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Supplement of

Identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions

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Characteristics of test vehicles and vehicle exhaust sampling

The selected vehicles represent the most frequent vehicle classes in the French fleet in circulation, according to the following criteria: European emission standards (EURO classes), motorization (diesel or petrol), engine capacity (large-, intermediate-, small-engined cars, defined as vehicles with the following capacities: below 1.4 L, from 1.4 to 2 L, above 2 L), and the presence or not of an after-treatment system. According to André et al. (2014), Euro 3 and Euro 4 vehicles accounted in 2011 for the largest part of the French fleet in circulation, followed by Euro 5 and Euro 2 vehicles. They also estimated that diesel vehicles with medium engine displacement (1.4 to 2.0 liters) accounted for 78 % of the diesel vehicles, while petrol vehicles with small displacement (less than 1.4 liters) were the most numerous (62 % of petrol vehicles). Chassis dynamometer experiments have been conducted before the field campaign, and the small differences between the French fleet and the local fleet are discussed in Fallah Shorshani et al. (2015). Finally, three diesel and one petrol vehicles have been chosen as a good representation of the French fleet in circulation in 2011, as follows:

– Petrol Euro 2 with small engine displacement (< 1.4 l) – below referred as E2P

– Petrol Euro 4 with small engine displacement (< 1.4 l) – below referred as E4P

– Diesel Euro 3 with medium engine displacement (1.4 – 2 l) – E3D

– Diesel Euro 4 with medium engine displacement (1.4 – 2 l) - E4D

– Diesel Euro 4 with medium engine displacement (1.4 – 2 l) and equipped with a particulate filter, instead a Euro 5 diesel vehicle) – referred as E4D-PF. Note that this vehicle met Euro 5 standard for PM emissions thanks to the presence of the particle filter, but not the Euro 5 standard for NO_x emissions.

No high-emitting vehicles has been selected (all test vehicles followed their own EU regulations).

vehicles	Vehicle fuel	EURO class	Vehicle model	Year	Mileage km	Engine dCi	Emission control device
E4P	Petrol	EURO 4	Renault Clio 3	2006	82,000	1.4	TWC
E2P	Petrol	EURO 2	Ford Ka	1999	72,000	1.3	CC
E3D	Diesel	EURO 3	Xsara Picasso HDI	2003	140,000	1.9	DOC
E4D	Diesel	EURO 4	Renault Kangoo	2005	146,000	1.5	DOC
E4D-PF	Diesel	EURO 4	Audi TDI	2009	73,800	1.9	DOC+PF

Table S1: Detailed characteristics of vehicles run on chassis dynamometer. TWC: three-way catalyst; DOC: diesel oxidation catalyst; PF: particle filter; CC: catalyst converter

vehicles	Flow rates (l.min-1)		Sampling duration (min, nb cycles)	Mean dilution ratios	
	F1	F2		Road cycle	Urban cycle
E3D	5	40	15 min (1 cycle) for F1 30 min (2 cycles) for F2	22	41
E4D	5-10*	30-40-50*	15 min (1 cycle) for F1 30 min (2 cycles) for F2	23	37
E4D-PF	30	50	30 min (2 cycles)	18	28
E2P	30	50	30 min (2 cycles)	17	28
E4P$	50	-	30 min (2 cycles)	-	23

Table S2: Description of vehicle exhaust sampling: Sample flow rates, sampling time durations and dilution ratios. F1 is the filter dedicated to EC/OC analyses and F2 the filter dedicated to the other analyses. *: The selected flow rates were finally the same as the ones of the E3D vehicle. $: This vehicle has not been kept for the main vehicle tests.

PM_{10} mass and chemistry measured at the traffic site

	PM_{10}	$PM_{2.5}$	OC	EC	NO	NO_2	NO_x
Unit	*µg/m³*	*µg/m³*	*µg/m³*	*µg/m³*	*µg/m³*	*µg/m³*	*µg/m³*
median	24.1	18.4	5.4	5.9	43.6	51.8	103.8
min	4.9	4.9	1.6	1.8	6.4	20.1	27.1
max	45.1	35.4	8.6	12.6	212.4	86.5	298.9

Table S3: 4-h Concentrations of PM_x (TEOM-FDMS), organic and elemental carbons and nitrogen oxides

