

1 **Supplementary information for manuscript:**

2 **Technical Note: Emission factors, chemical composition and**
3 **morphology of particles emitted from Euro 5 diesel and gasoline light**
4 **duty vehicles during transient cycles**

5 Evangelia Kostenidou¹, Alvaro Martinez-Valiente², Badr R'Mili¹, Baptiste Marques¹,
6 Brice Temime-Roussel¹, Michel André³, Yao Liu³, Cédric Louis³, Boris Vanseventant³,
7 Daniel Ferry⁴, Carine Laffon⁴, Philippe Parent⁴ and Barbara D'Anna¹

8

9 ¹ Aix-Marseille Université, UMR 7673 CNRS, LCE, Marseille, France

10 ² IRCELYON, UMR 5256 CNRS, Université de Lyon, Villeurbanne, France

11 ³ AME-EASE, Univ Gustave Eiffel, IFSTTAR, Univ Lyon, F-69675 Lyon, France

12 ⁴ Aix-Marseille Université, CNRS, CINaM, Marseille, France

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32 **Table S1.** EF of regulated gas phase species: CO₂ in g km⁻¹, CO, THC and NO_x in mg
 33 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		
GDI3	CO ₂				150±31	129±17
	CO				694±821	308±329
	NO _x				1217±498	1387±526
	THC				112.5±116	73±112.3
GDI5	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		
PFI4	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		
D3	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
D4	CO ₂	210±4		142±0.1		
	CO	601±45		9±0.2		
	NO _x	396±8		510±160		
	THC	91±28		10±1		

34

35

36

37

38

39

40 **Table S2:** PAHS identified in diesel and gasoline Euro 5 vehicles emissions. They have
 41 been classified as unsubstituted PAHs (UnSubPAHs), methylated PAHs (MPAHs),
 42 oxygenated PAHs (OPAHs), nitro-substituted derivatives (NPAHs) and amino PAHs
 43 (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	
	Benzo[fluorene]	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	
	1H- 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 ₉ H ₈ O	132
		Benzocycloheptenone	C ₁₁ H ₈ O	156
	Naphthoquinone	C ₁₀ H ₆ O ₂	158	
	Dibenzofuran	C ₁₂ H ₈ O	168	
	Fluorenone	C ₁₃ H ₈ O	180	
	Dibenzopyran	C ₁₃ H ₁₀ O	182	
	Hydroxydibenzofuran	C ₁₂ H ₈ O ₂	184	

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

Family	Compound	Molecular formula	m/z
OPAH	Anthrone	C ₁₄ H ₁₀ O	194
	Xanthone	C ₁₃ H ₈ O ₂	196
	Cyclcopenta-phenanthrene-one	C ₁₅ H ₈ O	204
	Aceanthraquinone	C ₁₆ H ₈ O ₂	232
	Benzo[cd]pyrenone	C ₁₉ H ₁₀ O	254
NPAH	Nitro-anthracene/ Nitro-phenanthrene	C ₁₄ H ₉ NO ₂	223
	Dinitrofluorene	C ₁₃ H ₈ N ₂ O ₄	256
	Aminopyrene/ Carbazole	C ₁₆ H ₁₁ N	217
APAH	Aminobenzanthrone	C ₁₈ H ₁₃ NO	259
	Dibenzocarbazole	C ₂₀ H ₁₃ N	267
	Amino benzopyrene		

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

64 **Table S3:** Fraction (%) of major PAHs emitted from the GDI5, PFI4 and D4 cars during
 65 Artemis driving cycles: Cold Urban (CU) and Motorway (MW).

Compound	GDI5		PFI4		D4	
	CU	MW	CU	MW	CU	MW
<u>UnsPAHs</u>						
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
<u>MPAHs</u>						
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
<u>OPAHs</u>						
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
<u>NPAHs</u>						
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
<u>APAHs</u>						
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

66

67

68

69 **Table S4.** Major inorganic species found in fresh and used lubricant oil, TAE diesel
70 and gasoline fuels (analysis by ICP-MS). Other elements such as Cr, Ni, Al and Mg
71 were found in concentration below 3 ppm.
72

		Fresh lubricant oil	Old lubricant oil (Diesel)	Old lubricant oil (Gasoline)	Gasoline TAE 85 Fuel	Gasoline Fuel
Sulfur		0.14wt %	0.14wt%	0.12wt%	9 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
Silicon	(ppm)	5	15	11	31	138
Molybdenum	(ppm)	≤ 3	94	≤ 5	≤ 3	≤ 5
Copper	(ppm)	≤ 3	16	7	≤ 3	≤ 5

73

74

75

76

77

78

79

80

81

82

83

84

85

86

87

88

89 **Table S5:** EF for all gasoline and diesel vehicles and for all tested conditions. All values
 90 are expressed in $\mu\text{g km}^{-1}$. BDL stands for Below Detection Limit.

