

Supplement of

5 **Development and application of an analytical method for the quantification of tire wear in atmospheric deposition**

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Table S1 Reference tire samples

Sample ID	Manufacturer	Size	Season	Vehicle category
CMCTT-1	Orium	195/65 R15 95V	All season	Car/LDV
CMCTT-2	Bridgestone	215/45 R17	Winter	Car/LDV
CMCTT-3	Atlas	195/55 R16 87H	Winter	Car/LDV
CMCTT-4	Zeetex	205/55 R16	Winter	Car/LDV
CMCTT-5	Goodyear	225/50 R17 94H	Winter	Car/LDV
CMCTT-6	Eskimo Sava	175/65 R14	Winter	Car/LDV
CMCTT-7	Azenis	225/40Z R18 (92Y)	Summer	Car/LDV
CMCTT-8	Bridgestone	175/65 R14 82T	Summer	Car/LDV
CMCTT-9	StarMaxx	205/55 R16 91H	Winter	Car/LDV
CMCTT-10	Dunlop	205/55 R16 91V	Summer	Car/LDV
CMCTT-11	Continental	195/65 R15 T	Winter	Car/LDV
CMCTT-12	Continental	185/65 R15 T	Winter	Car/LDV
CMCTT-14	Star Performer	235/35Z R19	Winter	Car/LDV
CMCTT-14	Bridgestone	175/65 R14 82T	Summer	Car/LDV
CMCTT-15	Michelin	195/70 R15C	Winter	Car/LDV
CMCTT-16	Pirelli	205/55 R16	Winter	Car/LDV
CMCTT-17	Platin	205/45 R16	Summer	Car/LDV
CMCTT-18	Michelin	185/65 R15	Winter	Car/LDV
CMTTT-1	Bridgestone	385/65R 22.5	All season	Truck/Bus
CMTTT-2	Continental	275/70 R22.5	All season	Truck/Bus
CMTTT-3	Bridgestone	315/80 R22.5	Summer	Truck/Bus
CMTTT-4	Continental Re-thread	275/70R 22.5	Not known	Truck/Bus
CMTTT-5	Continental	315/80R 22.5	All season	Truck/Bus

15 **Table S1. Details of the used tire samples that were collected from local tire dealers, cryo-milled and used as reference material.**

