Comparative sampling of gas phase volatile and semi-volatile organic fuel emissions from a combustion aerosol standard system

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Supplementary Information

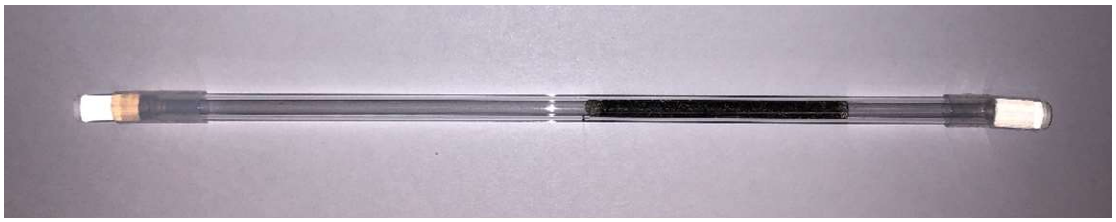


Figure S1: Graphene wool sampler showing the GW of 60 mm bed length housed in a glass tube with glass end caps held in place by Teflon sleeves. ***Source:*** *Adapted from (Schoonraad and Forbes, 2019b).*

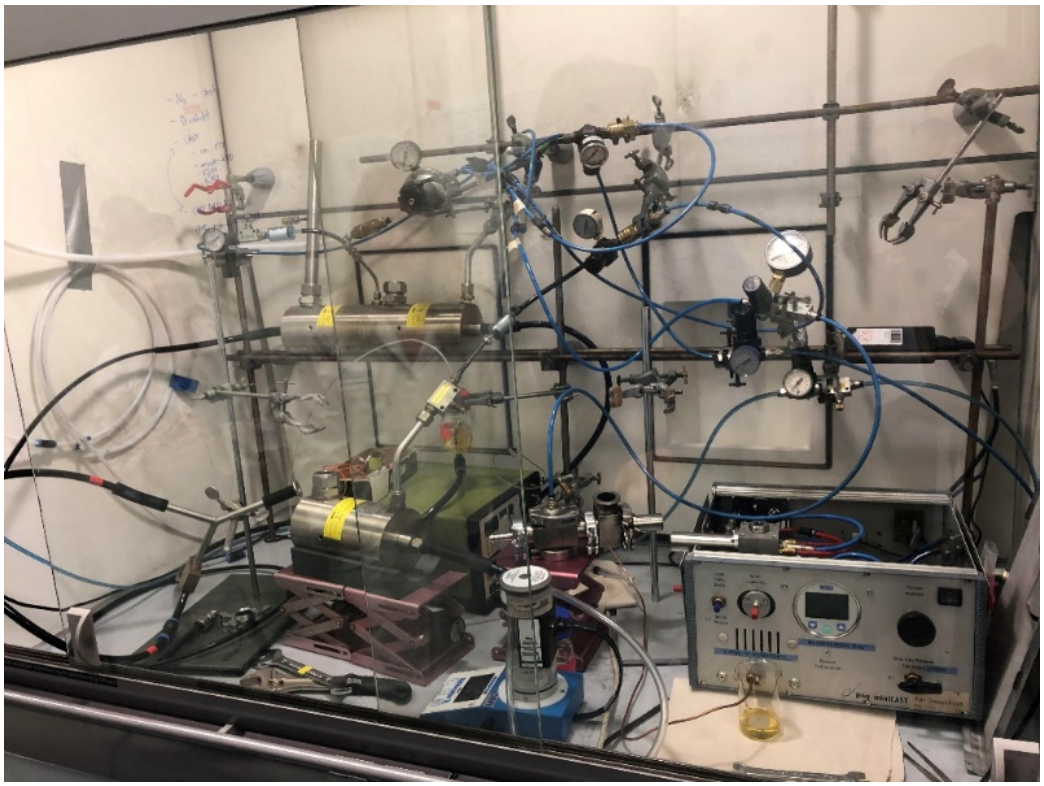


Figure S2: Photograph of the CAST generator sampling set-up.