Vehicle	Species	Artemis			WLTC	
		Cold Urban	Hot Urban	Motorway	Cold Start	Hot Start
GDI5	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		
	Sulfate	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		
PFI4	Organics	8.40±3.70	NA	1.00±0.26		
	PAHs	0.43±0.16	NA	0.04±0.05		
	Sulfate	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		
GDI1	BC	7140±500	960±190	1990±810		
GDI3	BC				5700±800	230±60
	Organics				103.5±52.23	41.23±8.38
	Sulfate				BDL	BDL
	Ammonium				BDL	BDL
	Nitrate				7.12±3.98	5.08±2.96
D4	Organics	61.0±38.2	NA	65.7±36.4		
	PAHs	2.04±0.19	NA	1.73±0.95		
	Sulfate	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		
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		
	Sulfate	NA	NA	1.34±1.26		
	Ammonium	NA	NA	0.38±0.21		
	Nitrate	0.28±0.02	0.18±0.06	0.18±0.09		
D3	BC				8.0±4.0	3.0±1.0
	Organics				0.74±0.25	0.28±0.01
	Sulfate				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

91

92

93

94

95

96

97

98

99

100 **Table S6:** Fuel consumption ($l\ km^{-1}$) and fuel densities ($kg\ l^{-1}$).

Vehicle	Fuel Consumption		Fuel density
GDI5	Cold Urban 0.085	Motorway 0.077	0.733
PFI4	Cold Urban 0.068	Motorway 0.048	0.733
GDI3	Cold start WLTC 0.064	Hot start WLTC 0.059	0.733
GDI1	Cold Urban 0.096	Motorway 0.063	0.733
D4	Cold Urban 0.077	Motorway 0.051	0.840
D3	Cold start WLTC 0.044	Hot start WLTC 0.047	0.840
D1	Cold Urban 0.063	Motorway 0.051	0.840

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

125

126

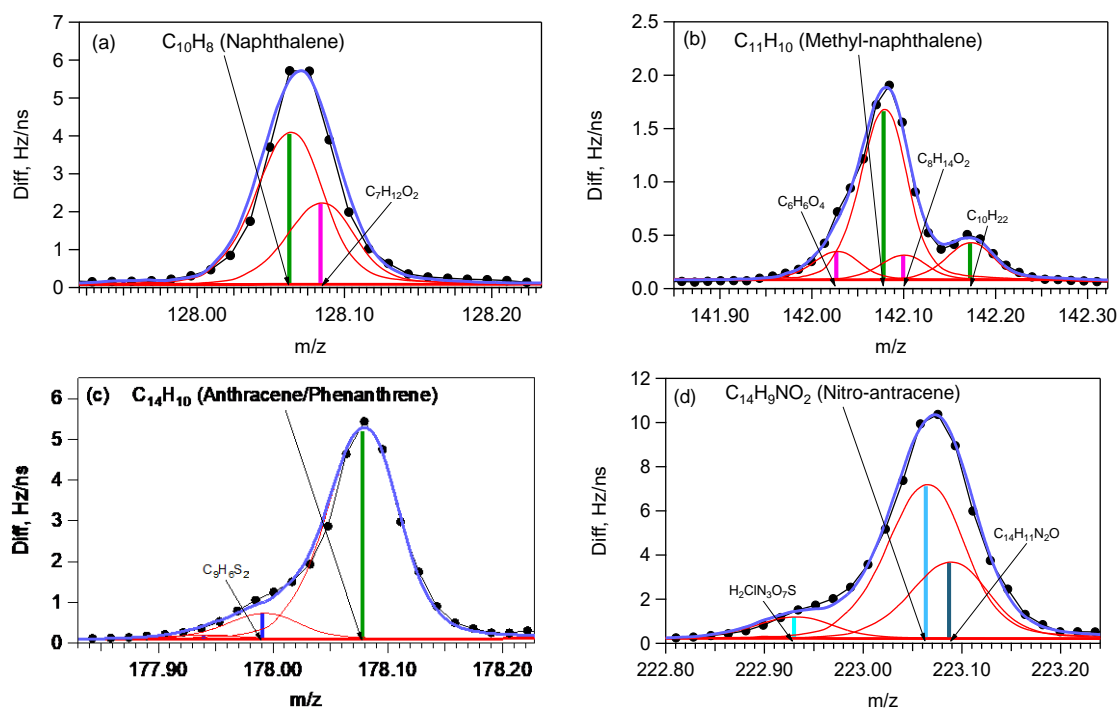
127

128

129

130

131



132 **Figure S1.** Examples of HR-AMS fitting for (a) naphthalene ($C_{10}H_8$) at m/z 128, (b)
 133 methyl-naphthalene ($C_{11}H_{10}$) at m/z 142, (c) anthracene/phenanthrene ($C_{14}H_{10}$) at m/z
 134 178 and (d) Nitro-anthracene ($C_{14}H_9NO_2$) at m/z 223.