S2 Sampling locations and passive sample collectors

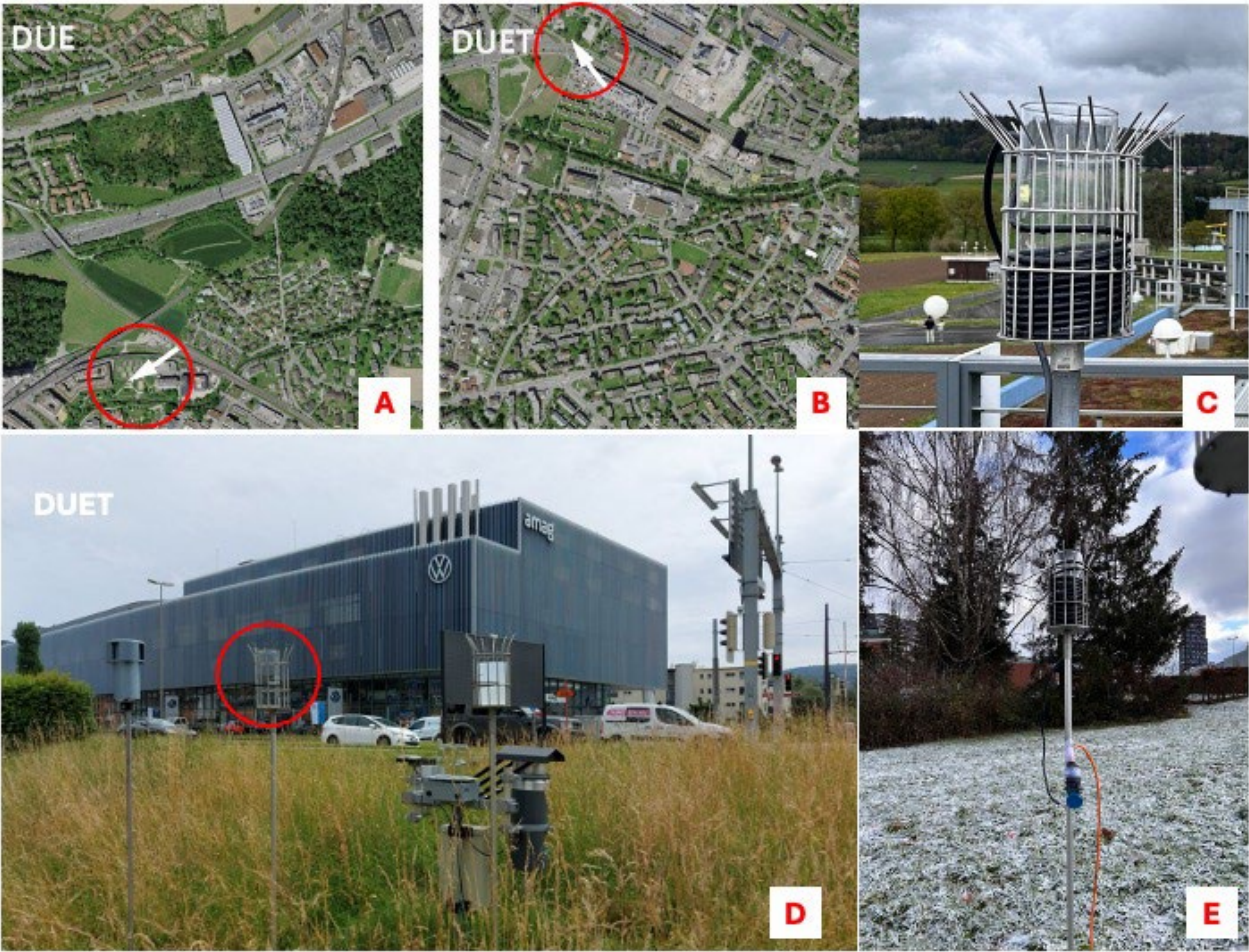


Figure S1. Aerial images indicating the environment of the sampling locations DUE and DUET (A and B, images from <https://www.swisstopo.admin.ch/de/orthobilder-swissimage-10-cm>). Photographs C and E show the passive samplers (cylindrical borosilicate glass containers) wrapped with heating cable (switches on below 5°C, switches off above 10°C) placed on a metallic pole 1.5 m above ground, and photograph D shows the DUET sampling site next to Ueberlandstrasse with a daily traffic volume of 19'000 vehicles.

S3 Solvent cleaning

Deuterated polystyrene and deuterated polyisoprene were spiked into the CMTT samples. We found that sequential solvent cleaning with THF, DCM, and acetone was effective in removing deuterated polymers from CMTT as seen from Py-GC-MS analyses of pure CMTT, spiked CMTT, and solvent-cleaned CMTT samples (Figure S2). Notably, the deuterated polymer markers were no longer detectable after the cleaning process. Additionally, the employed thermal desorption procedure indicated above helps to remove volatile components such as limonene and toluene, as well as small organic molecules. Employing this combination of density separation, solvent cleaning, and thermal desorption therefore efficiently removed the possibly interfering lighter microplastics ($d \leq 1$ g/mL), other non-tire related polymers, and small-sized organic molecules.

