration statistics (ng m^{-3}) of target polyol tracers determined from filter and PUF samples.

Polyol species	Q_f				Q_b				PUF			
	No. of obs.	Median	Average ± Stdev	Range	No. of obs.	Median	Average ± Stdev	Range	No. of obs.	Median	Average ± Stdev	Range
Isoprene SOA tracers												
C5-alkene triol1	89	0.28	3.59 ± 10.0	0.013 – 69.4	56	0.056	0.14 ± 0.28	0.0046 – 1.86	31	0.0064	0.0083 ± 0.0088	0.0003 – 0.045
C5-alkene triol2	85	0.61	1.88 ± 4.13	0.015 – 27.7	59	0.062	0.13 ± 0.21	0.0051 – 1.07	37	0.0031	0.0065 ± 0.013	0.0003 – 0.077
C5-alkene triol3	96	0.57	10.4 ± 31.6	0.0025 – 221	59	0.12	0.28 ± 0.42	0.0039 – 1.99	67	0.017	0.033 ± 0.041	0.0021 – 0.18
∑C5-alkene triols	102	0.94	14.5 ± 43.9	0.016 – 318	77	0.093	0.41 ± 0.79	0.0042 – 4.92	73	0.017	0.037 ± 0.051	0.0003 – 0.24
2-methylthreitol	102	0.52	2.35 ± 3.60	0.042 – 21.8	95	0.047	0.41 ± 1.11	0.0009 – 7.12	61	0.026	0.19 ± 0.43	0.0016 – 2.44
2-methylerythritol	102	1.22	7.14 ± 13.4	0.10 – 87.2	80	0.15	0.89 ± 1.98	0.0008 – 11.6	65	0.047	0.55 ± 1.12	0.0064 – 6.25
∑2-methyltetrols	102	1.74	9.49 ± 16.9	0.16 – 109	96	0.15	1.15 ± 2.89	0.0009 – 18.7	66	0.061	0.72 ± 1.50	0.0016 – 8.01
Biomass burning tracer												
levoglucosan	102	45.3	65.9 ± 71.1	4.47 – 415	8	0.37	0.60 ± 0.74	0.018 – 2.28	63	0.015	0.023 ± 0.036	0.0025 – 0.25
Sugars and sugar alcohols												
meso-erythritol	102	0.93	1.15 ± 0.80	0.17 – 4.99	12	0.040	0.074 ± 0.085	0.0019 – 0.21	22	0.012	0.013 ± 0.012	0.0012 – 0.061
fructose	102	3.05	14.9 ± 62.9	1.12 – 473	60	0.055	0.11 ± 0.18	0.0008 – 1.21	64	0.054	0.12± 0.14	0.0003 – 0.59
mannose	102	0.33	0.41 ± 0.31	0.0021 – 1.62	37	0.0060	0.017 ± 0.026	0.00 – 0.13	62	0.0042	0.018 ± 0.063	0.00 – 0.38
glucose	102	7.46	13.8 ± 31.3	1.22 – 239	74	0.20	0.31 ± 0.35	0.0024 – 2.01	60	0.11	0.48 ± 0.87	0.0032 – 5.15
xylitol	92	0.81	0.89 ± 0.63	0.048 – 3.13	23	0.036	0.049 ± 0.048	0.0068 – 0.22	0	/	/	/
arabitol	102	5.13	7.35 ± 6.99	0.50 – 39.3	10	0.034	0.13 ± 0.22	0.0021 – 0.68	23	0.011	0.026 ± 0.034	0.0002 – 0.15
manitol	102	6.87	11.3 ± 11.6	0.65 – 74.2	18	0.072	0.091 ± 0.10	0.0040 – 0.43	56	0.060	0.10 ± 0.13	0.0058 – 0.63

Table S5. Statistics for log $K^{m}_{p,WIOM}$ and log $K^{t}_{p,OM}$ of individual polyol tracers.

