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Supplement of

Technical note: Emission factors, chemical composition, and morphology of particles emitted from Euro 5 diesel and gasoline light-duty vehicles during transient cycles

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Table S1. EF of regulated gas phase species: CO_2 in g km^{-1}, CO, THC and NO_x in mg km^{-1}.

		Artemis			WLTC	
		Cold Urban	Hot Urban	Motorway	Cold Start	Hot Start
GDI1	CO_2	221±11	197±5	151±5		
	CO	104±47	5±0.5	326±207		
	NO_x	110±44	102±6	30±23		
	THC	45±20	0.8±0.3	2.1±0.9		
GDI2	CO_2				150±31	129±17
	CO				694±821	308±329
	NO_x				1217±498	1387±526
	THC				112±116	73±112
GDI3	CO_2	191±5	173±7	130±2		
	CO	714±228	557±561	586±206		
	NO_x	153±60	30±12	9±3		
	THC	219±0.4	25±14	8±2		
PFI	CO_2	155±2		112±2		
	CO	106±16		112±2		
	NO_x	69±13		7±1		
	THC	5.5±0.4		2.0±0.3		
D1	CO_2	168±18	147±7	144±14		
	CO	453±208	95±44	3±1.6		
	NO_x	697±120	741±112	890±233		
	THC	57±20	30±3	1.7±2		
D2	CO_2				120±1.5	116±1.8
	CO				54±11	27±7.5
	NO_x				240±25	232±32
	THC				14.7±3	12.4±2.5
D3	CO_2	210±4		142±0.1		
	CO	601±45		9±0.2		
	NO_x	396±8		510±160		
	THC	91±28		10±1		

Table S2. PAHs identified in diesel and gasoline Euro 5 vehicles emissions. They have been classified as unsubstituted PAHs (UnSubPAHs), methylated PAHs (MPAHs), oxygenated PAHs (OPAHs), nitro-substituted derivatives (NPAHs) and amino PAHs (APAHs).

Group	Compound	Molecular formula	m/z
UnSubPAH	Naphthalene	$C_{10}H_8$	128
	Acenaphthylene	$C_{12}H_8$	152
	Acenaphthene	$C_{12}H_{10}$	154
	Fluorene	$C_{13}H_{10}$	166
	Paracyclene	$C_{14}H_8$	176
	Anthracene/ Phenanthrene	$C_{14}H_{10}$	178
	Benzo[def]fluorene	$C_{15}H_{10}$	190
	Pyrene/ Fluoranthene/ Acephenanthrylene	$C_{16}H_{10}$	202
	Benzofluorene	$C_{17}H_{12}$	216
	Benz[a]anthracene/ Triphenylene/ Chrysene	$C_{18}H_{12}$	228
	Corannulene/ Dicyclopenta[cd,mn]pyrene	$C_{20}H_{10}$	250
	Benzo[b]fluoranthene/ Benzo[j]fluoranthene/ Benzo[k]fluoranthene/ Benzo[a]pyrene/ Benzo[e]pyrene	$C_{20}H_{12}$	252
	Indio[1,2,3-cd]pyrene/ Benzo[ghi]perylene	$C_{22}H_{12}$	276
	Dibenzanthracene/ Pentacene	$C_{22}H_{14}$	278
	1*H*-Benzo[*ghi*]cyclopenta[*pqr*]perylene	$C_{23}H_{12}$	288
MPAH	Methyl-naphthalene	$C_{11}H_{10}$	142
	Dimethyl-naphthalene	$C_{12}H_{12}$	156
	Methyl-acenaphthene	$C_{13}H_{12}$	168
	Methyl-fluorene	$C_{14}H_{12}$	180
	Methyl-phenanthrene	$C_{15}H_{12}$	192
	Dimethyl-fluorene	$C_{15}H_{14}$	194
	Ethyl-phenanthrene	$C_{16}H_{14}$	206
	Trimethyl-phenanthrene	$C_{17}H_{16}$	220
	Retene/ Tetramethyl phenanthrene	$C_{18}H_{18}$	234
	Methylbenzo[ghi]fluoranthene	$C_{19}H_{12}$	240
	Methylbenz[a]anthracene/ methyl chrysene	$C_{19}H_{14}$	242
	Di-methylbenz(a)anthracene	$C_{20}H_{16}$	256
	Methyl cholanthrene	$C_{21}H_{16}$	268
OPAH	Indanone	C_9H_8O	132
	Benzocycloheptenone	$C_{11}H_8O$	156
	Naphthoquinone	$C_{10}H_6O_2$	158
	Dibenzofuran	$C_{12}H_8O$	168
	Fluorenone	$C_{13}H_8O$	180
	Dibenzopyran	$C_{13}H_{10}O$	182
	Hydroxydibenzofuran	$C_{12}H_8O_2$	184

Table S2. PAHS identified in diesel and gasoline Euro 5 vehicles emissions. They have been classified as unsubstituted PAHs (UnSubPAHs), methylated PAHs (MPAHs), oxygenated PAHs (OPAHs), nitrogen-substituted derivatives (NPAHs) and amino PAHs (APAHs) *(continued).*

Family	Compound	Molecular formula	m/z
OPAH	Anthrone	$C_{14}H_{10}O$	194
	Xanthone	$C_{13}H_8O_2$	196
	Cyclcopenta-phenanthrene-one	$C_{15}H_8O$	204
	Aceanthraquinone	$C_{16}H_8O_2$	232
	Benzo[cd]pyrenone	$C_{19}H_{10}O$	254
NPAH	Nitro-anthracene/ Nitro-phenanthrene	$C_{14}H_9NO_2$	223
	Dinitrofluorene	$C_{13}H_8N_2O_4$	256
APAH	Aminopyrene/ Carbazole	$C_{16}H_{11}N$	217
	Aminobenzanthrone	$C_{18}H_{13}NO$	259
	Dibenzocarbazole Amino benzopyrene	$C_{20}H_{13}N$	267

Table S3. Intercomparison of PAHs mass concentration (ng m^{-3}) measured from the extract of one quartz filter (GC-MS analysis) and on-line AMS measurements for the emission of the GDI3 vehicle.