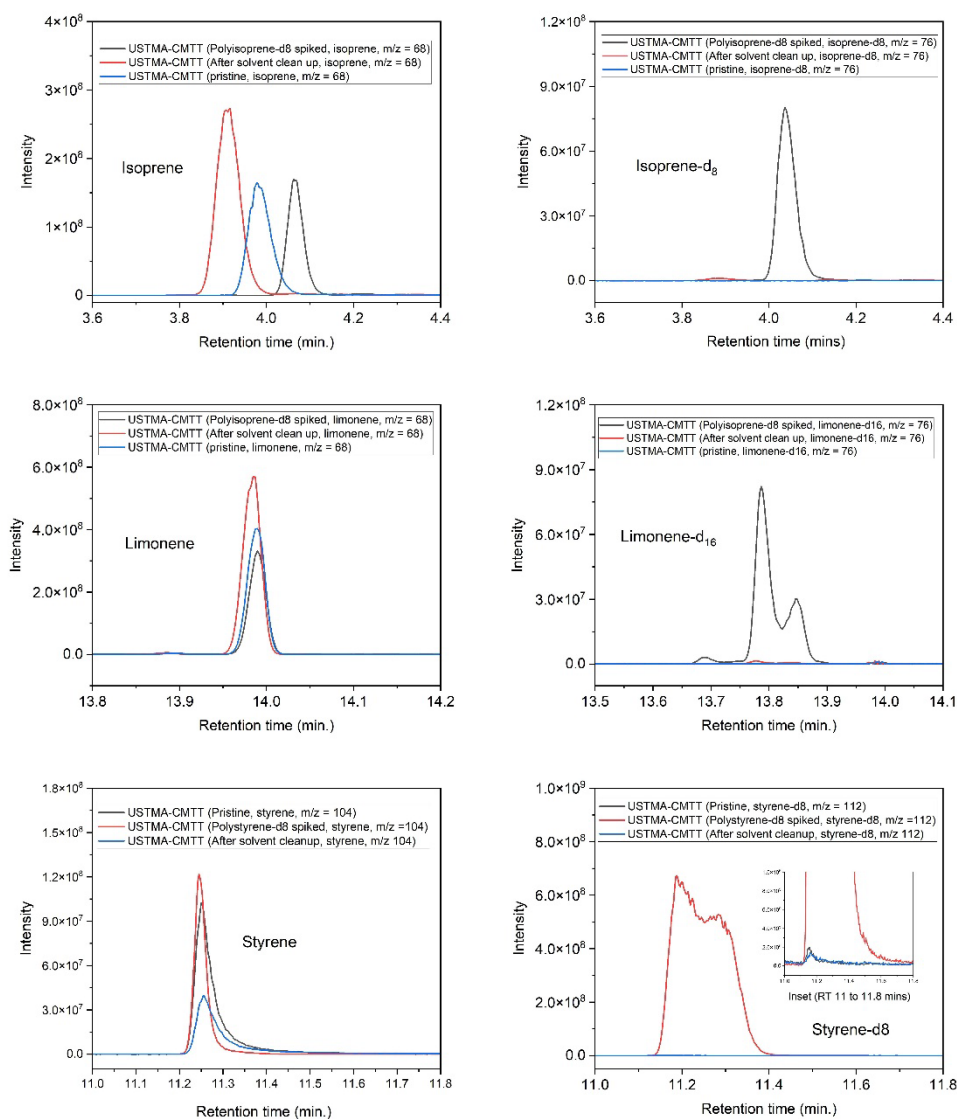
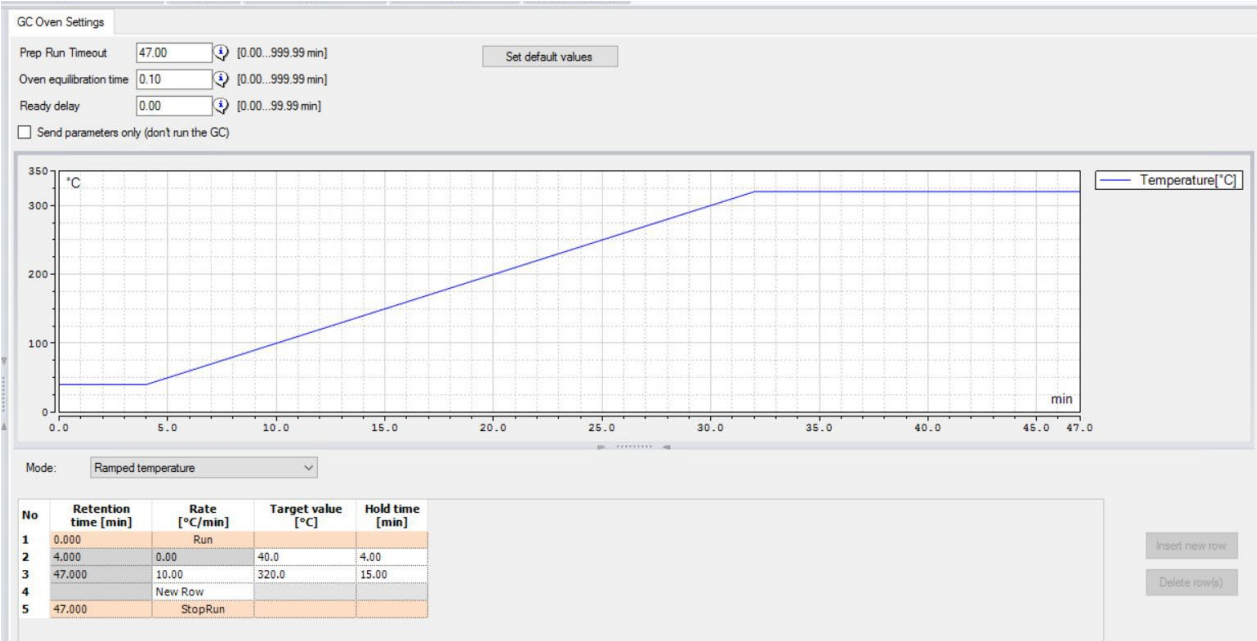