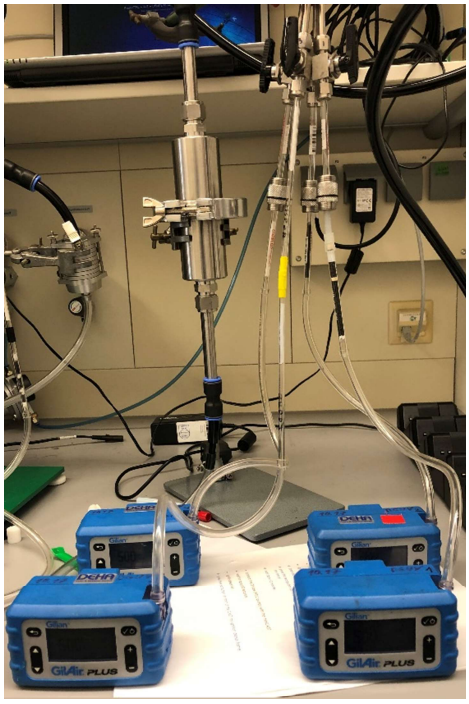


Figure S3: Photograph of the sampler setup for the activated charcoal, GW and PDMS samplers, respectively, during CAST sampling events. *Note: The fourth sampling point was for another experiment and is not reported on here.*

Table S1: Standards and internal standards used in this study.

Standard	Supplier
Naphthalene	Alfa Aesar
Fluorene	Fluka
Acenaphthene	Fluka
Acenaphthylene	Supelco
Phenanthrene	Alfa Aesar
Anthracene	Fluka
1-Methylnaphthalene	Aldrich
1,2-Dimethylnaphthalene	Alfa Aesar
2-Methylnaphthalene	Supelco
Biphenyl	Supelco
1-Methylfluorene	Aldrich
Fluoranthene	Fluka
Pyrene	Sigma-Aldrich
Benzene	Carl Roth
Toluene	Carl Roth
M-Xylene	Fluka
O-Xylene	Vwr
Ethylbenzene	Alfa Aesar

Benzaldehyde	Sigma Aldrich
Styrene	Fluka
Phenol	Merck
Indene	Aldrich
Indane	Fluka
Alkane Standard Solution C8-C20	Sigma-Aldrich
Benzene D6	Fluka
Toluene D8	Sigma Aldrich
O-Xylene D10	Sigma Aldrich
Naphthalene D8	Sigma Aldrich
Biphenyl D10	Cil - Cambridge Isotope Institute
Acenaphthylene D8	Cil-Cambridge Isotope Laboratories
Acenaphthene D10	Sigma Aldrich
Fluorene D10	Supelco
Phenanthrene D10	Cil-Cambridge Isotope Laboratories
Anthracene D10	Cil - Cambridge Isotope Institute
N-Heptane D16	Sigma Aldrich
N-Dodecane D26	Sigma Aldrich
N-Hexadecane D34	Aldrich

Table S2: Ambient conditions at the start of sampling events for this study

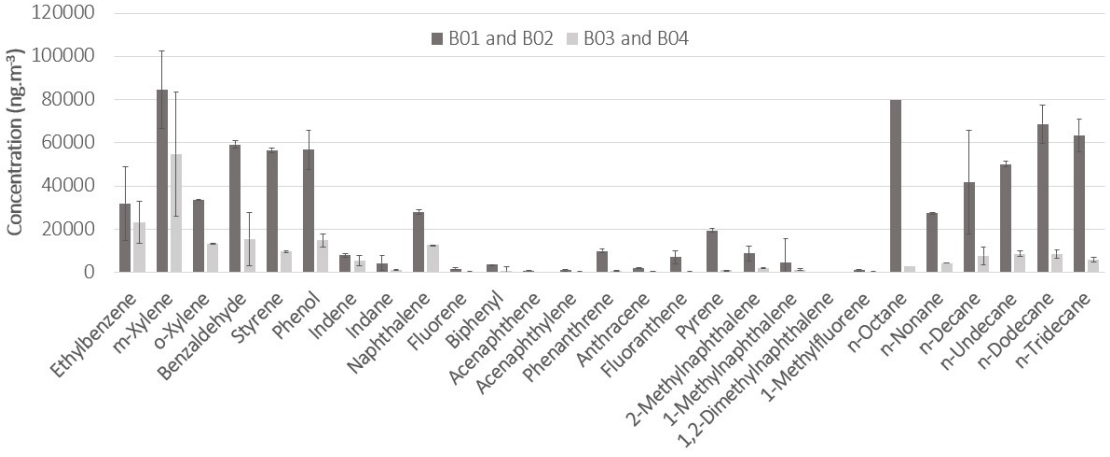
Measurement	Barometric Pressure (hPa)	Wet Bulb (°C)	Dry Bulb (°C)
B0 1	955.5	20.4	26.8
GTL 1	955.8	20.4	26.8
GTL 2	955.9	10.7	27.0
RME 1	956.0	10.7	27.0
RME 2	956.1	9.0	27.7
B0 2	956.2	9.0	27.7

Table S3: Mean FTIR results for the sampling events of the undiluted fuel emissions over each 10 min sampling period.