Molecular weight	**Compound**	**Concentration (ng m^{-3})** 3 cycles (1 urban hot + 2 motorway)	
		GC-MS	HR-ToF-MS
128	Naphthalene	45	245
178	Phenanthrene*/Anthracene	100	453
202	Pyrene/Fluoranthene*/Acephenanthrylene	111	480
228	Benzo[a]anthracène/Chrysène	25	69
252	Benzo[b]fluoranthene/Benzo[j]fluoranthene / Benzo[k]fluoranthene*/Benzo[a]pyrene/* Benzo[e]pyrene/Perylene	77	34
276	Indéno[123cd]pyrène/Benzo[ghi]perylène	31	25
142	Methyl-naphthalene*	27	80
180	Methyl-fluorene	24	53
168	Dibenzofuran	26	28
180	Fluorenone	76	75
208	Anthraquinone*	26	28

* compounds used for PAHs calibration and quantification during GC-MS analysis.

Table S4. Fraction (%) of major PAHs emitted from the GDI3, PFI and D3 vehicles during Artemis driving cycles: Cold Urban (CU) and Motorway (MW).

Compound	**GDI3**		**PFI**		**D3**	
	CU	MW	CU	MW	CU	MW
UnsPAHs						
Naphthalene	10.3	9.6	14.3	13.6	16.9	19.1
Acenaphthylene	4.3	7.8	4.5	5.4	8.3	9.7
Acenaphthene	2.4	3.6	2.0	2.6	4.2	5.2
Fluorene	1.9	2.5	2.2	3.2	5.0	4.3
Anthracene/Phenanthrene	5.3	15.9	4.1	8.9	6.9	8.2
Pyrene/Fluoranthene/Acephenanthrylene	5.9	13.7	3.3	5.8	2.1	1.9
Benz[a]anthracene/Triphenylene/Chrysene	2.2	1.6	1.7	1.0	1.3	0.7
Paracylene	1.7	3.5	1.0	1.2	2.1	2.8
Benzo[def]fluorene	1.4	1.5	1.1	1.9	3.4	2.1
Benzo[a, e]pyrene/Benzo[b,j,k]fluoranthene	2.3	1.1	3.8	0.6	0.7	0.4
Cyclopenta[cd]pyrene/Benzo[ghi]fluoranthene	3.3	2.0	2.5	1.2	1.6	1.0
Dibenzoanthracene/Pentacene	0.5	0.2	1.5	0.8	0.2	0.1
Indio[1,2,3-cd]pyrene/Benzo[ghi]perylene	3.0	0.6	6.6	0.7	0.4	0.3
Coronene	1.9	0.3	5.3	0.6	0.1	0.1
MPAHs						
Methyl-naphthalene	3.4	2.9	4.6	4.4	7.6	8.2
Dimethyl-naphthalene	1.9	1.9	2.6	2.9	5.4	5.5
Methyl-acenaphthene	1.3	1.7	1.3	2.4	3.3	3.3
Methyl-fluorene	1.1	2.1	1.0	2.1	3.4	2.9
Methyl-phenanthrene	0.7	2.3	1.1	1.7	4.7	3.1
Ethyl-phenanthrene	1.3	1.3	1.0	2.2	3.8	2.3
OPAHs						
Indanone	2.4	1.8	0.9	1.2	0.4	0.9
Anthraquinone	2.2	0.9	3.9	8.7	2.6	3.9
Dibenzofuran	1.0	1.0	0.7	1.3	0.5	1.6
Fluorenone	1.6	2.7	1.1	2.0	0.3	3.1
Dibenzopyran	1.5	1.1	1.3	2.4	0.3	0.4
Benzo[cd]pyrenone	1.4	0.6	0.8	0.5	0.1	0.1
NPAHs						
Nitro-fluorene	0.9	0.1	0.8	0.4	0.5	0.2
Nitro-anthracene/Nitro-phenanthrene	8.1	8.6	0.9	1.2	0.1	0.1
Nitro-pyrene	0.5	0.1	0.8	0.2	0.1	0.03
Nitrochrysene	0.4	0.03	0.7	0.2	0.06	0.04
APAHs						
Aminopyrene/Carbazole	0.8	0.6	0.5	0.6	1.5	0.5
Dibenzocarbazole/Amino benzopyrene	5.3	0.4	2.4	3.5	0.3	0.2
Dibenz[a,j]acridine	0.1	0.03	1.1	1.2	0.2	0.2

Table S5. Major inorganic species found in fresh and used lubricant oil, TAE diesel and gasoline fuels (analysis by ICP-MS). Other elements such as Cr, Ni, Al and Mg were found in concentration below 3 ppm.