Species	No. of obs.	Log $K^{m}_{p,WIOM}$			Log $K^{t}_{p,OM}$[a]		
		Median	Average	Range	Median	Average	Range
Isoprene SOA tracers							
C5-alkene triol 1	53	-1.03	-1.15 ± 0.86	-3.64 – 1.38	-3.23	-3.09 ± 0.44	-3.70 – -1.63
C5-alkene triol 2	63	-1.24	-1.41 ± 0.75	-3.71 – 1.06	-3.70	-3.62 ± 0.37	-4.24 – -2.67
C5-alkene triol 3	83	-1.17	-1.22 ± 0.87	-4.34 – 1.02	-3.01	-2.90 ± 0.48	-3.70 – -1.63
2-methylthreitol	101	-2.37	-2.47 ± 0.75	-4.82 – -0.80	-1.90	-1.87 ± 0.52	-2.81 – -0.62
2-methylerythritol	95	-2.32	-2.34 ± 0.75	-4.35 – -0.17	-1.91	-1.90 ± 0.51	-2.81 – -0.62
Biomass burning tracer							
levoglucosan	65	0.39	0.25 ± 0.93	-2.41 – 2.00	-0.12	-0.038 ± 0.59	-1.00 – 1.29
Sugars ang sugar alcohols							
meso-erythritol	31	-1.78	-1.83 ± 0.67	-3.63 – -0.64	-0.80	-0.65 ± 0.48	-1.35 – 0.69
fructose	85	-1.52	-1.58 ± 0.93	-3.83 – 0.88	1.14	1.17 ± 0.62	0.015 – 2.72
mannose	74	-2.58	-2.52 ± 1.00	-4.63 – 0.27	1.23	1.28 ± 0.66	0.18 – 2.81
glucose	88	-3.12	-3.15 ± 0.98	-5.71 – -0.45	0.31	0.34 ± 0.65	-0.75 – 1.92
xylitol	22	-2.96	-2.99 ± 0.73	-4.17 – -1.69	3.43	3.37 ± 0.57	2.11 – 4.39
arabitol	30	-1.69	-1.73 ± 1.30	-3.90 – 1.53	3.15	3.25 ± 0.77	2.05 – 4.81
manitol	65	-2.53	-2.63 ± 0.99	-5.25 – -0.72	2.31	2.33 ± 0.70	1.15 – 3.98

[a] Obtianed from Table 1.

Figure S1

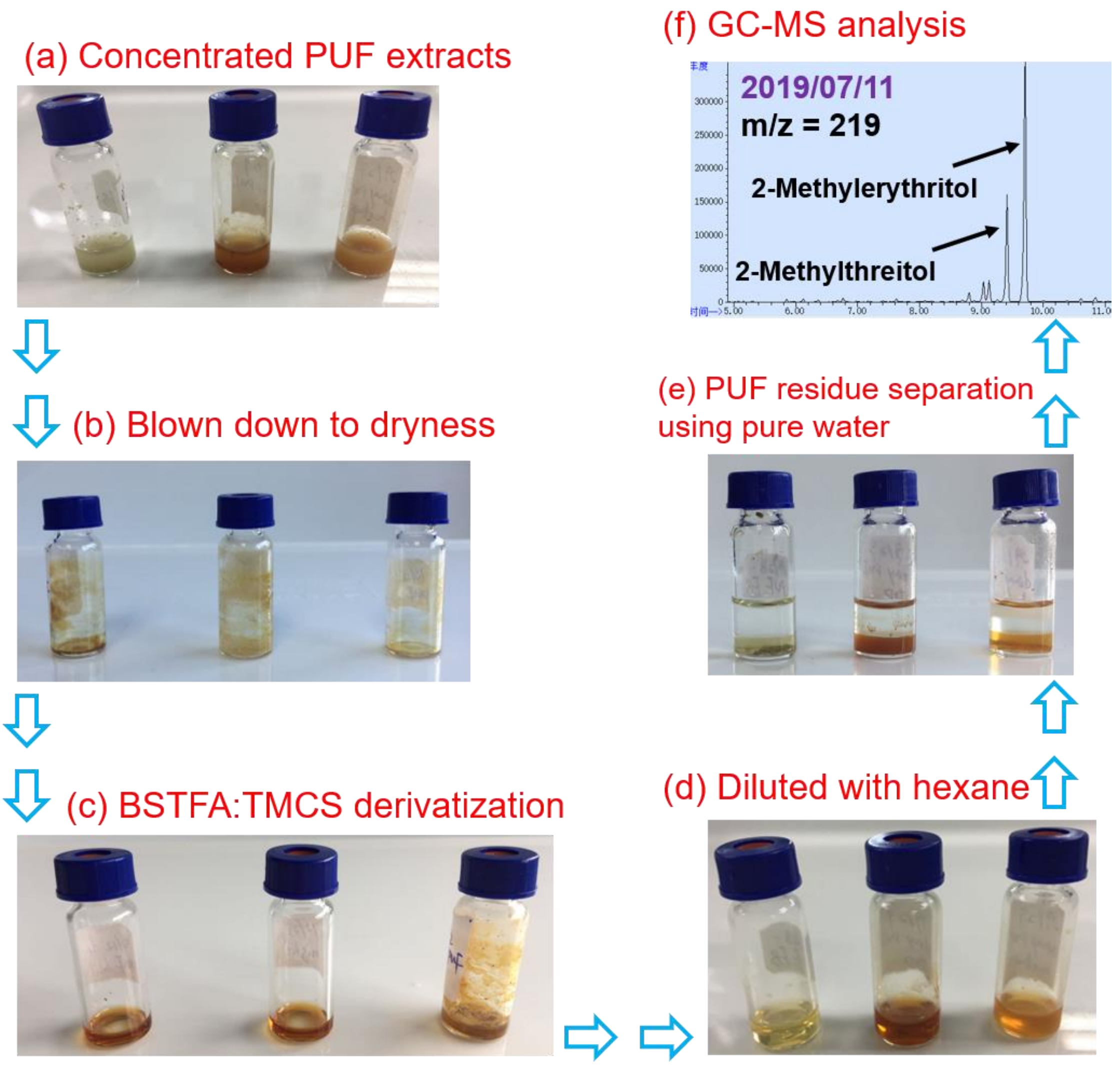

Figure S1. Revised procedures for analysis of gaseous polyols in PUF extracts.