Figure S2. Removal of non-volatile organic chemicals and soluble polymer fraction from the spiked samples upon washing with organic solvents.

S4 GC-MS configuration



65 **Figure S3. Temperature program applied during GC–MS analysis. The oven was initially held at 40 °C for 4 min, followed by a temperature increase at 10 °C/min up to 320 °C.**

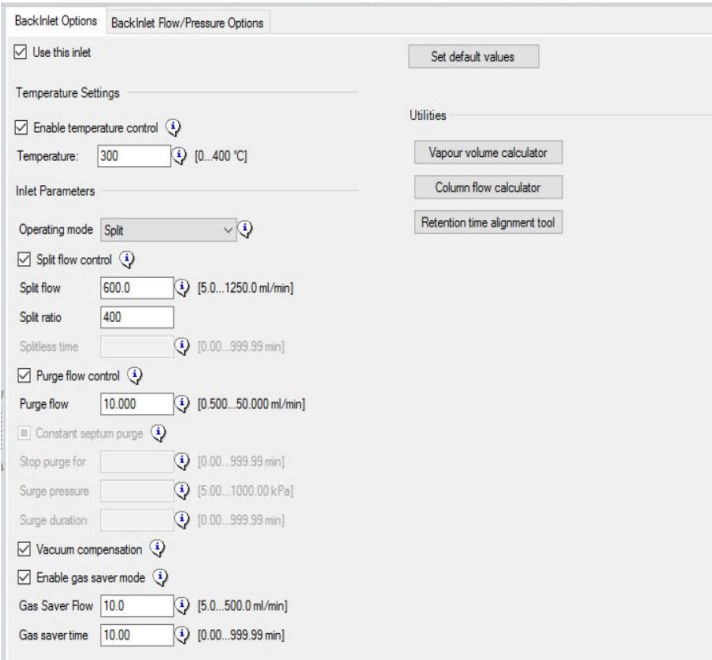
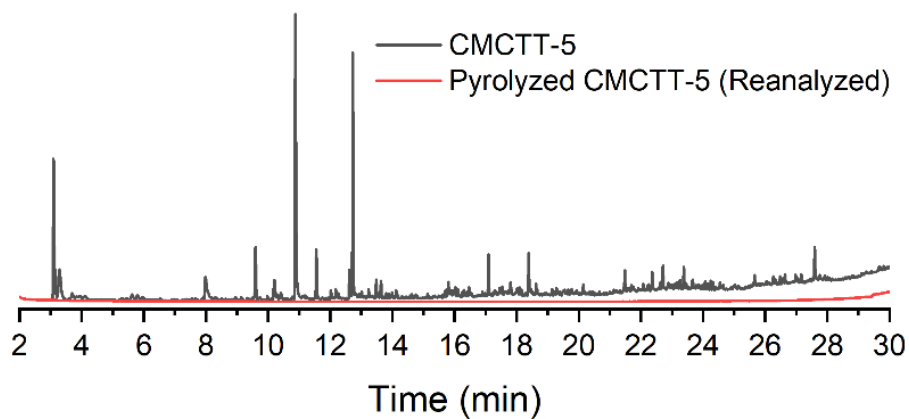