		Fresh lubricant oil	Old lubricant oil (Diesel)	Old lubricant oil (Gasoline)	Diesel TAE 85 Fuel	Gasoline Fuel
Sulphur		0.14wt %	0.14wt%	0.12wt%	16 ppm	34 ppm
Calcium	(ppm)	1630	1441	1829	≤ 3	≤ 5
Phosphor	(ppm)	638	614	709	≤ 3	≤ 5
Zinc	(ppm)	849	728	857	≤ 3	≤ 5
Iron	(ppm)	≤ 3	66	75	≤ 2	≤ 5
Silicium	(ppm)	5	15	11	31	138
Molybdenum	(ppm)	≤ 3	94	≤ 5	≤ 3	≤ 5
Copper	(ppm)	≤ 3	16	7	≤ 3	≤ 5

Table S6. EF for all gasoline and diesel vehicles and for all tested conditions. All values are expressed in μg km^{-1}. BDL stands for Below Detection Limit.

Vehicle	Species	Artemis			WLTC	
		Cold Urban	Hot Urban	Motorway	Cold Start	Hot Start
GDI1	BC	7140±500	960±190	1990±810		
GDI2	BC				5700±800	230±60
	Organics				103.5±52.23	41.23±8.38
	Sulphate				BDL	BDL
	Ammonium				BDL	BDL
	Nitrate				7.12±3.98	5.08±2.96
GDI3	BC	3180±137	200±160	767±330		
	Organics	66.3±64.8	5.34±4.42	25.3±13.5		
	PAHs	1.54±0.81	0.13±0.01	1.10±0.73		
	Sulphate	0.34±0.07	0.06±0.03	0.06±0.04		
	Ammonium	0.28±0.04	0.02±0.01	0.09±0.08		
	Nitrate	1.31±0.41	0.12±0.09	0.48±0.43		
PFI	BC	135.25±8.15	NA	22.27±11.23		
	Organics	8.40±3.70	NA	1.00±0.26		
	PAHs	0.43±0.16	NA	0.04±0.05		
	Sulphate	0.28±0.11	NA	0.04±0.03		
	Ammonium	0.24±0.14	NA	0.03±0.01		
	Nitrate	0.88±0.45	NA	0.03±0.01		
D1	BC	76.0±55.0	8.0±4.0	9.0±3.9		
	Organics	11.0±0.81	0.15±0.05	1.91±1.32		
	Sulphate	BDL	BDL	1.34±1.26		
	Ammonium	BDL	BDL	0.38±0.21		
	Nitrate	0.28±0.02	0.18±0.06	0.18±0.09		
D2	BC				8.0±4.0	3.0±1.0
	Organics				0.74±0.25	0.28±0.01
	Sulphate				4.19±3.20	0.28±0.05
	Ammonium				0.68±0.53	0.06±0.02
	Nitrate				0.14±0.09	0.03±0.01
D3	BC	378.38±136.59	NA	927.72±139.16		
	Organics	61.0±38.2	NA	65.7±36.4		
	PAHs	2.04±0.19	NA	1.73±0.95		
	Sulphate	0.18±0.06	NA	0.22±0.13		
	Ammonium	0.15±0.01	NA	0.15±0.06		
	Nitrate	0.25±0.05	NA	0.82±0.53		

Table S7. Fuel consumption (l km^{-1}) and fuel densities (kg l^{-1}).

Vehicle	Fuel Consumption		Fuel density
GDI1	Cold Urban 0.096	Motorway 0.063	0.733
GDI2	Cold start WLTC 0.064	Hot start WLTC 0.059	0.733
GDI3	Cold Urban 0.085	Motorway 0.077	0.733
PFI	Cold Urban 0.068	Motorway 0.048	0.733
D1	Cold Urban 0.063	Motorway 0.051	0.840
D2	Cold start WLTC 0.044	Hot start WLTC 0.047	0.840
D3	Cold Urban 0.077	Motorway 0.051	0.840