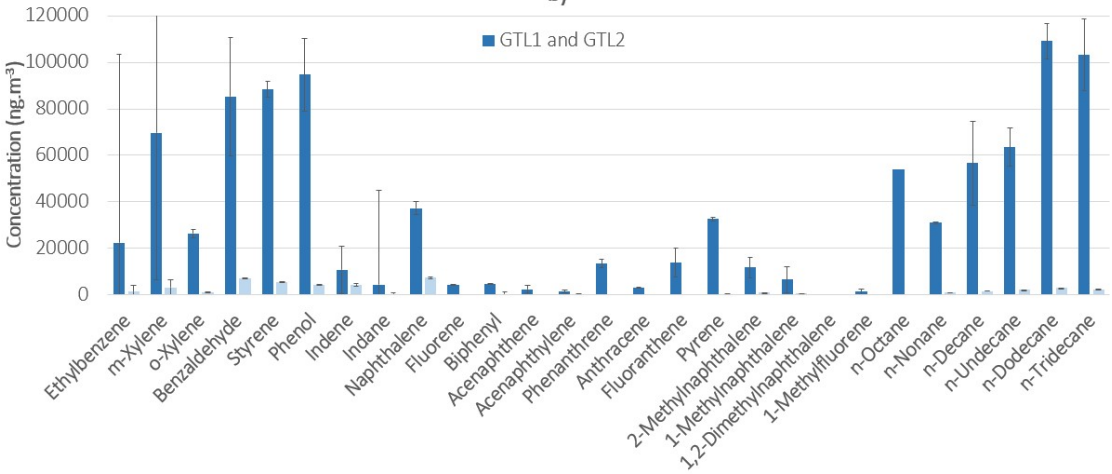
Sample	H_2O (%)	CO_2 (%)	CO (ppm)	O_2 (%)
B0 1	0.58	0.58	9.51	10.30
B0 2	0.57	0.58	9.48	10.30
B0 3	0.65	0.58	9.40	10.20
B0 4	0.66	0.58	9.42	10.20
Mean	0.62	0.58	9.45	10.25
SD	0.05	0.00	0.05	0.06
%RSD	7.42	0.13	0.55	0.56

GTL 1	0.56	0.58	7.89	10.31
GTL 2	0.56	0.58	7.86	10.31
GTL 3	0.66	0.58	7.63	10.50
GTL 4	0.65	0.58	7.65	10.45
Mean	0.61	0.58	7.76	10.39
SD	0.06	0.00	0.14	0.10
%RSD	9.10	0.21	1.77	0.94
RME 1	0.62	0.60	7.25	10.26
RME 2	0.62	0.60	7.30	10.28
RME 3	0.67	0.60	7.32	10.45
RME 4	0.67	0.59	7.64	10.41
Mean	0.64	0.60	7.38	10.35
SD	0.03	0.00	0.18	0.10
%RSD	4.79	0.63	2.43	0.93

a)



b)