Figure S2

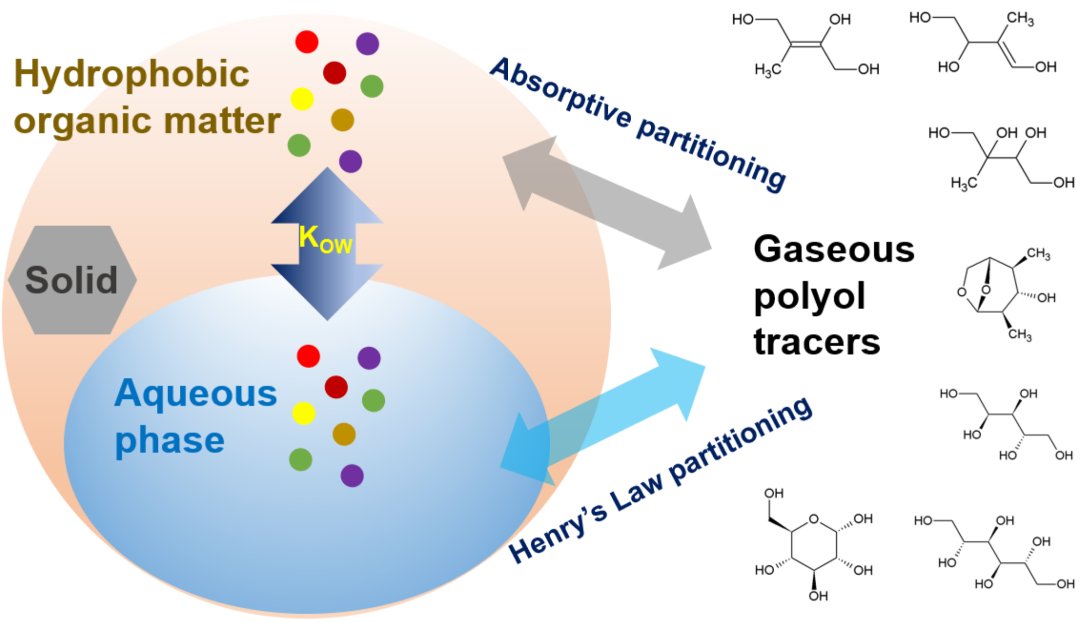

Figure S2. Proposed scheme for gas-particle partitioning of polyol tracers.