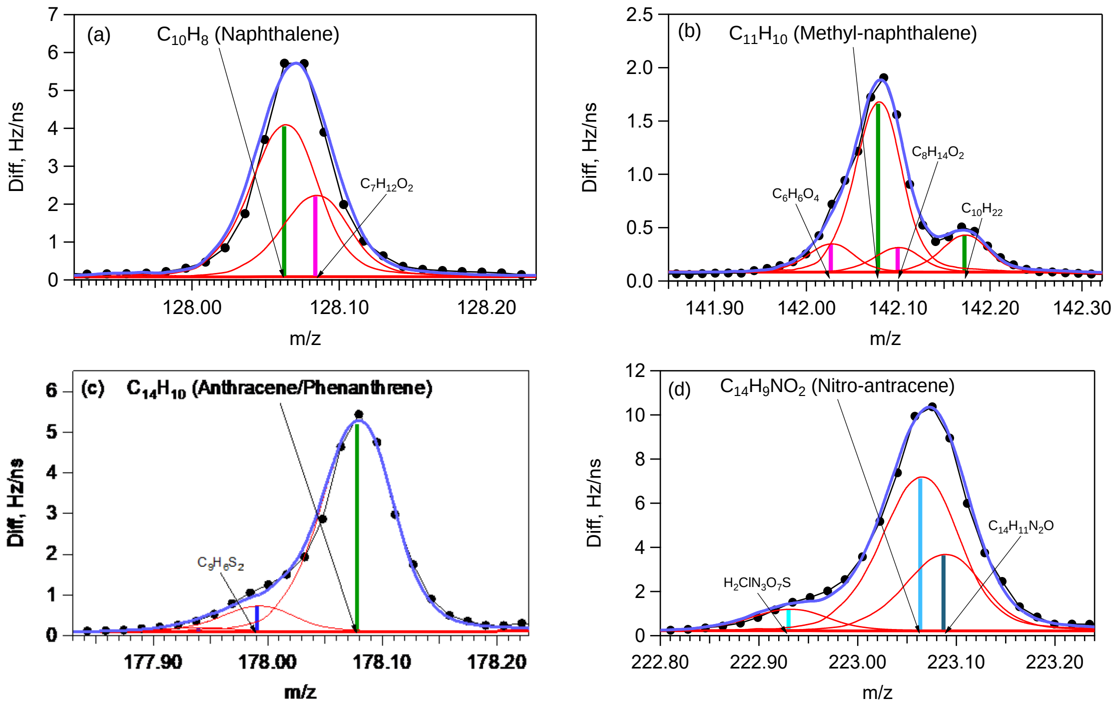

Figure S1. Examples of HR-AMS fitting for (a) naphthalene ($C_{10}H_8$) at *m/z* 128, (b) methyl-naphthalene ($C_{11}H_{10}$) at *m/z* 142, (c) anthracene/phenanthrene ($C_{14}H_{10}$) at *m/z* 178 and (d) Nitro-anthracene ($C_{14}H_9NO_2$) at *m/z* 223.

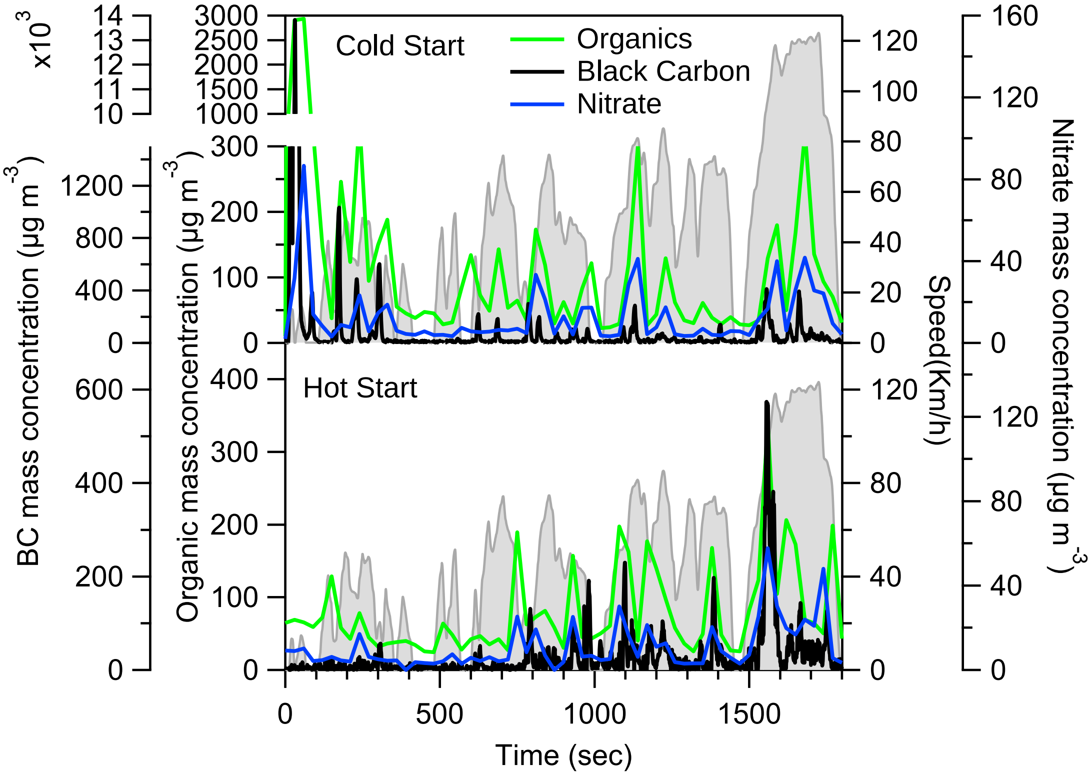

Figure S2. Time series of organics, nitrate and BC for WLTC cycle cold start (upper plot) and hot start (lower plot) for the GDI2 vehicle.