Figure S4. Gas chromatograph operating parameters showing the configured carrier gas flow rates, inlet split ratio, purge flow, and the programmed oven temperature profile used in the analysis.

S4 Repeated pyrolysis of CMTT sample



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Figure S5. Comparison of the chromatograms of the repeated measurement of a CMCTT-5 sample. The red line shows the chromatogram of the re-analysis of a CMCTT-5 sample that has already been pyrolyzed at 500°C.

S6 Comparison of pure polymers and CMTT

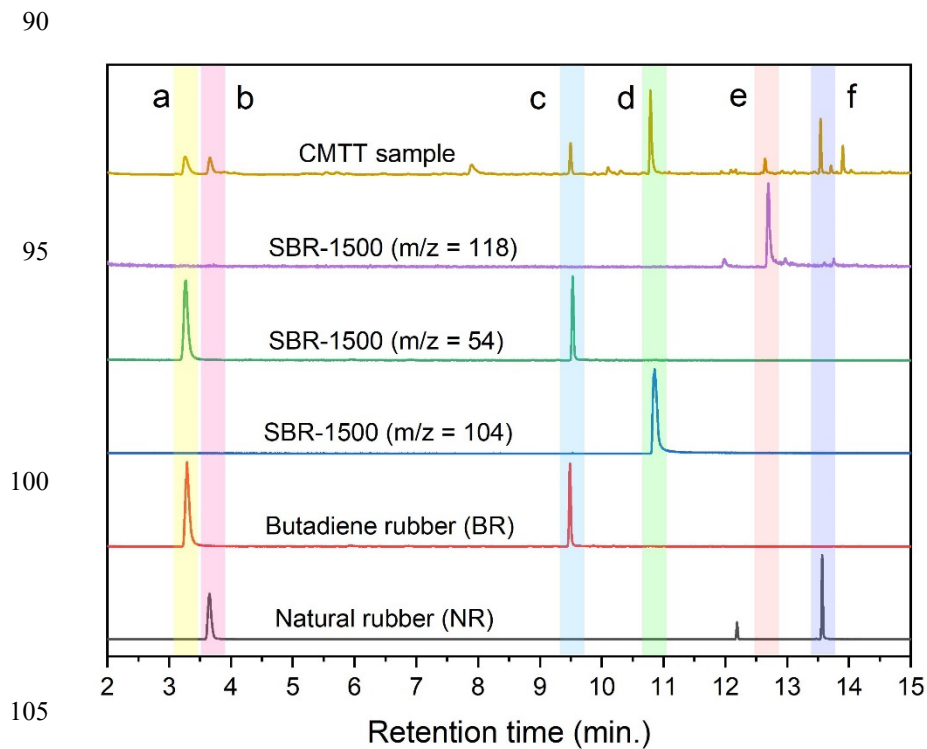


Figure S6. Comparison of the characteristic pyrolysis markers (a = butadiene, b = isoprene, c = 4-vinylcyclohexene, d = styrene, e = α -methylstyrene, and f = limonene) observed in pure polymer standards with their corresponding pyrolysis products in a CMTT sample at 500 °C, indicating the existence of each marker in a tire tread sample.