135

136

137

138

139

140

141

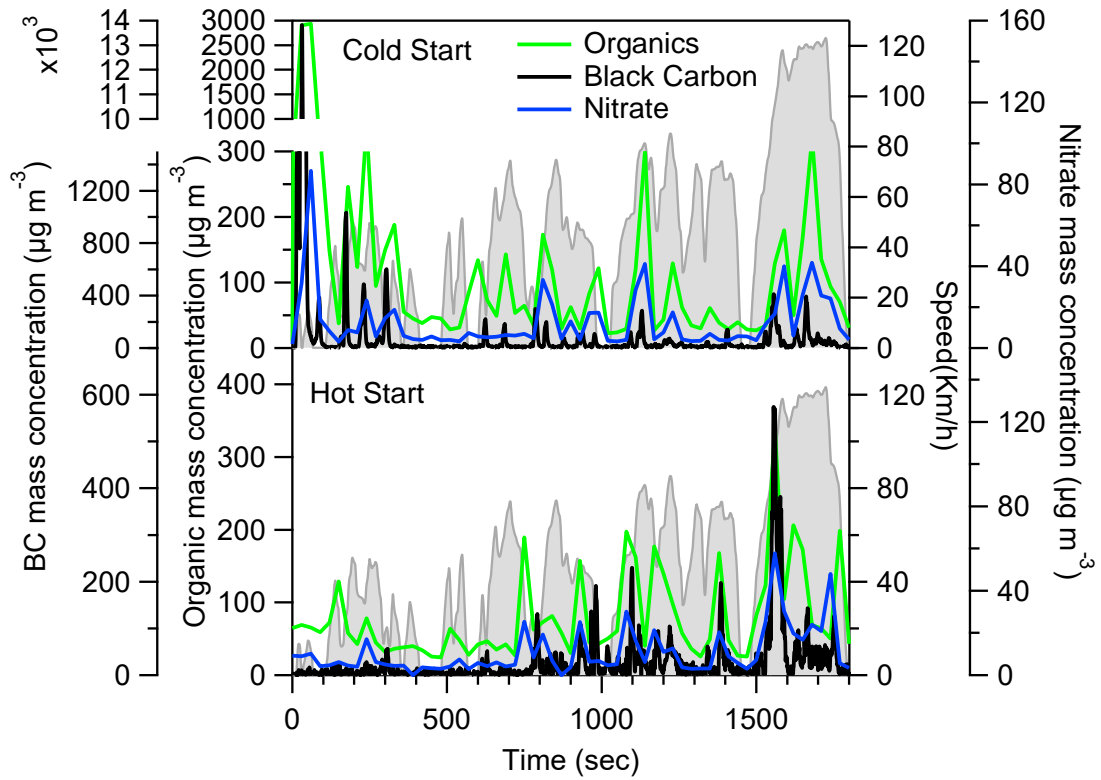
142

143

144

145

146



147

148 **Figure S2.** Time series of organics, nitrate and BC for WLTC cycle cold start (upper
 149 plot) and hot start (lower plot) for the GDI3 vehicle.