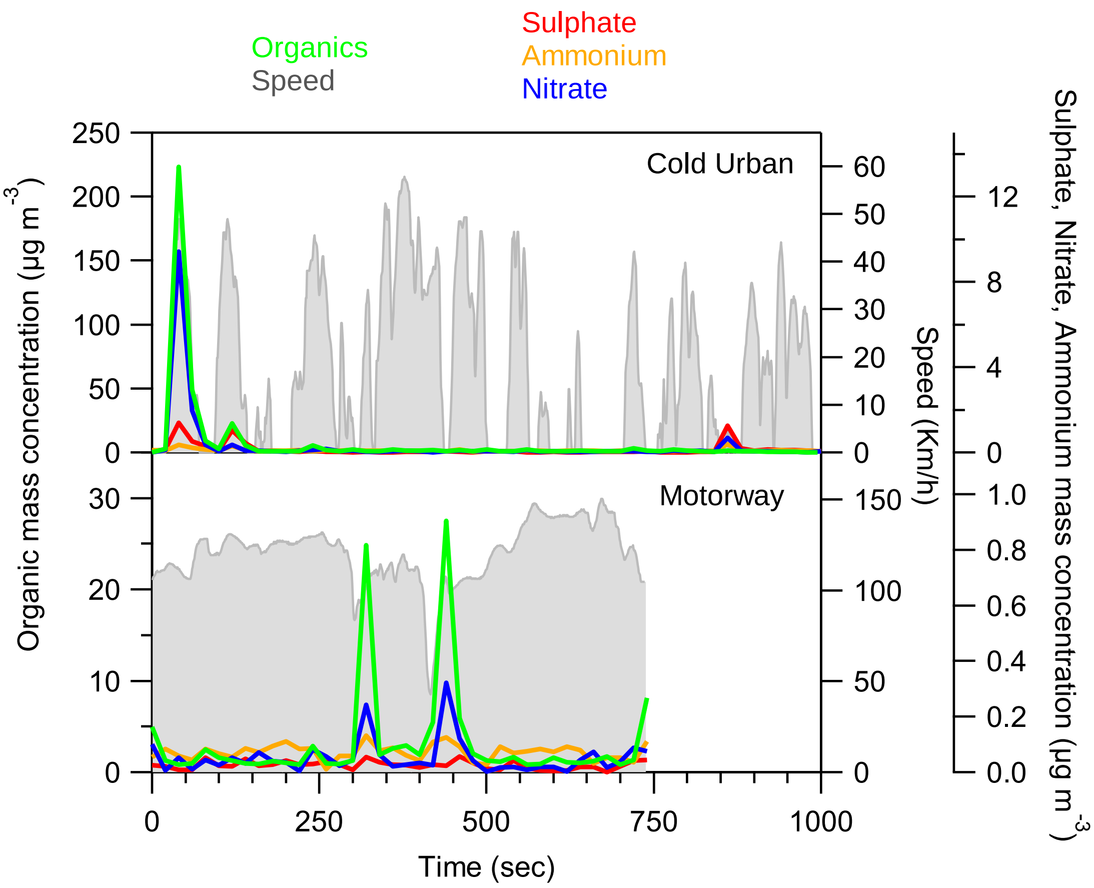

Figure S3. Time series of organics, sulphate, nitrate and ammonium for Artemis cold urban (upper) and motorway cycles (lower) for the PFI vehicle. BC measurements are not available for this vehicle.

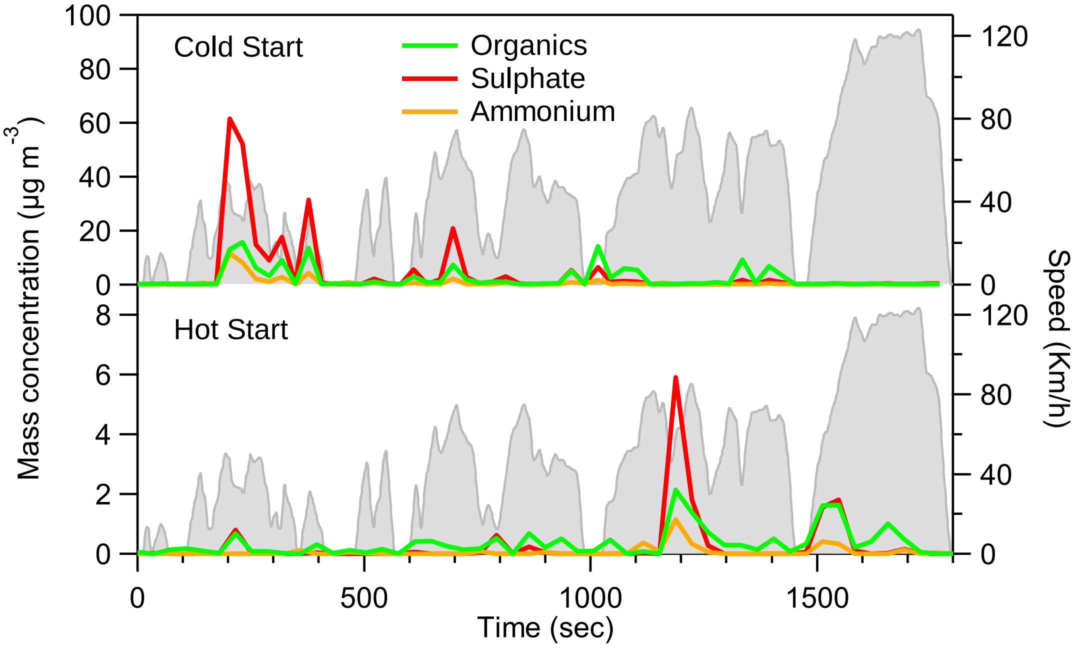

Figure S4. Time series of organics, sulphate and ammonium for WLTC cold start (upper) and hot start (lower) for the D2 vehicle.