Figure S3

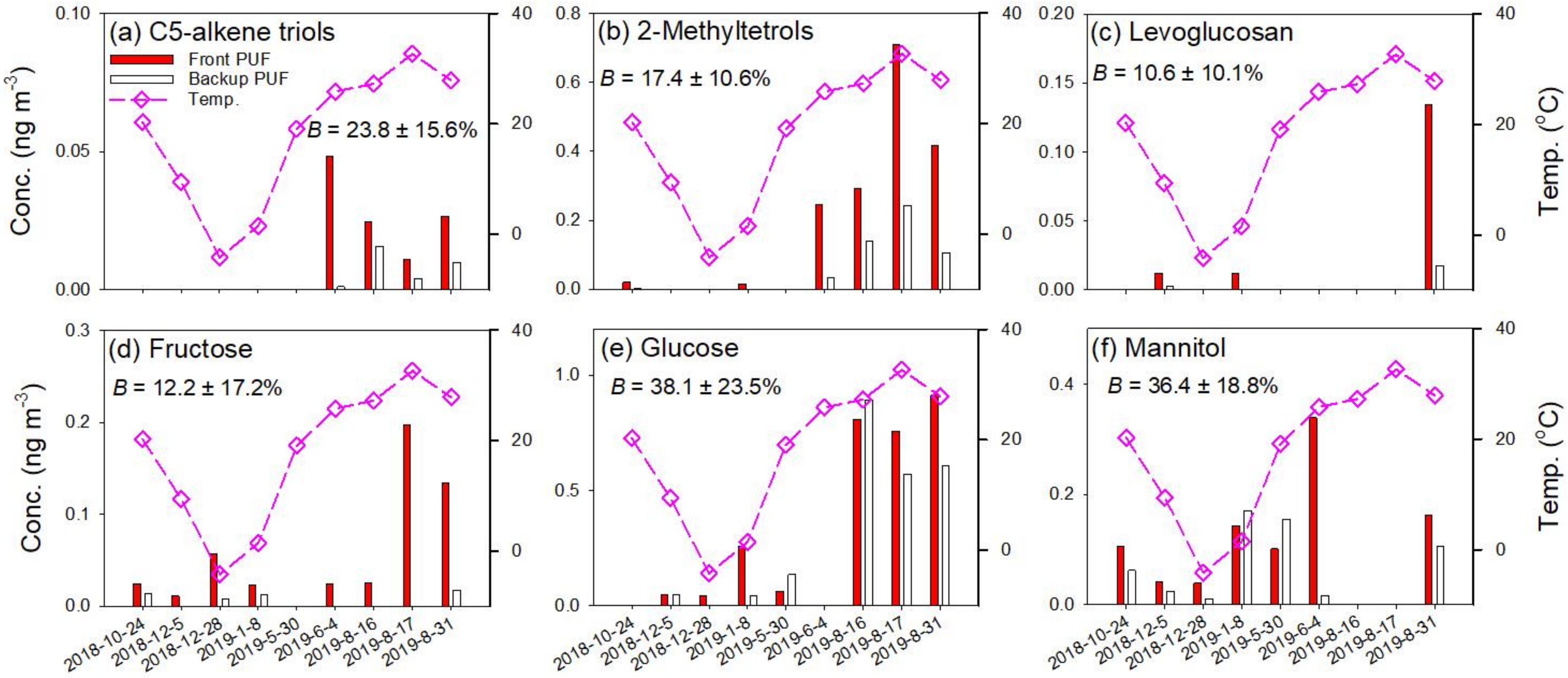

Figure S3. Concentrations of (a) C5-alkene triols, (b) 2-methylterols, (c) levoglucosan, (d) fructose, (e) glucose, and (f) mannitol in 9 pairs of front and backup PUF samples for breakthrough analysis.

Figure S4

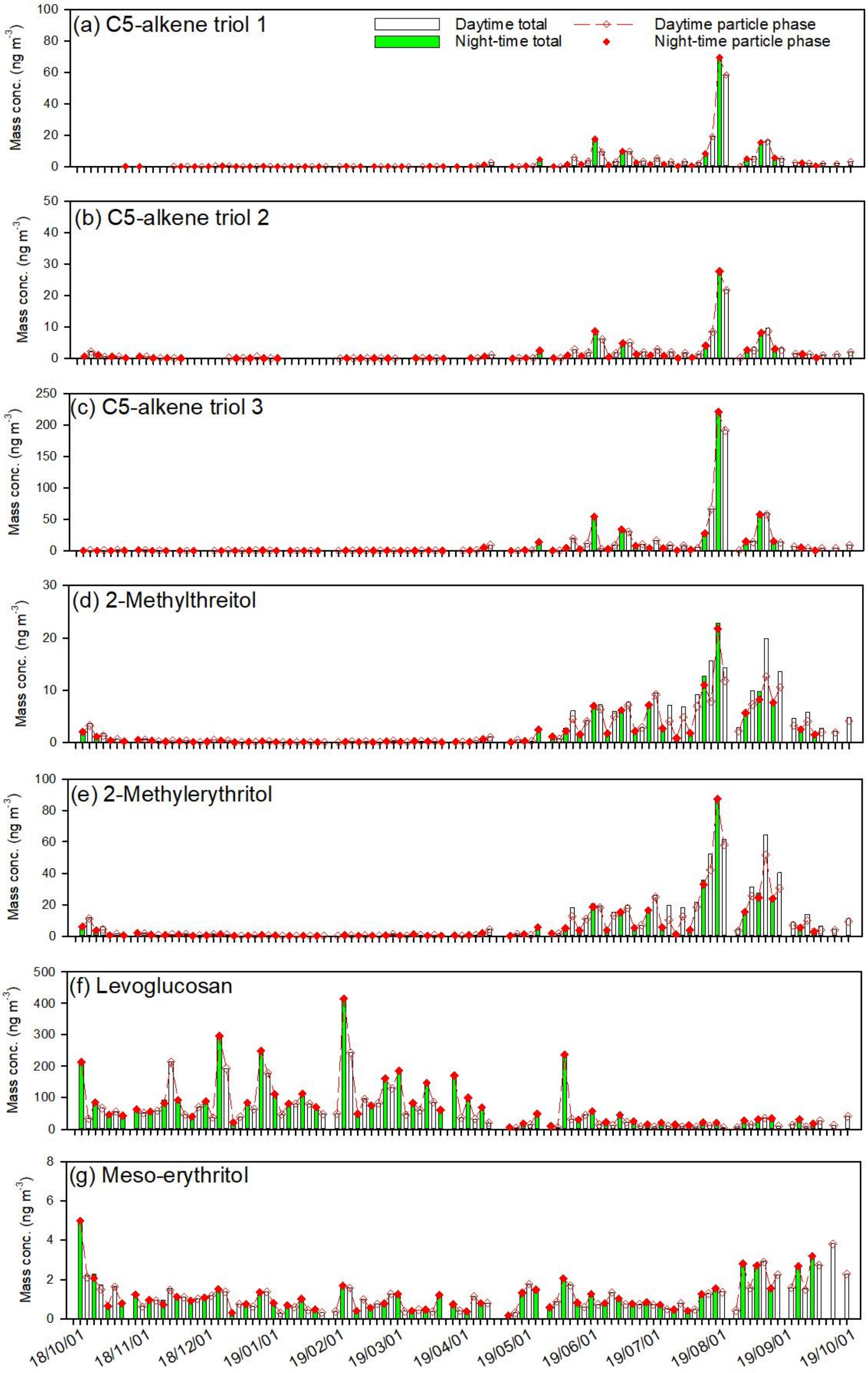

Figure S4. Temporal variations of total and Q_f concentrations of individual polyol tracers.