150

151

152

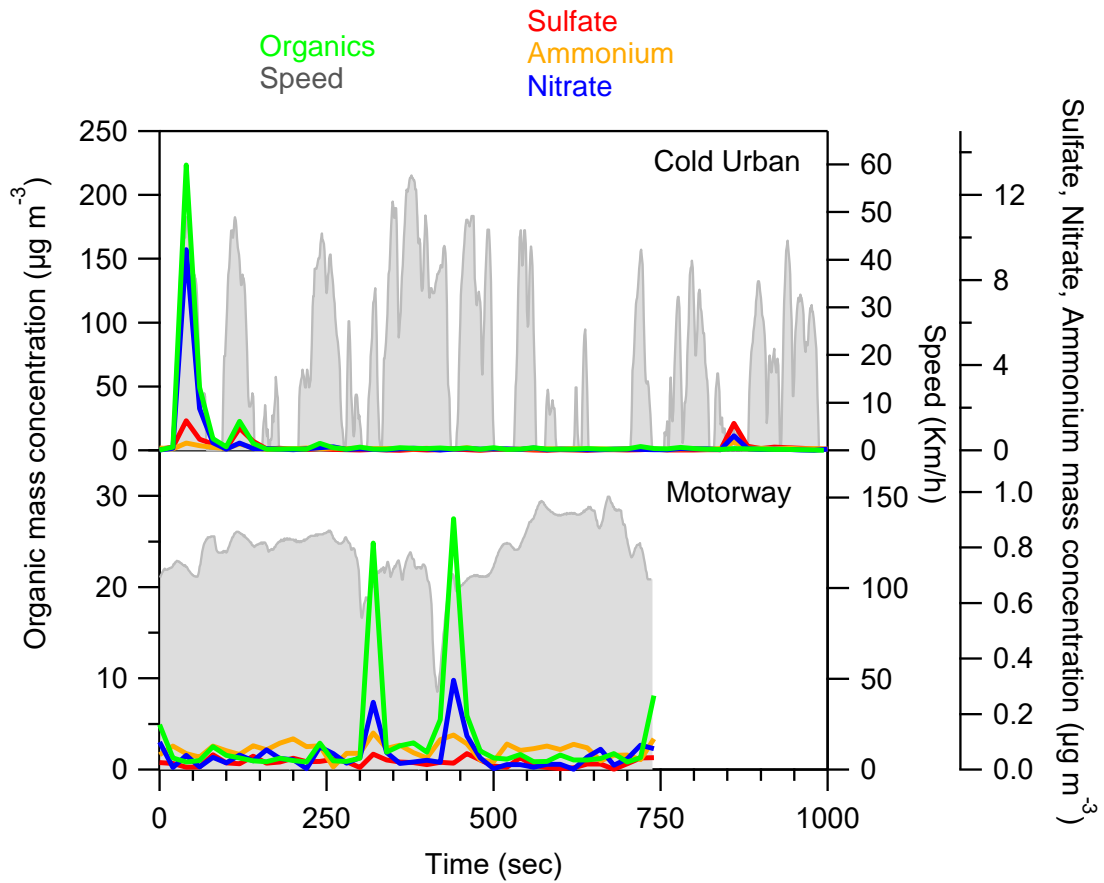
153

154

155

156

157



158

159 **Figure S3.** Time series of organics, sulfate, nitrate and ammonium for Artemis cold
 160 urban (upper) and motorway cycles (lower) for the PFI4 vehicle. BC measurements are
 161 not available for this car.
 162