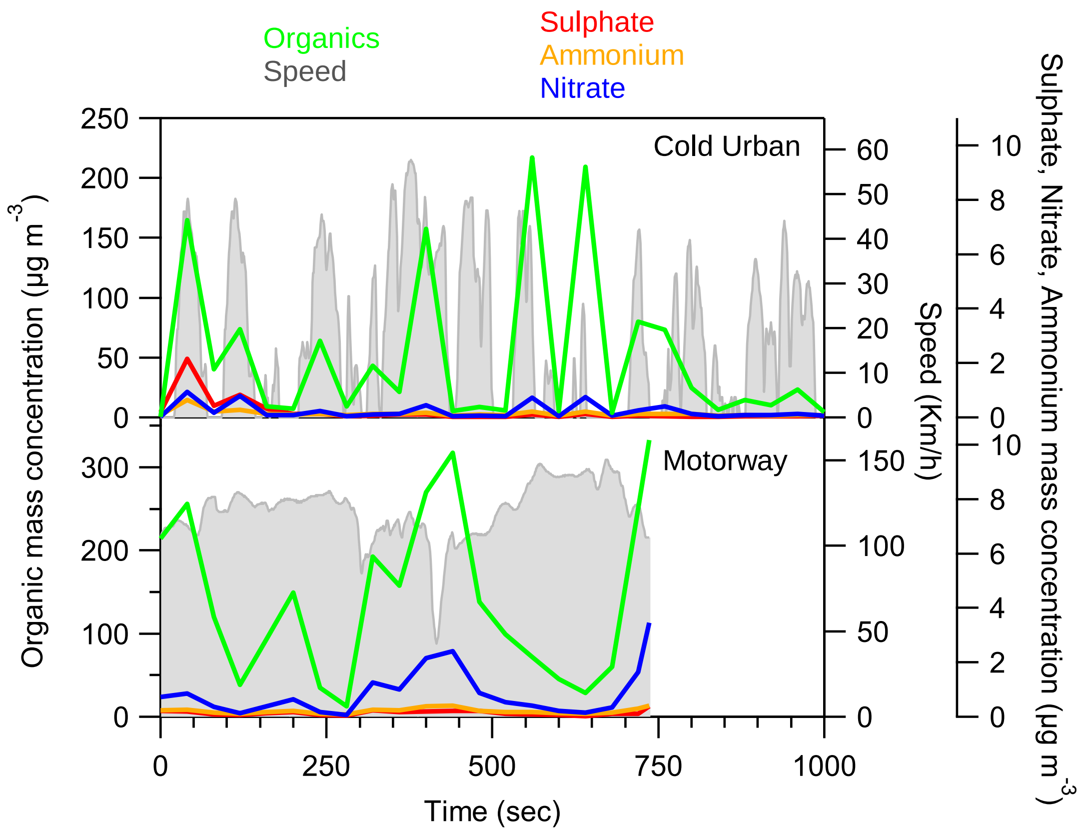

Figure S5. Time series of organics, sulphate, nitrate and ammonium for Artemis cold urban cycle (upper) and a motorway (lower) for the D3 vehicle.

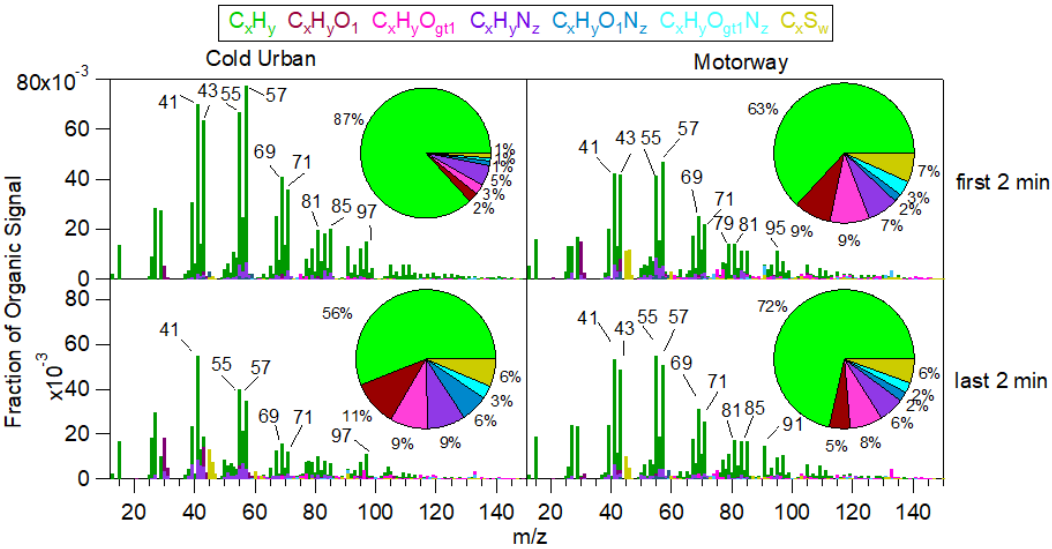

Figure S6. AMS HR spectra speciation for organic fragments for the PFI vehicle (ARTEMIS cycle).