	Cl^-	NO_3^-	SO_4^{2-}	Oxalates	Na^+	NH_4^+	K^+
Unit	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*
median	17.6	476.5	1227.9	120.2	75.5	366.7	70.8
min	6.2	2.8	166.6	8.6	6.3	22.2	14.0
max	188.2	1571.6	2198.6	285.9	273.2	784.0	120.4

	Mg^{2+}	Ca^{2+}
Unit	*ng/m³*	*ng/m³*
median	15.5	373.5
min	0.6	7.3
max	2820.0	981.4

Table S4: 4-h Concentrations of major ions

	Al	As	Ba	Ca	Cd	Co	Cr
Unit	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*
median	361.1	0.108	12.0	819.9	0.011	0.201	5.8
min	31.6	<DL	<DL	42.3	0.011	0.037	<DL
max	1118.4	0.643	65.8	4347.9	4.439	0.814	60.3

	Cu	Fe	Mn	Na	Pb	Pd	Rb
Unit	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*
median	48.4	1011.4	11.7	321.9	3.7	0.103	0.309
min	3.3	67.5	0.4	41.0	0.5	0.103	0.001
max	146.9	5164.7	56.8	881.4	14.5	3.916	1.670

	Sb	Se	Sn	Sr	Ti	V	Zn
Unit	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*	*ng/m³*
median	4.7	0.19	9.9	0.95	5.3	0.514	28.6
min	0.4	<DL	0.7	0.02	1.4	0.105	18.3
max	10.1	1.40	36.0	13.90	53.9	1.921	881.4

	Zr
Unit	*ng/m³*
median	1.6
min	1.6
max	35.1

Table S5: 4-h Concentrations of metals and trace elements

	Phe	An	Fla	Pyr	BaA	Chr	BeP
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	0.131	0.0099	0.235	0.301	0.087	0.063	0.037
min	0.001	0.0026	0.054	<DL	0.016	<DL	<DL
max	0.307	0.0772	0.528	0.921	1.047	0.470	0.366

	BbF	BkF	BaP	BghiP	DBahA	IP	Cor
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	0.058	0.017	0.029	0.031	<DL	0.019	0.015
min	0.019	0.005	0.005	<DL	<DL	0.005	<DL
max	0.403	0.124	0.292	0.257	0.060	0.270	0.174

Table S6: 4-h Concentrations of Polycyclic Aromatic Hydrocarbons

	C12	C13	C14	C15	C16	C17	C18
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	<DL	<DL	<DL	<DL	<DL	0.172	0.381
min	<DL	<DL	<DL	<DL	<DL	<DL	<DL
max	0.332	0.898	0.847	0.356	0.479	1.658	1.857

	C19	C20	C21	C22	C23	C24	C25
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	0.475	1.207	3.254	5.939	7.017	5.864	4.045
min	<DL	<DL	<DL	<DL	0.256	0.140	0.165
max	2.174	3.724	10.788	18.691	18.679	16.246	10.062

	C26	C27	C28	C29	C30	C31	C32
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	2.409	2.574	0.839	2.314	0.834	2.004	0.393
min	0.086	0.064	<DL	<DL	<DL	<DL	<DL
max	6.900	6.288	4.354	5.253	3.177	5.909	2.061

	C33	C34	C35	C36	C37	C38	C39
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	0.818	<DL	<DL	<DL	<DL	<DL	<DL
min	<DL	<DL	<DL	<DL	<DL	<DL	<DL
max	2.597	1.398	1.620	0.337	0.317	0.337	0.440

	C40	Pristane	Phytane	H3	H4	Manno	Levo
Unit	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*	*ng/m^3*
median	<DL	<DL	<DL	0.366	0.343	0.94	11.1
min	<DL	<DL	<DL	<DL	<DL	<DL	<DL
max	0.389	0.172	0.140	1.679	1.488	4.47	47.5

Table S7: 4-h Concentrations of n-alkanes from C12 to C40, 2 branched alkanes, 2 hopanes (H3: 17α21βNorhopane ; H4: 17α21βhopane) and 2 anhydrosugars (mannosan; levoglucosan)