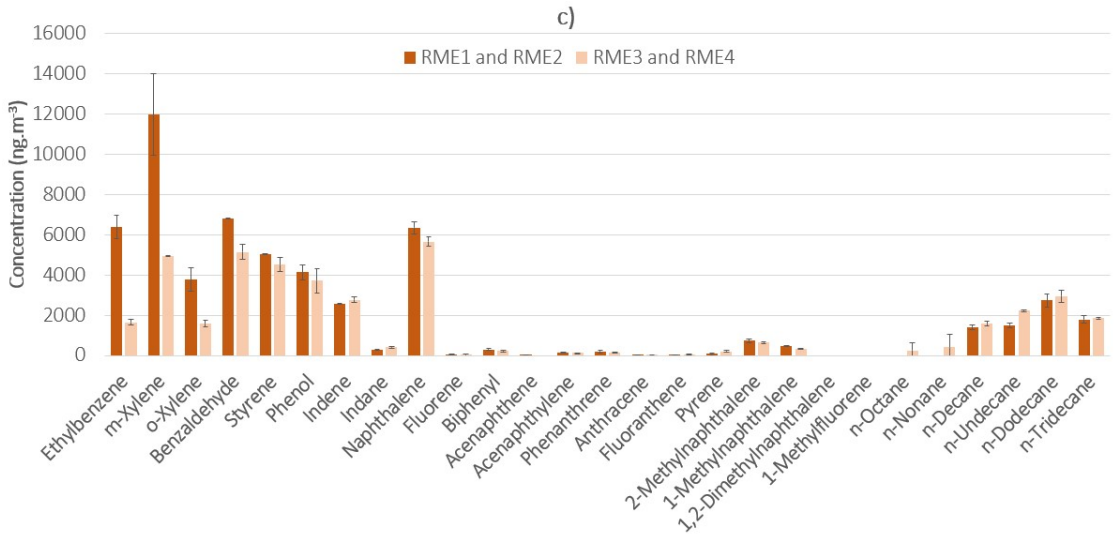


Figure S4: Comparison of sampling event replicates for B0 a), GTL b) and RME c)

Table S4: Concentrations of target analytes detected upon analysis of blank samplers. *(n.d.) denotes that the specific target analyte was not detected.*

Analyte	Concentration detected (ng)		
	PDMS	GW	Activated charcoal
Benzene	6.72	n.d.	74.95
Toluene	35.60	n.d.	19.25
Ethylbenzene	n.d.	n.d.	n.d.
m-Xylene	n.d.	n.d.	n.d.
o-Xylene	0.01	n.d.	n.d.
Benzaldehyde	n.d.	n.d.	n.d.
Styrene	n.d.	n.d.	n.d.
Phenol	n.d.	n.d.	n.d.
Indene	n.d.	n.d.	n.d.
Indane	n.d.	n.d.	n.d.
Naphthalene	0.07	n.d.	n.d.
Fluorene	n.d.	n.d.	n.d.
Biphenyl	0.01	n.d.	n.d.
Acenaphthene	n.d.	n.d.	n.d.
Acenaphthylene	n.d.	n.d.	n.d.
Phenanthrene	0.01	n.d.	n.d.
Anthracene	0.01	n.d.	n.d.
Fluoranthene	n.d.	n.d.	n.d.
Pyrene	n.d.	n.d.	n.d.
2-Methylnaphthalene	n.d.	n.d.	n.d.
1-Methylnaphthalene	n.d.	n.d.	n.d.
1,2-Dimethylnaphthalene	n.d.	n.d.	n.d.
1-Methylfluorene	n.d.	n.d.	n.d.
n-Octane	n.d.	n.d.	n.d.

n-Nonane	n.d.	n.d.	n.d.
n-Decane	0.01	n.d.	n.d.
n-Undecane	0.01	n.d.	n.d.
n-Dodecane	n.d.	n.d.	n.d.
n-Tridecane	n.d.	n.d.	n.d.
n-Tetradecane	0.05	n.d.	n.d.
n-Pentadecane	0.07	n.d.	n.d.
n-Hexadecane	0.09	n.d.	n.d.
n-Heptadecane	n.d.	n.d.	n.d.
n-Octadecane	n.d.	n.d.	n.d.
n-Nonadecane	n.d.	n.d.	n.d.
n-Eicosane	n.d.	n.d.	n.d.

Table S5: Concentrations of target analytes detected upon thermal desorption of GW samplers after sampling the emissions of CAST combustion of different fuels with associated standard deviations between sampling duplicates. *(n.d.) denotes that the specific target analyte was not detected for a specific analyte/sampler combination.*