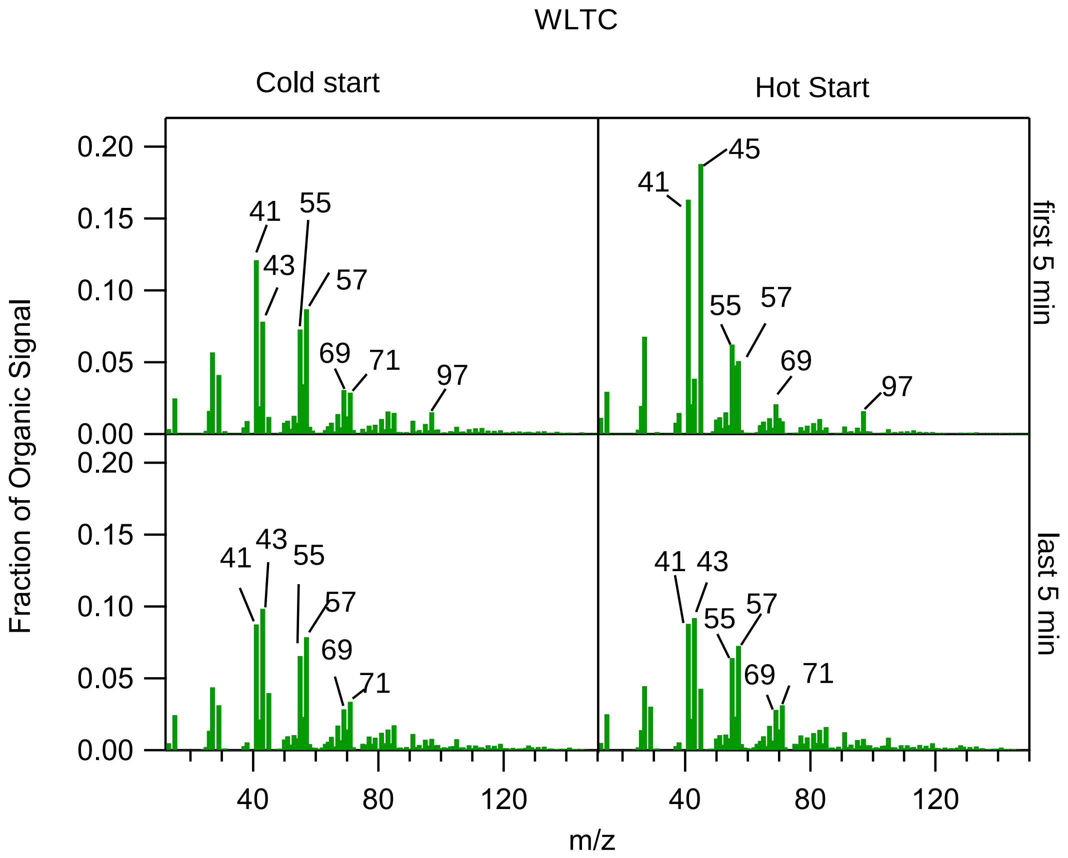

Figure S7. AMS UMR spectra for organic fragments for the GDI2 vehicle (WLTC).

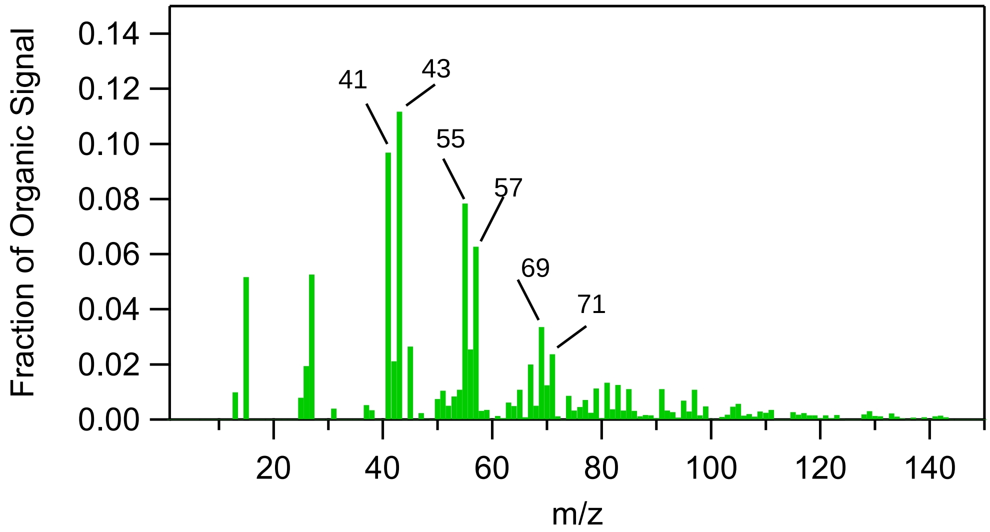

Figure S8. UMR mass spectrum for taken at the beginning of a motorway cycle (2 first minutes) for the D1 vehicle.