S7 Detailed CMCTT-5 chromatogram

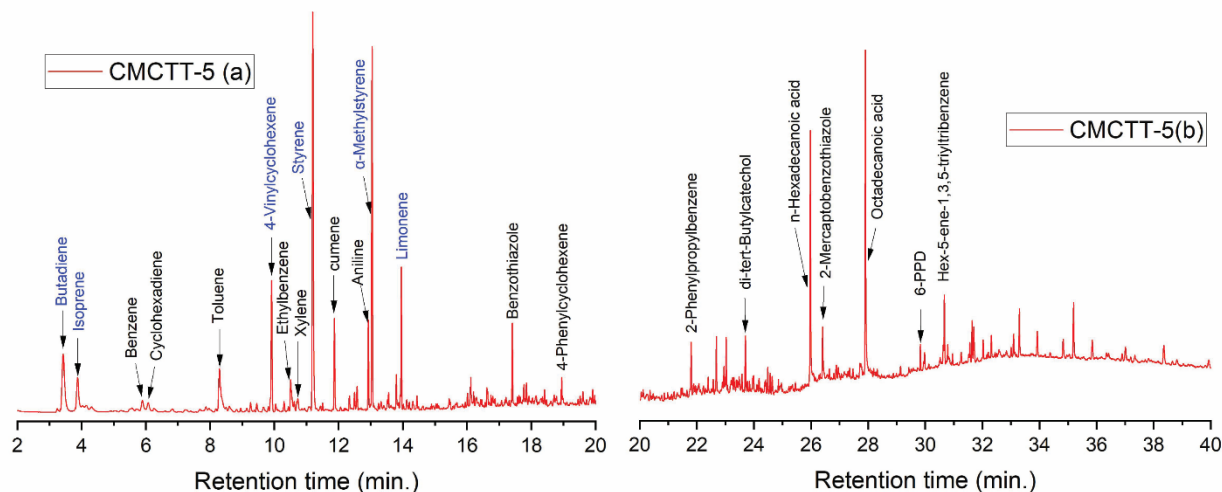


Figure S7. Full chromatogram of CMCTT-5 sample at pyrolysis temperature of 500°C split in part (a) and (b) at a retention time of 20 min. The y-axis is not shown but indicates signal height in arbitrary units. The most prominent pyrolysis products are labelled.

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S8 SBS in road wear

One of the pyrolysis markers used (α -methylstyrene) is also formed during the thermal decomposition of styrene-butadiene-styrene (SBS), a compound found in polymer-modified bitumen and also used in road asphalt.¹ Simple calculations suggest that the amount of SBS used in road construction in Switzerland is small and its contribution is negligible.

135 In Switzerland, bitumen makes up 1% of the total mass of the road material.² There is no literature available on the proportion of polymer bitumen in the total bitumen used in road construction in Switzerland. According to expert judgement about 20-40% of the bitumen used is polymer-modified. Therefore, the road material consists of less than 0.4% polymer-modified bitumen. The SBS content of polymer-modified bitumen is about 5%.³ This means that, on average, road material and road wear contain less than 0.02% SBS.

140 Tire and road wear material each contribute about 50% to the mass of tire and road wear particles (TRWP).⁴ The tire tread material contains an average of about 11% styrene-butadiene-rubber (SBR), the polymer that also forms α -methylstyrene during pyrolysis. However, in an average TRWP, the SBR content in tire wear exceeds the SBS content in road wear by more than a factor of 100.