	Average concentrations of target analyte ($\mu g.m^{-3}$)			%RSD of the duplicate measurements		
Target analytes	B0	GTL	RME	B0	GTL	RME
Benzene	96.63	21.65	26.57	10.09	12.28	5.96
Toluene	773.83	148.24	161.10	3.72	2.33	2.30
Ethylbenzene	23.19	1.36	6.39	0.63	14.06	9.05
m-Xylene	54.90	3.07	11.99	22.43	5.60	16.96
o-Xylene	13.36	1.12	3.79	2.91	8.52	15.63
Benzaldehyde	15.69	6.95	6.82	19.46	1.25	0.33
Styrene	9.78	5.62	5.03	24.03	10.74	0.52
Phenol	15.01	4.38	4.15	0.56	9.58	8.68
Indene	5.53	4.30	2.59	0.02	9.73	0.74
Indane	1.33	0.40	0.31	28.53	9.97	4.56
Naphthalene	12.83	7.40	6.37	13.75	12.64	4.89
Fluorene	0.28	0.07	0.07	61.87	141.11	31.98
Biphenyl	0.85	0.30	0.30	10.94	19.21	15.14
Acenaphthene	0.15	0.06	0.04	141.45	1.59	8.33
Acenaphthylene	0.42	0.23	0.16	84.21	1.13	11.05

Phenanthrene	0.81	0.21	0.22	34.41	0.37	30.69
Anthracene	0.07	0.04	0.01	24.32	63.85	142.59
Fluoranthene	0.44	0.12	0.05	28.34	34.07	7.66
Pyrene	1.18	0.29	0.09	38.74	10.01	29.98
2-Methylnaphthalene	2.06	0.90	0.75	30.84	4.45	12.39
1-Methylnaphthalene	1.46	0.52	0.47	29.26	15.43	4.34
1,2-Dimethylnaphthalene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1-Methylfluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-Octane	2.90	n.d.	n.d.	141.42	n.d.	n.d.
n-Nonane	4.45	n.d.	n.d.	28.04	1.78	n.d.
n-Decane	7.90	1.63	1.43	24.32	1.24	9.17
n-Undecane	8.72	2.24	1.52	13.65	8.92	7.10
n-Dodecane	8.76	3.02	2.75	18.82	2.74	11.17
n-Tridecane	6.06	2.14	1.80	33.12	9.88	10.07
n-Tetradecane	10.74	5.81	4.71	58.44	4.16	16.36
n-Pentadecane	3.62	3.44	3.02	54.29	32.67	0.62
n-Hexadecane	5.22	6.34	4.06	59.61	20.35	23.37
n-Heptadecane	2.16	1.66	1.17	40.45	17.83	26.03
n-Octadecane	2.25	2.10	0.74	50.89	62.41	8.76
n-Nonadecane	2.78	0.91	0.51	76.23	2.11	21.29
n-Eicosane	1.82	0.57	0.30	69.41	8.14	22.08
Total VOCs + SVOCs	1097.16	237.09	259.29			

Table S6: Concentrations of target analytes detected upon thermal desorption of PDMS samplers after sampling the emissions of CAST combustion of different fuels with associated standard deviations between sampling duplicates. *(n.d.) denotes that the specific target analyte was not detected for a specific analyte/sampler combination.*

	Average concentrations of target analyte ($\mu g.m^{-3}$)			%RSD of the duplicate measurements		
Target analytes	B0	GTL	RME	B0	GTL	RME

Benzene	374.65	76.74	71.51	8.72	8.89	7.15
Toluene	774.41	159.30	158.30	0.18	1.61	0.36
Ethylbenzene	7.91	2.07	2.57	18.31	1.64	29.13
m-Xylene	22.07	2.73	5.36	34.95	12.19	30.19
o-Xylene	7.31	1.01	2.38	17.10	38.32	19.83
Benzaldehyde	59.86	27.56	20.25	37.49	9.69	7.30
Styrene	6.53	5.14	3.79	16.97	17.68	11.63
Phenol	54.34	13.28	12.62	6.01	13.91	12.16
Indene	4.28	4.03	3.03	1.99	13.75	7.79
Indane	0.35	0.44	0.25	0.00	5.16	7.45
Naphthalene	13.45	8.96	6.55	23.13	3.17	6.07
Fluorene	0.66	0.09	0.09	61.04	141.31	50.64
Biphenyl	0.80	0.31	0.14	48.49	74.59	4.80
Acenaphthene	0.38	0.12	0.03	80.47	21.37	141.25
Acenaphthylene	0.21	0.31	0.27	141.26	7.57	4.26
Phenanthrene	1.07	0.22	0.21	71.78	76.52	52.34
Anthracene	0.25	n.d.	0.01	64.40	n.d.	142.86
Fluoranthene	0.61	0.05	0.05	5.45	5.17	30.53
Pyrene	0.51	0.16	0.10	119.65	47.45	2.00
2-Methylnaphthalene	3.07	1.11	0.86	75.32	24.08	3.62
1-Methylnaphthalene	2.10	0.78	0.55	32.75	14.58	7.71
1,2-Dimethylnaphthalene	0.38	n.d.	n.d.	141.36	n.d.	n.d.
1-Methylfluorene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-Octane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-Nonane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n-Decane	5.73	2.13	1.09	141.43	49.46	0.26
n-Undecane	8.19	3.25	1.52	141.42	38.41	10.44
n-Dodecane	16.44	4.42	3.92	72.83	64.28	66.00
n-Tridecane	16.87	4.56	1.66	97.65	84.11	2.39
n-Tetradecane	520.12	119.29	4.36	139.33	137.22	30.47
n-Pentadecane	150.05	31.72	2.20	131.22	130.84	0.39