Traffic characteristics

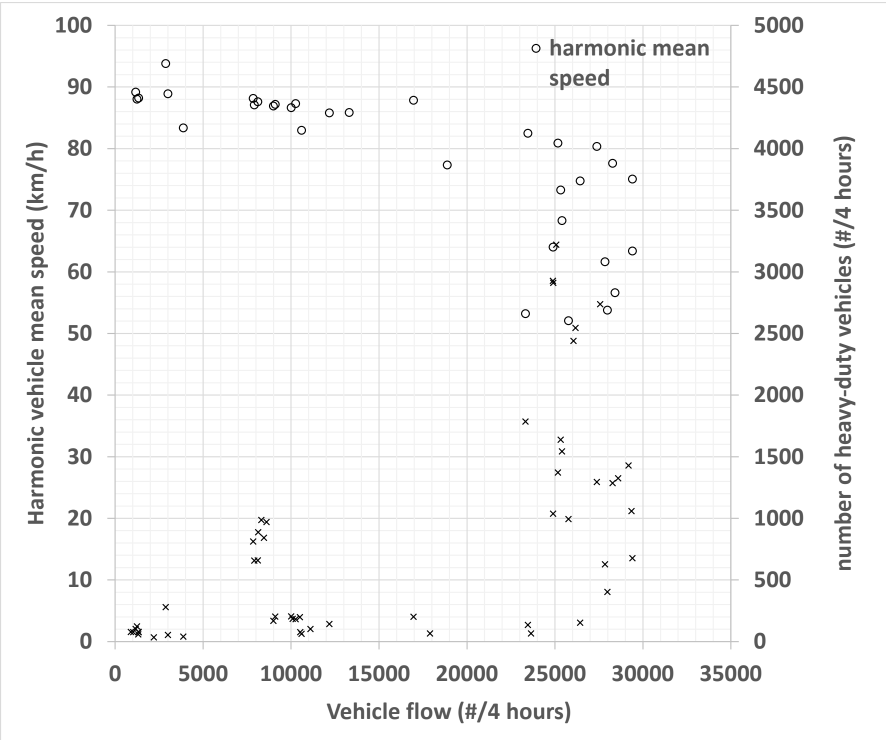


Figure S1: Harmonic vehicle mean speed (km/h) and number of heavy-duty vehicles versus the vehicle flow per period of 4 hours (corresponding to the sampling periods)

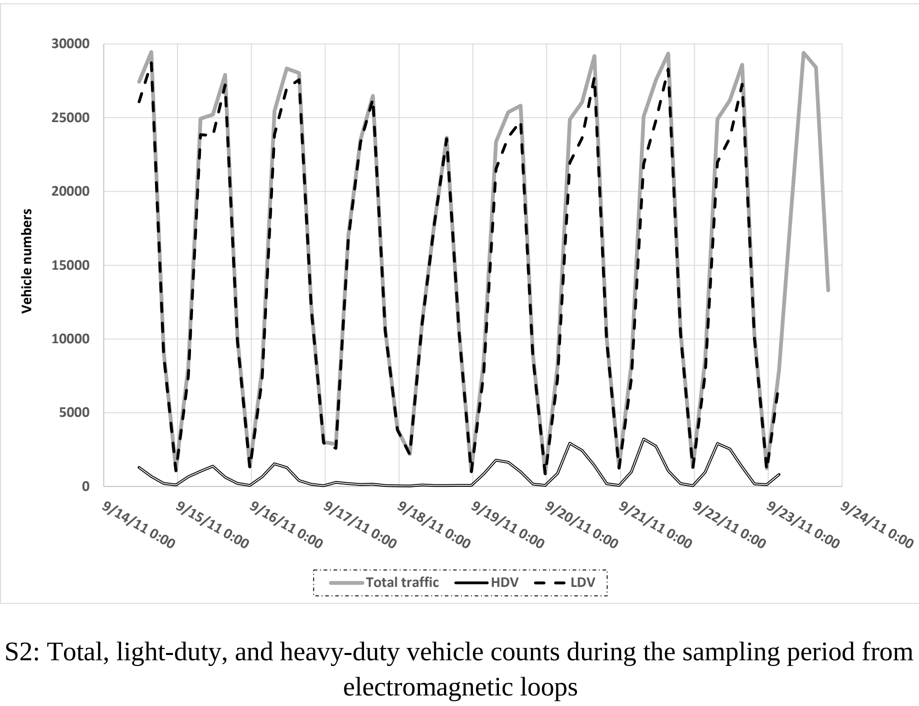


Figure S2: Total, light-duty, and heavy-duty vehicle counts during the sampling period from double electromagnetic loops