Figure S4 Continue

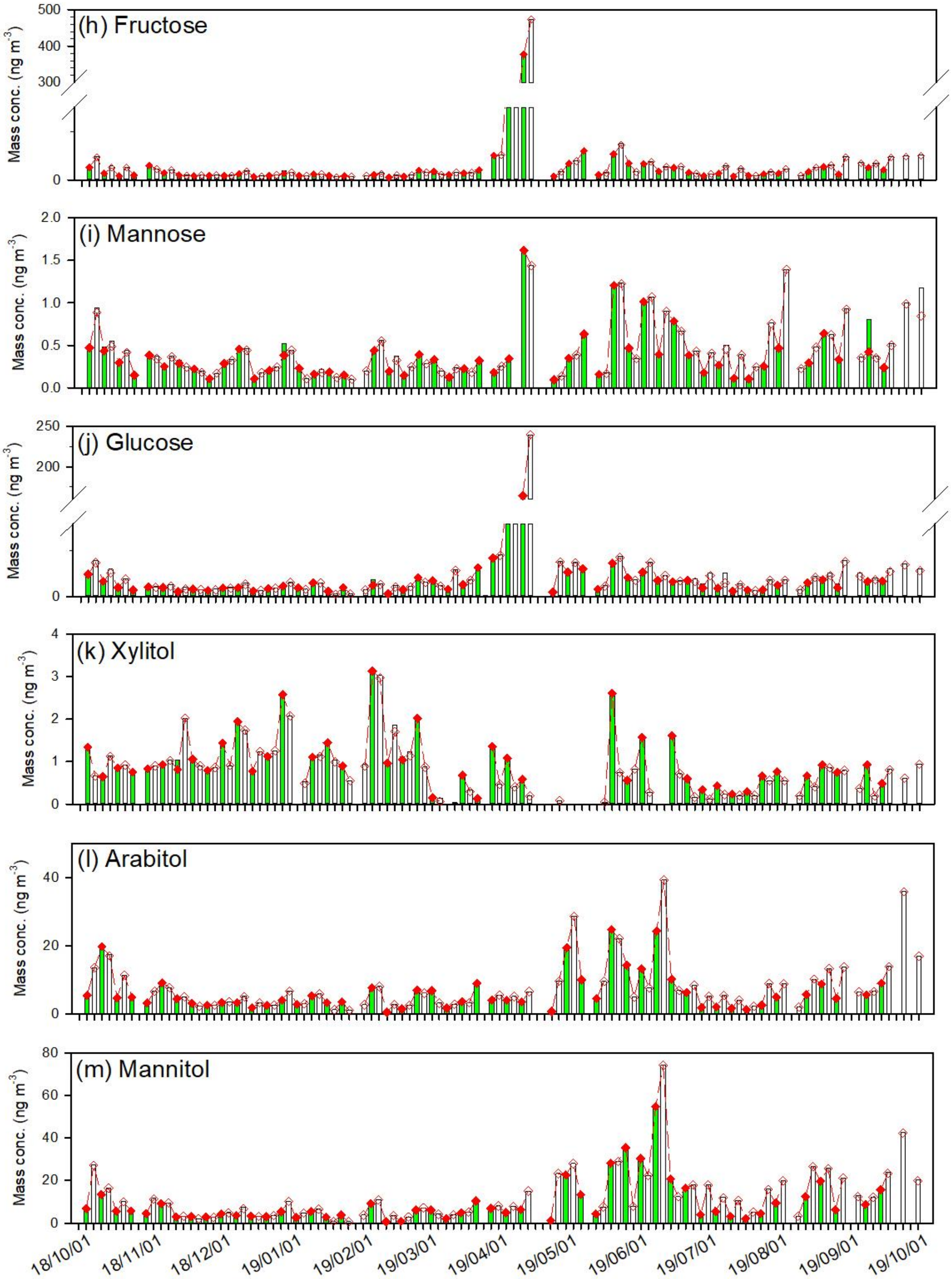

Figure S5

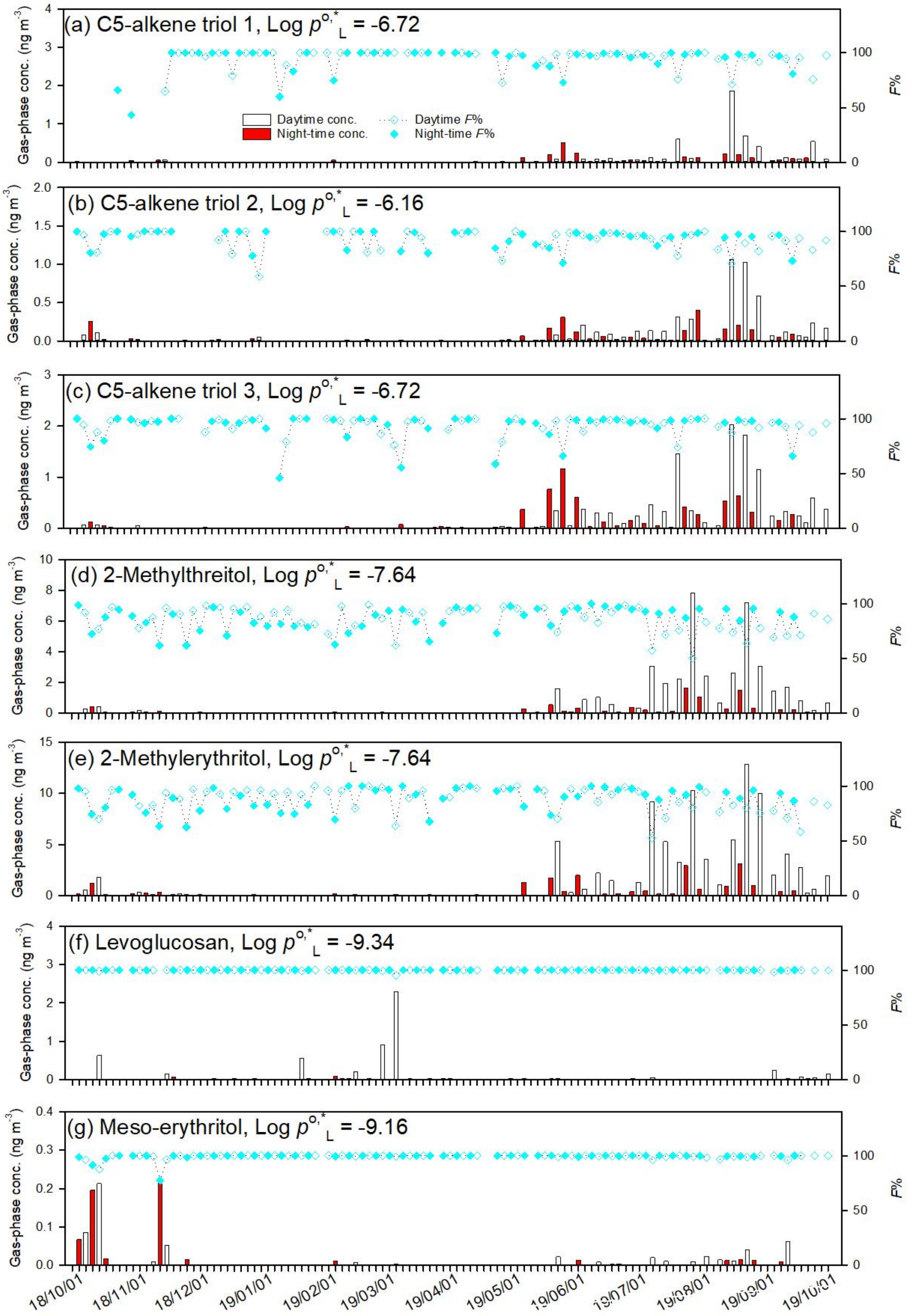

Figure S5. Temporal variations of gas-phase concentrations and particle-phase fractions (*F*%) of polyol tracers.