n-Hexadecane	1672.63	12.29	9.82	140.53	55.46	96.35
n-Heptadecane	7.50	1.57	0.93	53.58	57.03	28.53
n-Octadecane	10.30	2.13	1.09	46.23	69.11	6.49
n-Nonadecane	18.57	1.16	0.89	26.85	27.60	6.40
n-Eicosane	6.44	1.02	0.64	12.58	33.06	12.86
Total VOCs + SVOCs	3768.03	487.96	317.03			

Table S7a: LODs and LOQs (ng) of target analytes for different samplers, namely PDMS, GW and activated charcoal. PDMS and GW samplers were directly thermally desorbed whilst the activated charcoal extract was first extracted with CS_2 and the extract was injected into the GC port. *(-) denotes that content is unavailable for a specific analyte/sampler combination.*

	Abr.	LOD (ng)			LOQ (ng)		
Target analytes		PDMS	GW	Charcoal	PDMS	GW	Charcoal
Benzene	-	0.03	0.44	0.002	0.09	1.45	0.01
Toluene	-	0.001	0.01	0.002	0.004	0.04	0.01
Ethylbenzene	-	0.02	0.09	0.003	0.06	0.29	0.01
m-Xylene	-	0.05	2.27	0.004	0.15	7.58	0.01
o-Xylene	-	0.07	0.07	0.002	0.22	0.24	0.01
Benzaldehyde	-	0.07	0.13	-	0.22	0.42	-
Styrene	-	0.02	0.13	0.001	0.06	0.43	0.003
Phenol	-	0.04	0.09	0.003	0.14	0.31	0.01
Indene	-	0.05	0.06	-	0.15	0.19	-
Indane	-	0.03	0.06	-	0.11	0.19	-
Naphthalene	Naph	0.004	0.86	0.001	0.01	2.85	0.003
Fluorene	FluE	0.02	0.03	-	0.08	0.11	-
Biphenyl	Biph	0.01	0.01	-	0.04	0.04	-
Acenaphthene	AceE	0.02	0.04	-	0.07	0.13	-
Acenaphthylene	AceY	0.02	0.02	-	0.06	0.08	-
Phenanthrene	Phe	0.01	0.02	-	0.05	0.05	-
Anthracene	Anth	0.02	0.02	-	0.06	0.06	-
Fluoranthene	FluA	0.01	0.02	-	0.03	0.05	-

Pyrene	Pyr	0.01	0.01	-	0.03	0.05	-
2-Methylnaphthalene	2-Mnap	0.03	0.03	-	0.11	0.10	-
1-Methylnaphthalene	1-MNap	0.10	0.58	-	0.33	1.92	-
1,2-Dimethylnaphthalene	1,2-DiMNap	0.001	0.31	-	0.002	1.02	-
1-Methylfluorene	1-MF	0.03	0.05	-	0.10	0.16	-
n-Octane	n-Oct	4.00	3.95	-	13.33	13.16	-
n-Nonane	n-Non	0.79	3.95	-	2.63	13.16	-
n-Decane	n-Dec	0.19	0.63	-	0.62	2.10	-
n-Undecane	n-Und	0.07	0.26	-	0.24	0.87	-
n-Dodecane	n-Dod	0.05	0.07	-	0.17	0.24	-
n-Tridecane	n-Tri	0.06	0.05	-	0.21	0.17	-
n-Tetradecane	n-Tet	0.02	0.04	-	0.06	0.12	-
n-Pentadecane	n-Pent	0.03	0.03	-	0.09	0.12	-
n-Hexadecane	n-Hex	0.04	0.04	-	0.12	0.12	-
n-Heptadecane	n-Hept	0.02	0.03	-	0.07	0.10	-
n-Octadecane	n-OctD	0.03	0.04	-	0.10	0.14	-
n-Nonadecane	n-NonD	0.04	0.04	-	0.13	0.13	-
n-Eicosane	n-Eic	0.05	0.12	-	0.16	0.41	-