Meteorology

A Young meteorological station was installed at the traffic site to capture wind speed and direction, relative humidity, and temperature data. Other meteorological data were supplied by Météo France or measured on the rooftop of our laboratory at the University Grenoble-Alpes (http://www.lthe.fr/LTHE/MesuresEnLigne/MeteoOsugB.html). Since rain events heavily influencing the PM levels occurred during the field campaign and no local measurements have been done, rain data from two stations located in Grenoble conurbation were compared: Grenoble-LVD Météo-France station (45.217 5.848, 13 km away from the traffic site) and CERMO station (45.194 5.762, 6 km away from the traffic site). An excellent agreement is found between the two stations.

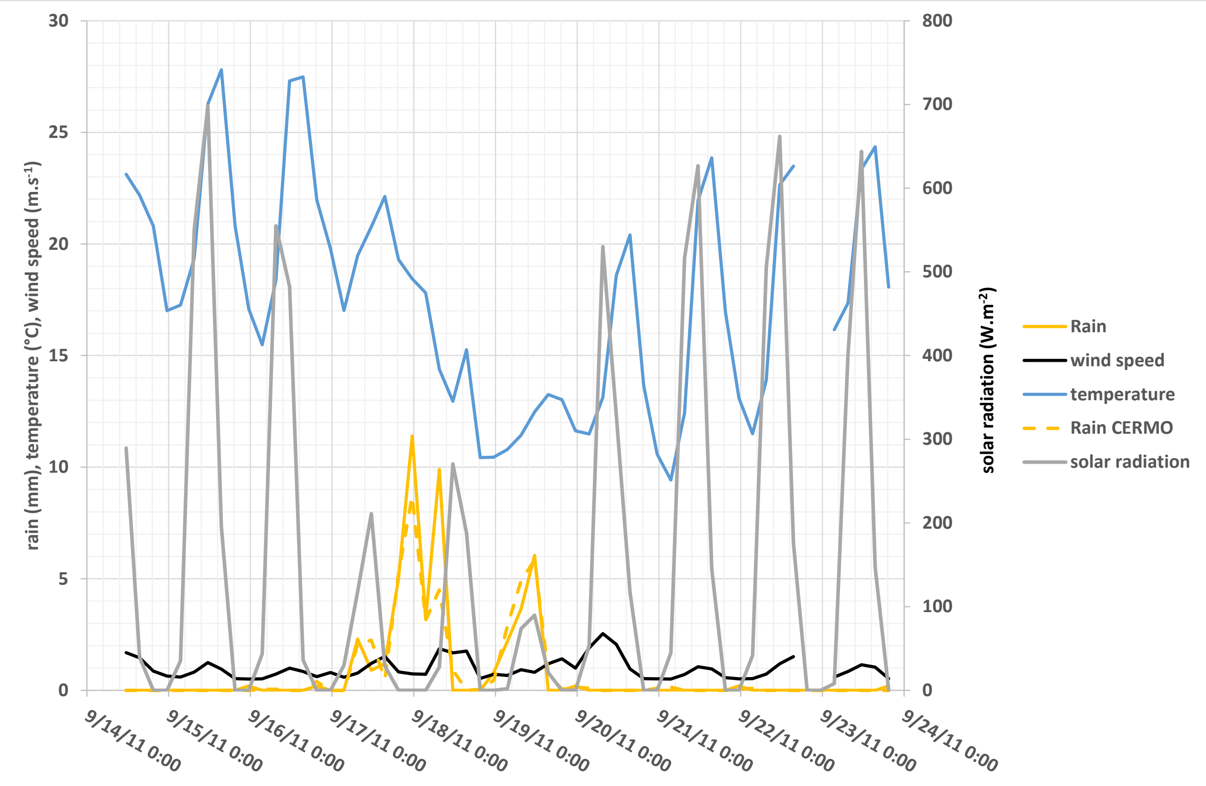


Figure S3: Temperature, wind speed, solar radiation and rain (Météo France and CERMO data) measured during the field campaign. Temperature and wind speed are measured near the traffic site.

Estimation of emission factors

We assume that particle and NO_x concentrations measured on the traffic site result from the addition of local traffic emissions and the urban background of Grenoble (Les Frênes site).