Figure S5 continue

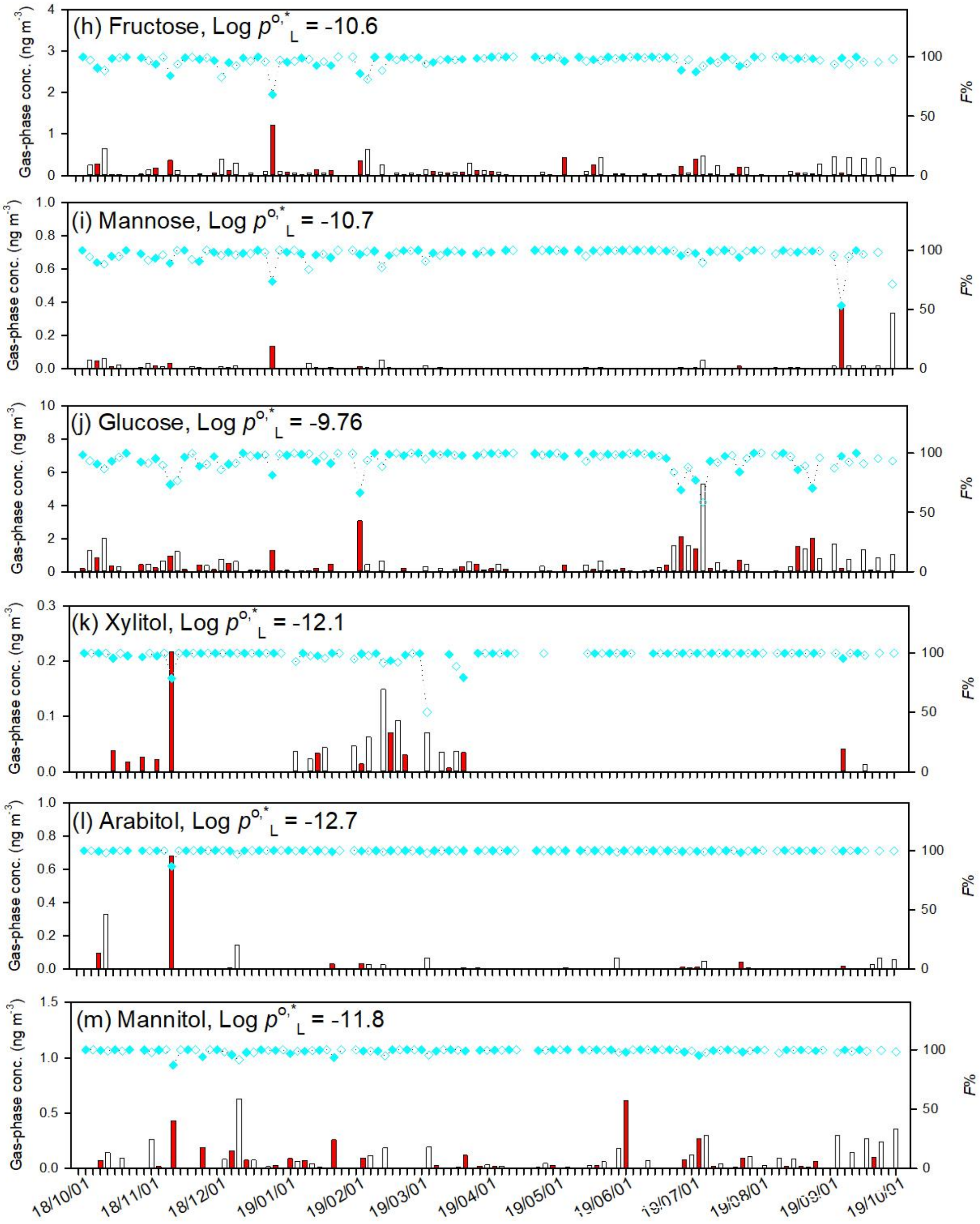

Figure S6

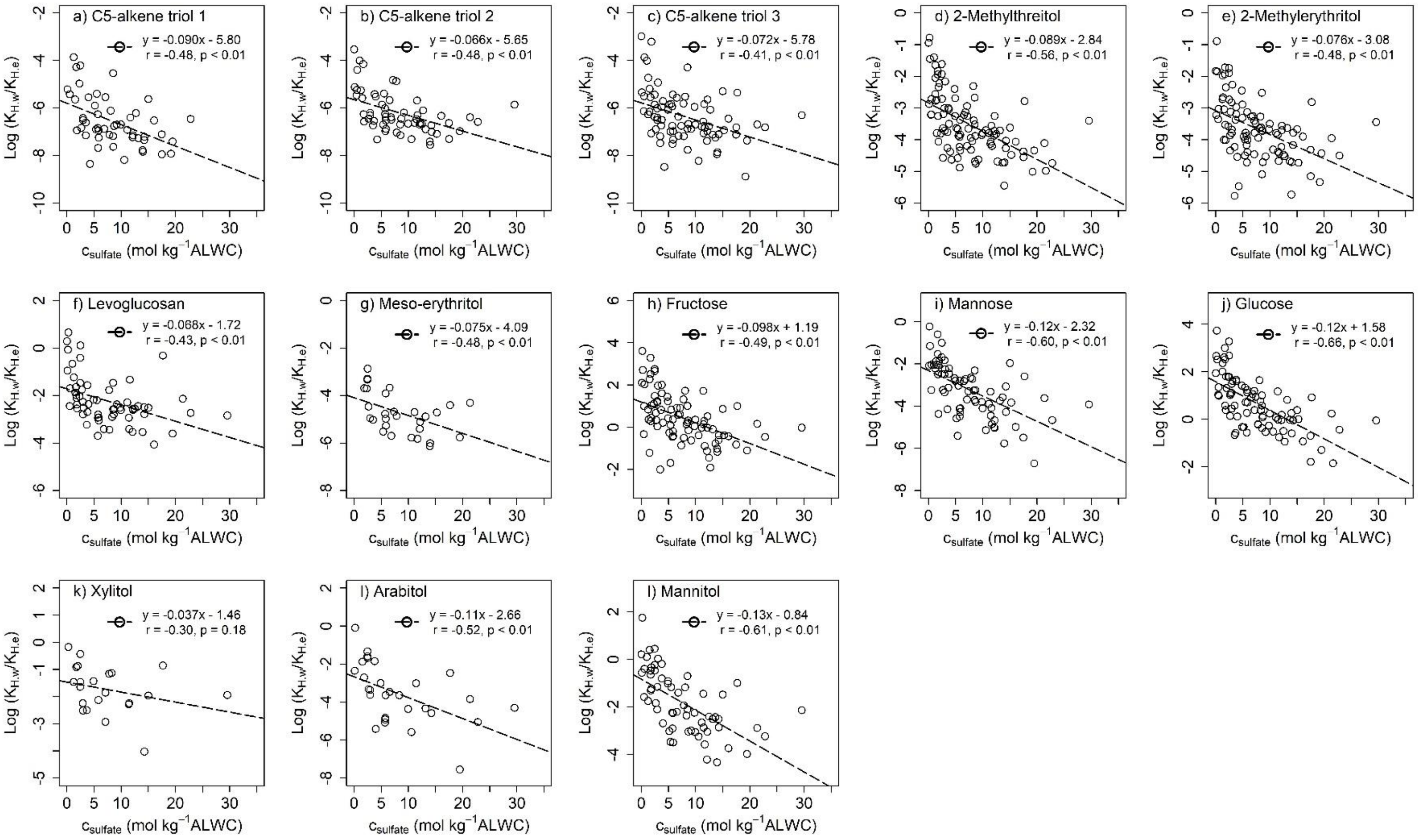

Figure S6. Modified Setschenow plots of log ($K_{H,w}/K_{H,e}$) vs. $c_{sulfate}$ for individual polyol tracers.

Figure S7