163

164

165

166

167

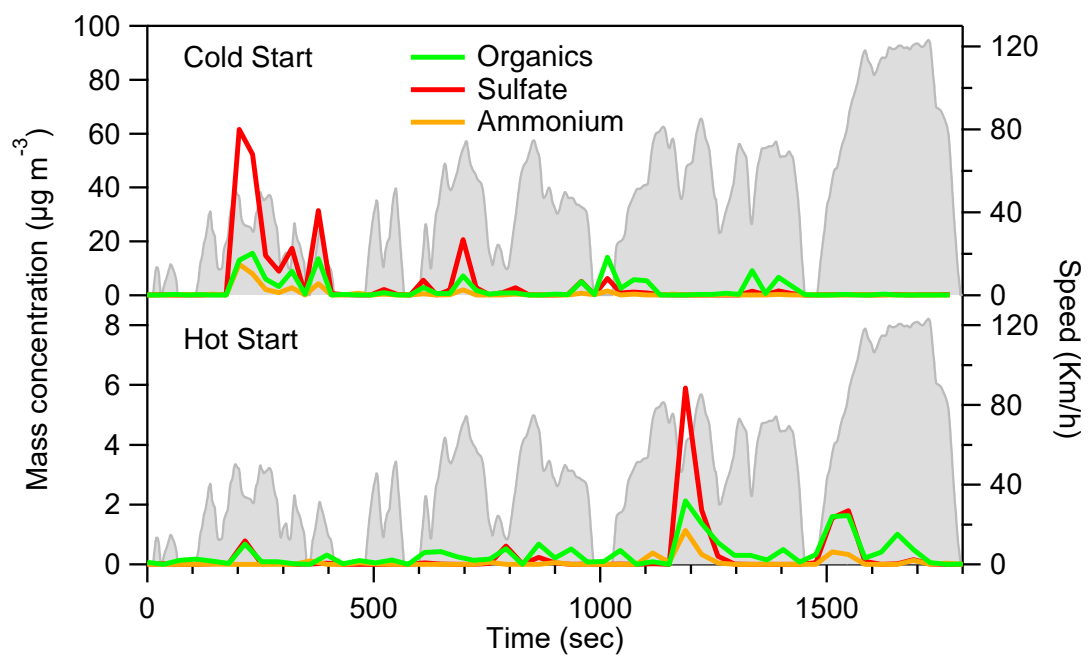
168

169

170

171

172



173

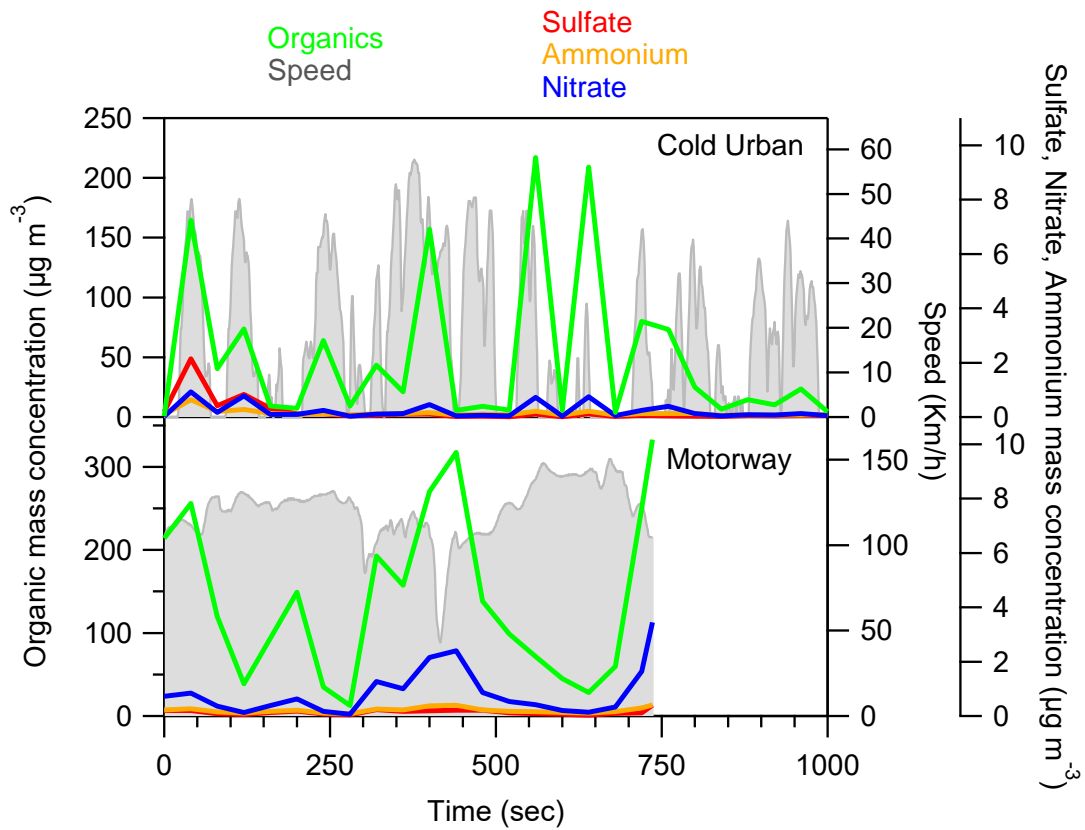
174 **Figure S4:** Time series of organics, sulfate and ammonium for WLTC cold start (upper)
 175 and hot start (lower) for the D3 vehicle.

176

177

178

179



180

181 **Figure S5:** Time series of organics, sulfate, nitrate and ammonium for Artemis cold
 182 urban cycle (upper) and a motorway (lower) for the D4 car.

183

184

185

186

187

188

189

190

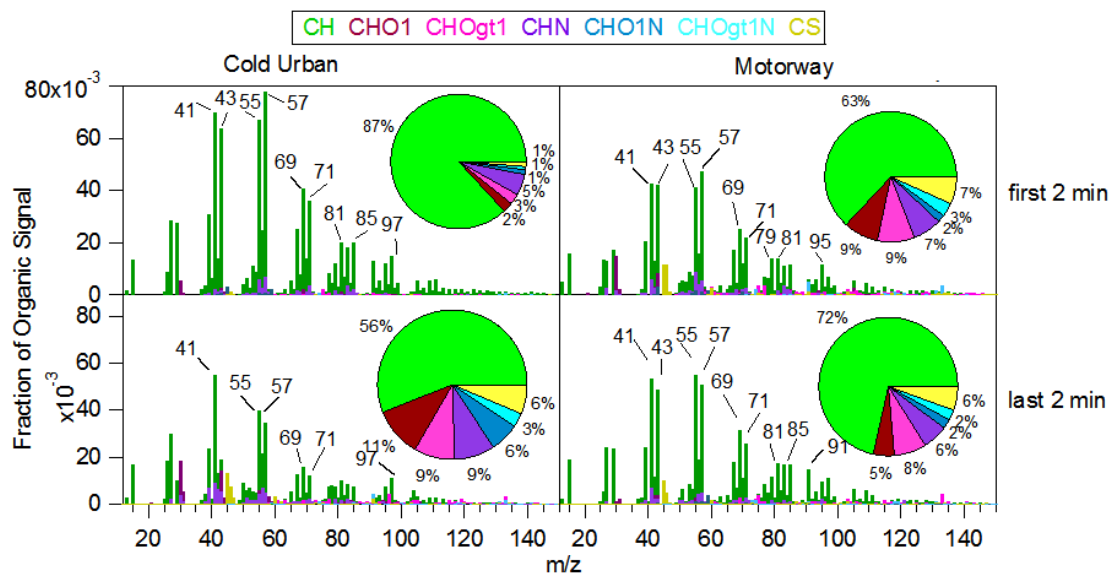
191

192

193

194

195



196

197 **Figure S6.** AMS HR spectra speciation for organic fragments for the PFI4 vehicle
 198 (ARTEMIS cycle).