Then, incremental concentrations of the pollutant p due to the local traffic are determined by difference (1).

$$\Delta C_p \ = C_p^{traffic\ site} - C_p^{urban\ background} \quad (1)$$

We assume that the atmospheric dilution affects similarly all pollutants emitted by the traffic (2). From this assumption, we could write:

$$\frac{EF_p}{\Delta C_p} = \frac{\mathrm{EF_{NO_x}}}{\Delta \mathrm{C_{NO_x}}} \quad (2)$$

With EF_p, the emission factor of pollutant *p*, ΔC_p the incremental concentrations of *p* assumed from the local traffic, EF_{NOx} the emission factor of NO_x et ΔC_{NOx}, the incremental concentrations of NO_x from the local traffic.

We estimate NO_x emissions (EF_{NOx}) from the local traffic from COPCETE data (SI, II. table 1), local traffic counts and the local vehicle fleet (determined by cameras, see Fallah Shorshani et al., 2015, II. table 2). No emission factor is available for two-wheelers, then the emission factor of petrol vehicles is used to estimate their emissions. COPCETE uses emission functions from European COPERT4 (Ntziachristos et al., 2009) averaged for fleet composition and speed. The average emission factors of NO_x for heavy-duty and light duty vehicles at the RN87 highway are estimated to be respectively 5.218 $g.veh^{-1}.km^{-1}$ and 0.523 $g.veh^{-1}.km^{-1}$.

Then, formula (2) allows the determination of hourly vehicle emissions from the RN87/E712 highway. The EF per vehicle can be calculated using N^{total} the total number of vehicles crossing the sampling area during the sampling period:

$$EF_p = \frac{\mathrm{EF_{NO_x}}}{\Delta \mathrm{C_{NO_x}}} . \frac{\Delta C_p}{N^{total}} \quad (3)$$

Emission factors calculated as above are average emission factors for the E712 vehicle fleet. In theory the emissions of pollutant p from local traffic come from the addition of heavy-duty traffic emissions and light duty traffic emissions (4).

$$E_p^{RN87} = EF_p^{LDV}.N^{LDV} + EF_p^{HDV}.N^{HDV} \quad (4)$$

With N^{LDV} and N^{HDV} are respectively the heavy-duty and light duty traffic counts.

In order to discriminate the respective contributions of heavy-duty EF_p^{HDV} and light duty vehicles EF_p^{LDV} to particulate emissions, Multiple Linear Regressions (MLR) are applied to data that show significant relationships with the traffic and for which corresponding emission data follow (or are sufficiently close to) the Normal distribution. There is no collinearity between light-duty and heavy-duty traffic data (VIF equal to 1.9 for the dataset of metals and 1.4 for the dataset of the organics species), while petrol and diesel traffic data are strongly correlated.

	NO_x	***PM***
	g/km	**g/km**
Diesel PC	0.555572	0.072830
Petrol PC	0.303579	0.045651
Hybrid PC	0.022623	0.044401
LPG PC	0.099782	0.045719
Diesel CUV	0.781215	0.089742
Petrol CUV	0.430468	0.051572
Lorries	5.165895	0.65918
Buses	6.85756	0.668866
TOTAL	0.710245	0.091522

Table S8: Emission factors of NO_x and PM (COPCETE data). PC: passenger cars, CUV: commercial utility vehicles

	%
HDV	3.78
Diesel CUV	15.73
2-wheelers	0.83
Diesel PC	54.52
Other PC	0.69
Petrol PC	24.34
Buses	0.12

Table S9: Mean fleet used to compute NO_x emissions

Calculation of Carbon Preference Index (CPI)

$$CPI = \frac{\sum C_i}{\sum C_j}$$

Where C_i and C_j represent concentrations of odd and even carbon numbers n-alkanes respectively