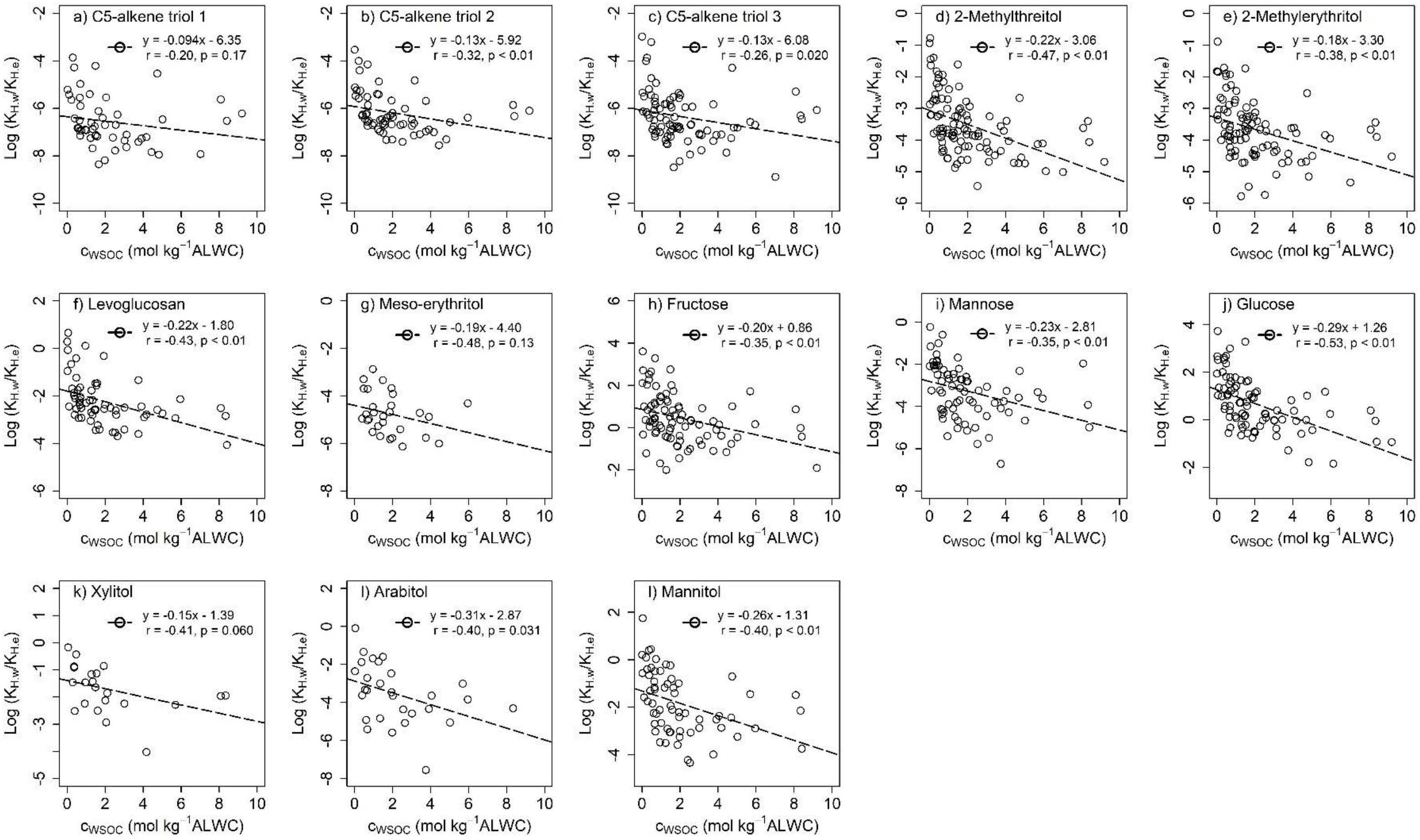

Figure S7. Modified Setschenow plots of log ($K_{H,w}/K_{H,e}$) vs. c_{WSOC} for individual polyol tracers (MW of WSOC was presumed as 200 g mol^{-1}).

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