Table S7b: LODs and LOQs (ng.m^{-3}) of target analytes for different samplers, namely PDMS, GW and activated charcoal. PDMS and GW samplers were directly thermally desorbed whilst the activated charcoal extract was first extracted with CS_2 and 1 µL of the 3 mL extract was injected into the GC port. *(-) denotes that content is unavailable for a specific analyte/sampler combination.*

	Abr.	LOD (µg.m^{-3})			LOQ (µg.m^{-3})		
Target analytes		PDMS	GW	Charcoal	PDMS	GW	Charcoal
Benzene	-	0.01	0.09	0.99	0.02	0.29	3.31

Toluene	-	0.0002	0.002	1.10	0.00	0.01	3.66
Ethylbenzene	-	0.004	0.02	1.78	0.01	0.06	5.94
m-Xylene	-	0.01	0.45	2.26	0.03	1.52	7.55
o-Xylene	-	0.01	0.01	1.49	0.04	0.05	4.95
Benzaldehyde	-	0.01	0.03	-	0.04	0.08	-
Styrene	-	0.003	0.03	0.62	0.01	0.09	2.08
Phenol	-	0.01	0.02	1.50	0.03	0.06	5.01
Indene	-	0.01	0.01	-	0.03	0.04	-
Indane	-	0.01	0.01	-	0.02	0.04	-
Naphthalene	Naph	0.001	0.17	0.48	0.00	0.57	1.59
Fluorene	FluE	0.005	0.01	-	0.02	0.02	-
Biphenyl	Biph	0.002	0.003	-	0.01	0.01	-
Acenaphthene	AceE	0.004	0.01	-	0.01	0.03	-
Acenaphthylene	AceY	0.004	0.005	-	0.01	0.02	-
Phenanthrene	Phe	0.003	0.003	-	0.01	0.01	-
Anthracene	Anth	0.004	0.004	-	0.01	0.01	-
Fluoranthene	FluA	0.002	0.003	-	0.01	0.01	-
Pyrene	Pyr	0.002	0.003	-	0.01	0.01	-
2-Methylnaphthalene	2-Mnap	0.01	0.01	-	0.02	0.02	-
1-Methylnaphthalene	1-MNap	0.02	0.12	-	0.07	0.38	-
1,2-Dimethylnaphthalene	1,2-DiMNap	0.0001	0.06	-	0.00	0.20	-
1-Methylfluorene	1-MF	0.01	0.01	-	0.02	0.03	-
n-Octane	n-Oct	0.80	0.79	-	2.67	2.63	-
n-Nonane	n-Non	0.16	0.79	-	0.53	2.63	-
n-Decane	n-Dec	0.04	0.13	-	0.12	0.42	-
n-Undecane	n-Und	0.01	0.05	-	0.05	0.17	-
n-Dodecane	n-Dod	0.01	0.01	-	0.03	0.05	-
n-Tridecane	n-Tri	0.01	0.01	-	0.04	0.03	-
n-Tetradecane	n-Tet	0.003	0.01	-	0.01	0.02	-
n-Pentadecane	n-Pent	0.01	0.01	-	0.02	0.02	-
n-Hexadecane	n-Hex	0.01	0.01	-	0.02	0.02	-

n-Heptadecane	n-Hept	0.004	0.01	-	0.01	0.02	-
n-Octadecane	n-OctD	0.01	0.01	-	0.02	0.03	-
n-Nonadecane	n-NonD	0.01	0.01	-	0.03	0.03	-
n-Eicosane	n-Eic	0.01	0.02	-	0.03	0.08	-