199

200

201

202

203

204

205

206

207

208

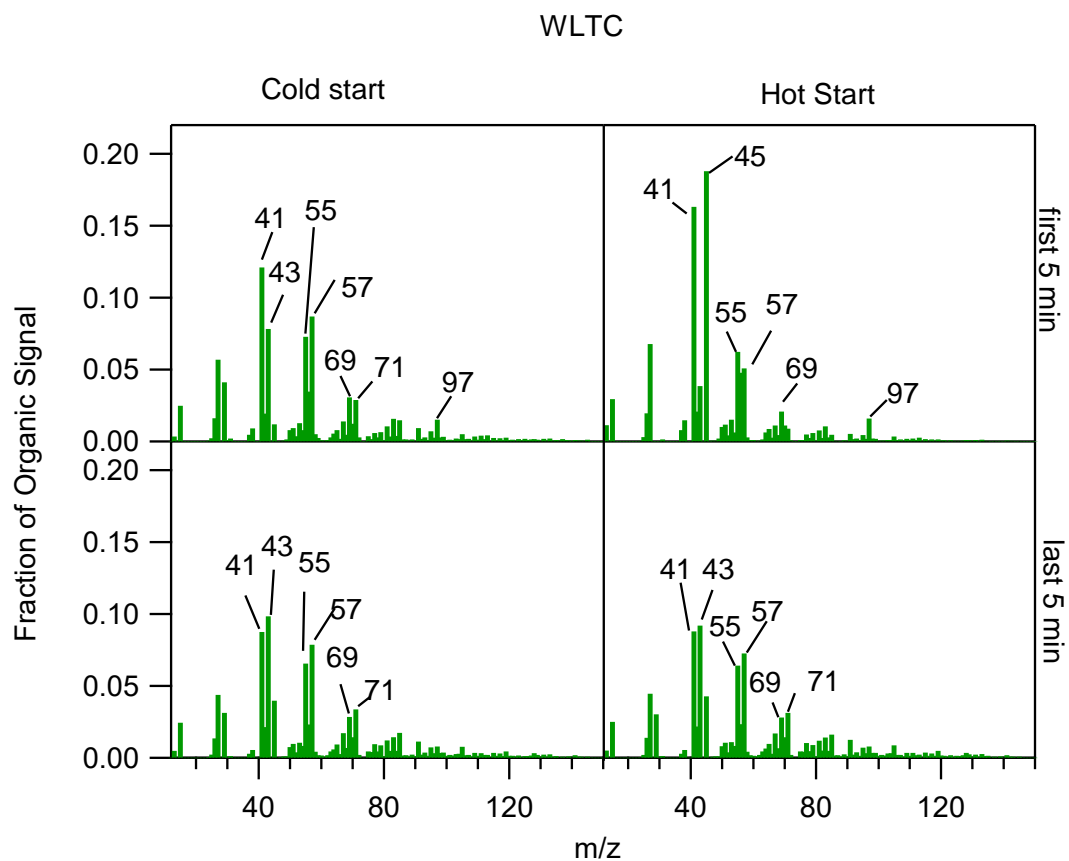
209

210

211

212

213



214

215 **Figure S7.** AMS UMR spectra for organic fragments for the GDI3 vehicle (WLTC).