Temporal variations of concentrations

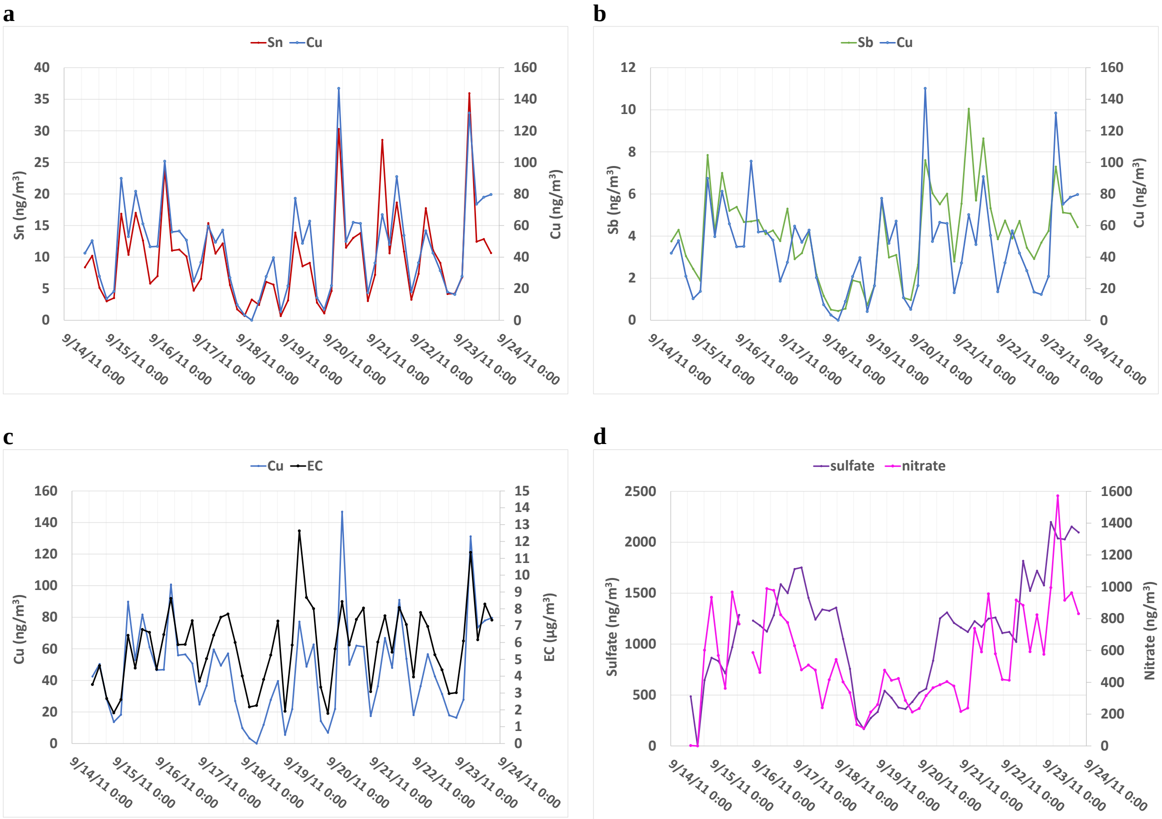
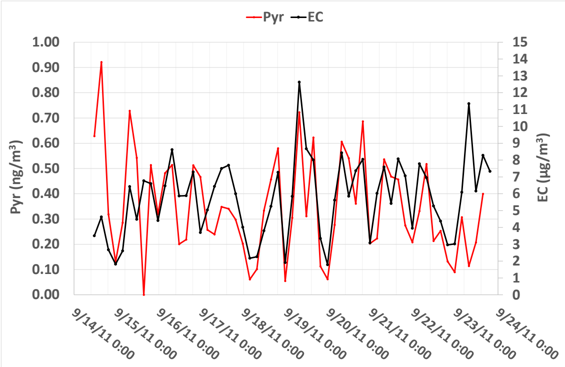


Figure S4: 4-hour concentrations measured at the traffic site: a: copper and tin; b: copper and antimony; c: copper and elemental carbon; d: sulfate and nitrate a



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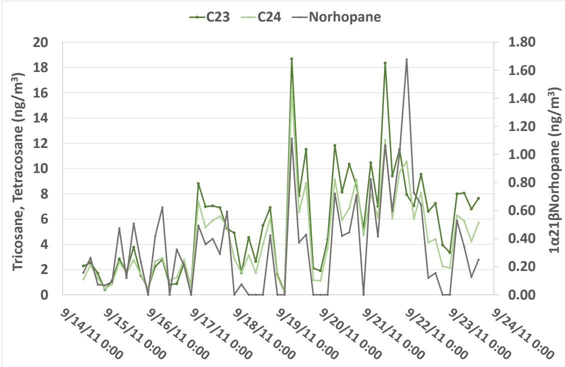