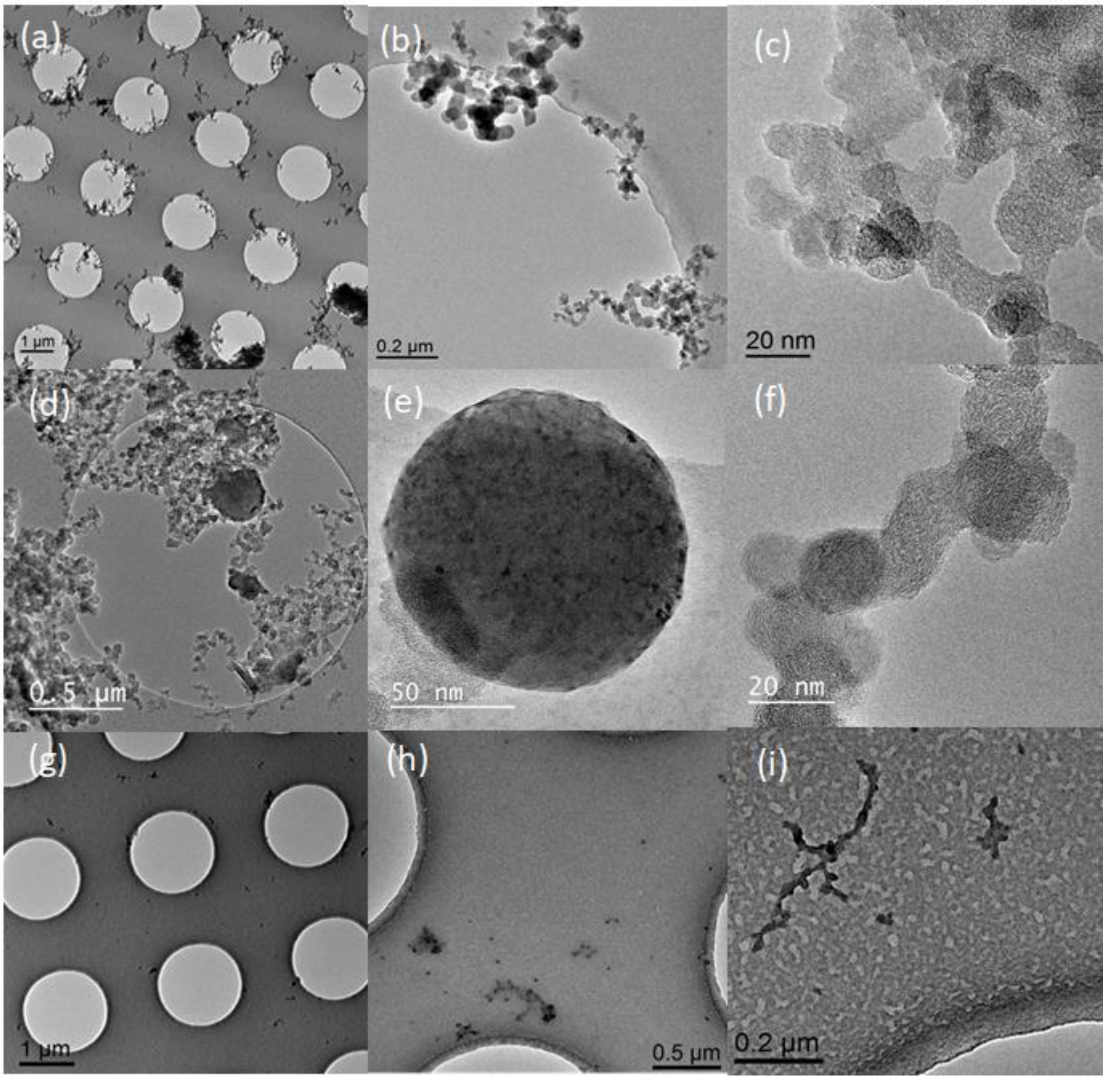

Figure S9. TEM images of samples collected during hot cycles: (a-c) GDI1 sampling the first 120 sec of the motorway cycle, dilution ratio 40; (d-f) GDI2 sampling the last 120 sec of a WLTC cycle, dilution ratio 46; (g-i) D1 vehicle sampling first 300 sec of the motorway cycle, dilution ratio 40.

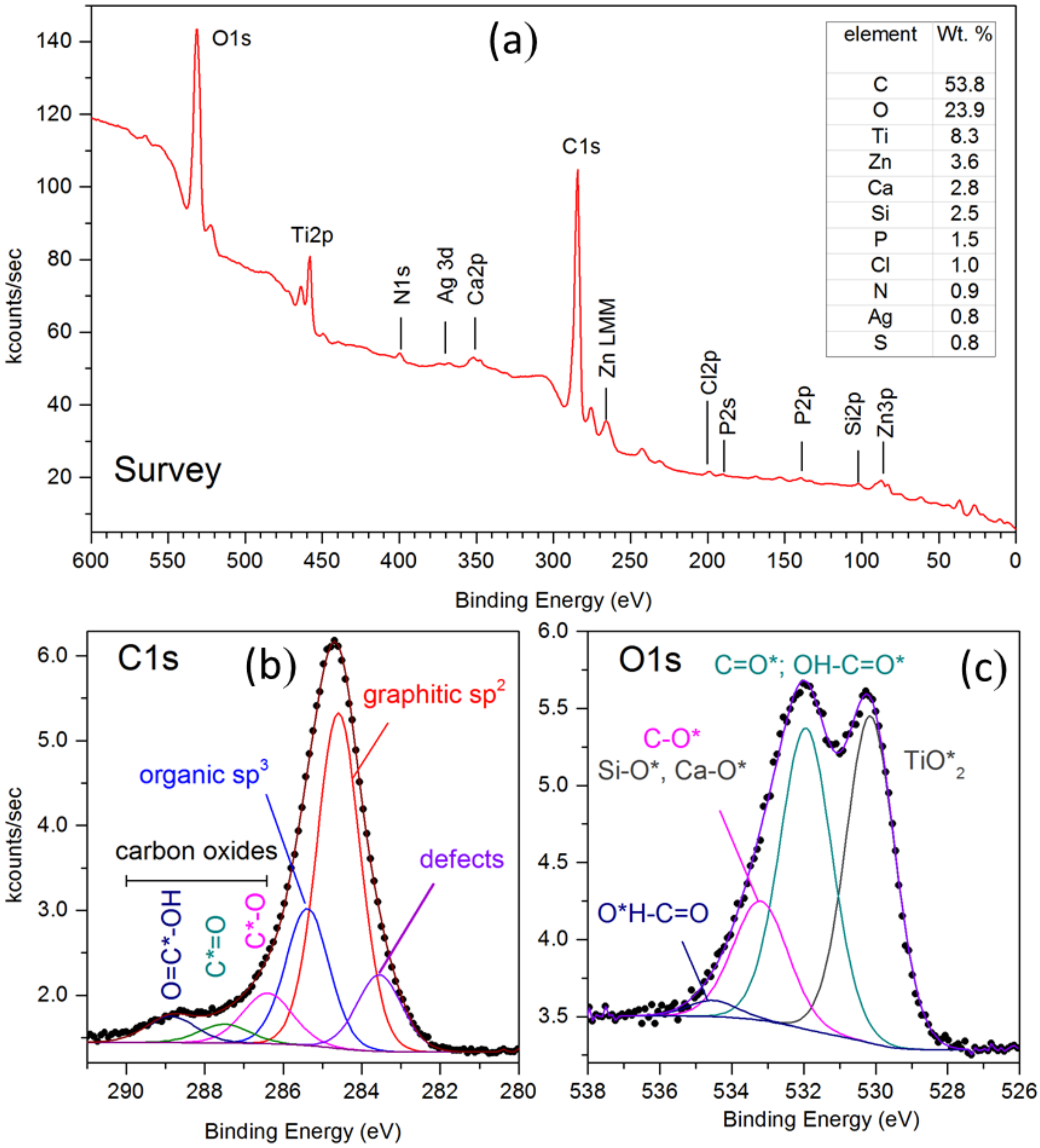

Figure S10. XPS spectra of particles collected from the PFI vehicle: (a) survey spectrum and elemental composition (table in insert); (b) deconvolution of the C1s spectrum; (c) deconvolution of the O1s spectrum.