216

217

218

219

220

221

222

223

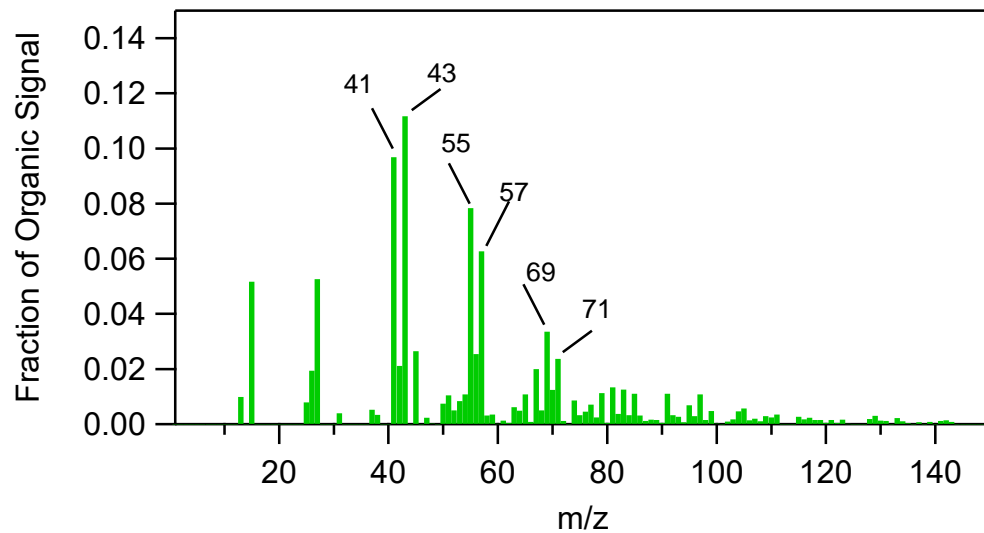
224

225

226

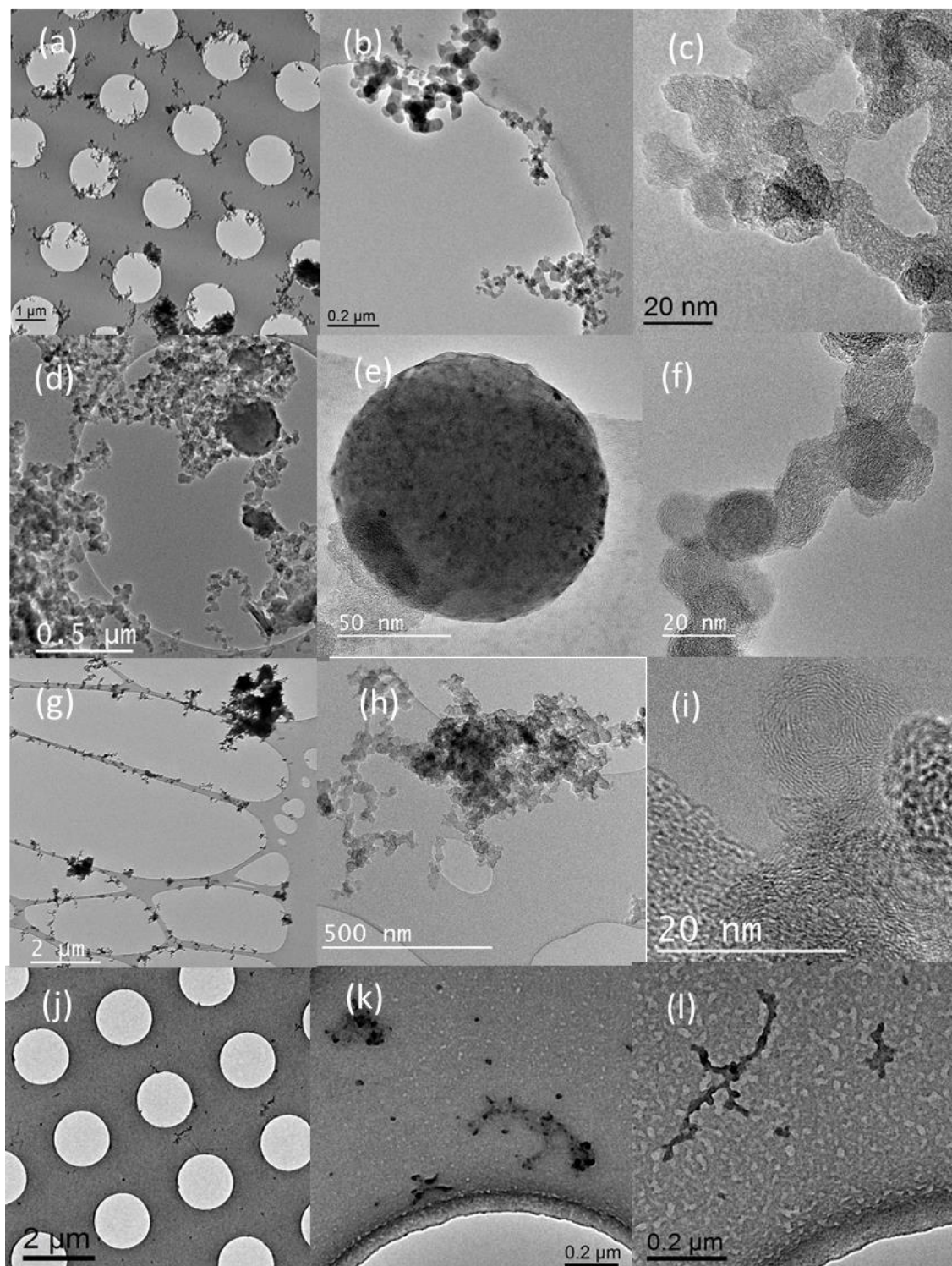
227

228



229
230
231

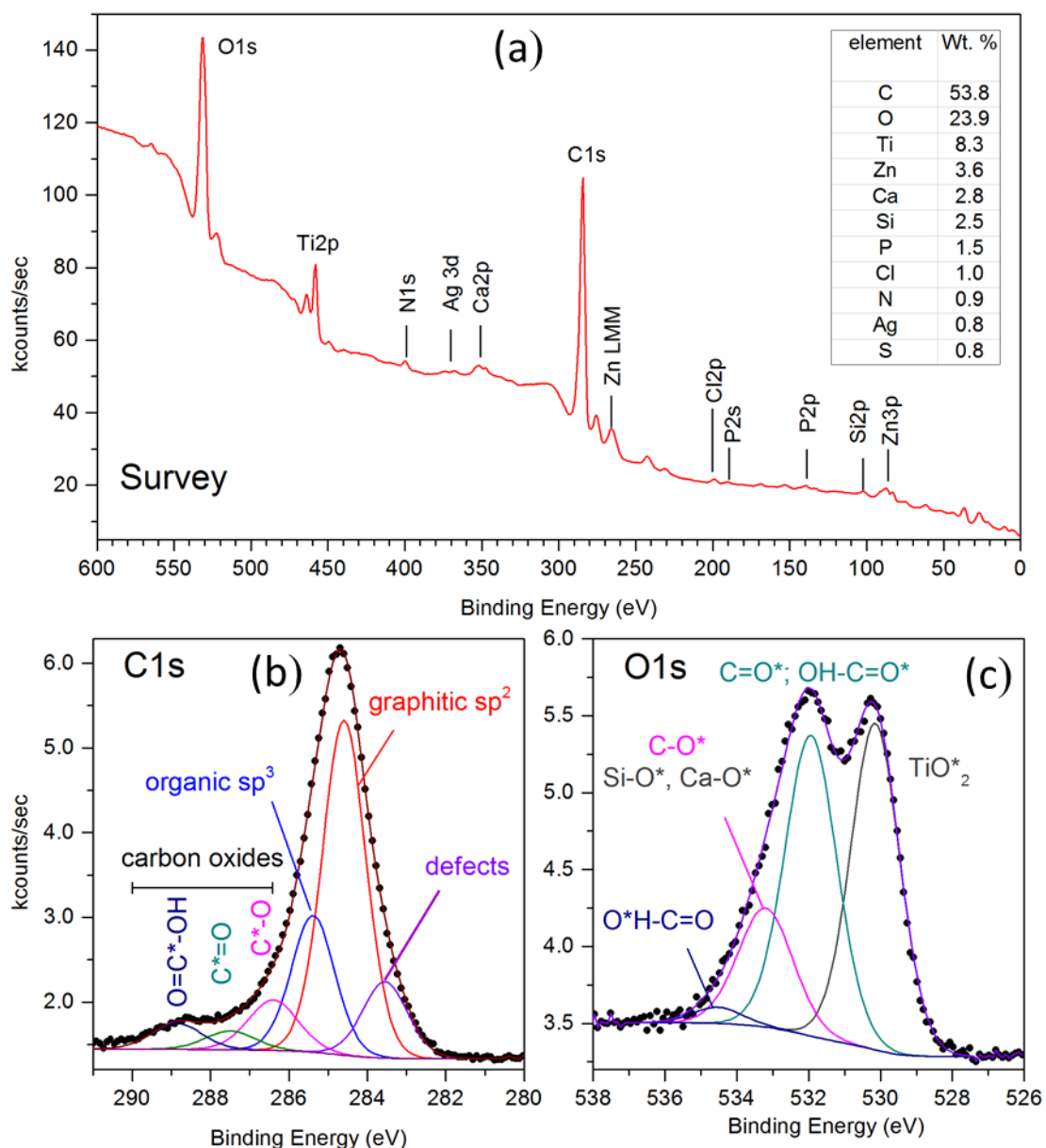
Figure S8: UMR mass spectrum for taken at the beginning of a motorway cycle (2 first minutes) for the D1 vehicle.



232

233 **Figure S9:** TEM images of samples collected during hot cycles: (a-c) GDI1 sampling
 234 the first 120 sec of the motorway cycle, dilution ratio 40; (d-f) GDI3 sampling the last
 235 120 sec of a WLTC cycle, dilution ratio 46; (g-i) D4 sampling the first 45 sec of the
 236 motorway cycle, dilution ratio 2; (j-l) D1 vehicle sampling first 300 sec of the motorway
 237 cycle, dilution ratio 40.
 238

239



240

241 **Figure S10.** XPS spectra of particles collected from the PF14 vehicle: (a) survey
 242 spectrum and elemental composition (table in insert); (b) deconvolution of the C1s
 243 spectrum; (c) deconvolution of the O1s spectrum.

244