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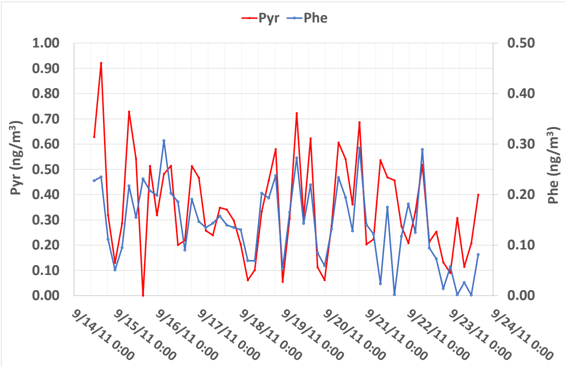

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Figure S5: 4-hour concentrations measured at the traffic site: a: elemental carbon and pyrene; b: tricosane, tetracosane and 17α21βNorhopane; c: pyrene and phenanthrene

Comparison with PM_{10} emission factors of the recent literature (brake wear elements)

PM_{10} EFs	This study	Johansson *et al.* 2009	Bukowiecki *et al*. 2009[$]		Bukowiecki *et al*. 2009[$§]	Gillies et al., 2001	Handler *et al.* 2008	Alves *et al.* 2015	Hulskotte *et al.* 2004	
Location	Grenoble, France	Stockholm, Sweden	Zürich, Switzerland		Reiden Switzerland	L.A., U.S.	Vienna, Austria	Braga, Portugal	The Netherlands	
Road type	Urban freeway 4 lanes	Roadside	City centre Street canyon 2 lanes		Inter urban freeway 4 lanes	Tunnel 2 bores with 3 lanes	Highway tunnel	Urban tunnel	Brake discs and pads analyses	
Traffic conditions	Mainly congested	Densely trafficked	Queues at red lights		Mainly free-flowing		Free flowing + congested			
Speed limit/inf.	90 km.h^{-1}		50 km.h^{-1}		120 km.h^{-1}	42.6/64.4 km.h^{-1}	80 km.h^{-1}			
Nb veh/day	65-95,000		22,000		50,000	3000 veh/hr	36-50,000	6,4-10,700	Passenger cars Average brake profile	
%HDV	0.3-12%		10%[$]		15%[$]	2.6%	4-12.6%	10%	Low braking 8 mg.veh^{-1}.km^{-1}	High braking 15 mg.veh^{-1}.km^{-1}
Results expected	Brake + resuspension	Brake + resuspension	Brake + resuspension	Brake only	Brake only	Brake + resuspension	Brake + resuspension	Brake + resuspension		
Ba μg.veh^{-1}.km^{-1}	66		145	39.1	11.9	1040	55	670		
Cr μg.veh^{-1}.km^{-1}	43	41				20		60	30	55
Cu μg.veh^{-1}.km^{-1}	300	542	476.6	108.1	28.2	530	156	110	291	546
Fe mg.veh^{-1}.km^{-1}	6.71		6.83	1.85	0.56	12.39	3.4	0.51	5.75	10.78
Mn μg.veh^{-1}.km^{-1}	62	110				70	42	60	43	80
Sb μg.veh^{-1}.km^{-1}	27	144	74.1	17.9	32.3	220	100	50	64	120
Sn μg.veh^{-1}.km^{-1}	55	126	72.5	16.1	8.7	70	25		83	155
Ti μg.veh^{-1}.km^{-1}	28					60	47	300	32	61
Cu/Fe*	0.046 ±0.015		0.070	0.058	0.050	0.043	0.046	0.216	0.051	0.051
Cu/Sb*	12.6 ±4.7	3.8	6.4	6.0	0.9	2.4	1.6	2.2	4.5	4.6
Cu/Sn*	5.6 ±1.8	4.3	6.6	6.7	3.2	7.6	6.2		3.5	3.5
Cu/Mn*	5.7 ±2.9	4.9				7.6	3.7	1.8	6.8	6.8

Table S10: Comparison with PM_{10} emission factors of the recent literature. $: traffic EFs related to an average 10% or 15% HDV and calculated from the three particle size fractions: 2.5-10; 1-2.5; and 0.1-1 µm for Zürich and the two size fractions 2.5-10 and 1-2.5 µm for Reiden; §: estimation for brake wear only. *The ratios are calculated from the published data.