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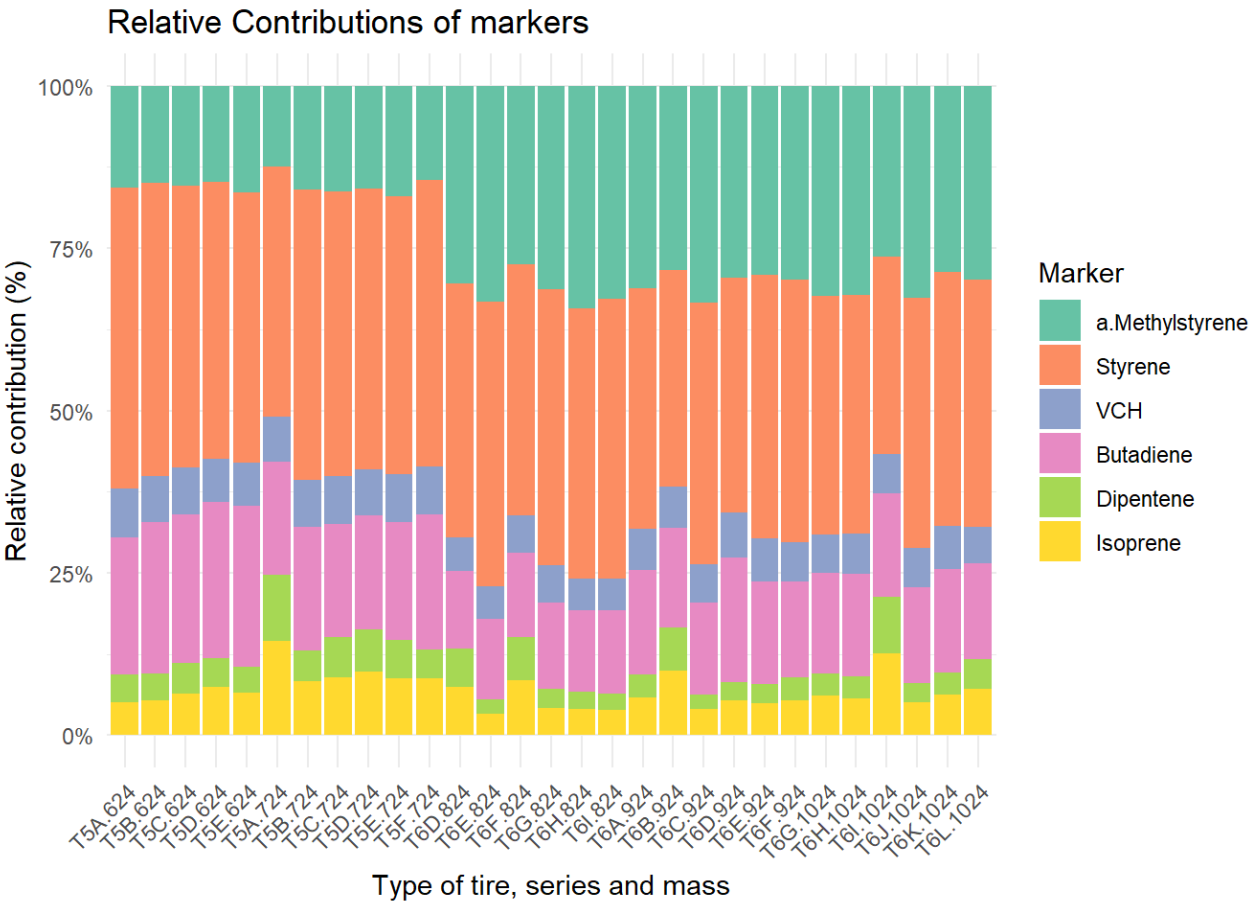


Figure S8. Relative contribution of the six pyrolysis markers for repeated measurement of CMCTT-5 and CMCTT-6. The labels of the samples analyzed (color bars) are the following. The first letter indicated the type of CMTT (T5 for CMCTT-5 and T6 for CMCTT-6), the third letter indicates the mass of CMTT sample (the mass increases with the sequence of letters), and the last three numbers indicate the date of analysis, i.e. (M)MY.

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S10 Principal Component Analysis of CMTT sample data

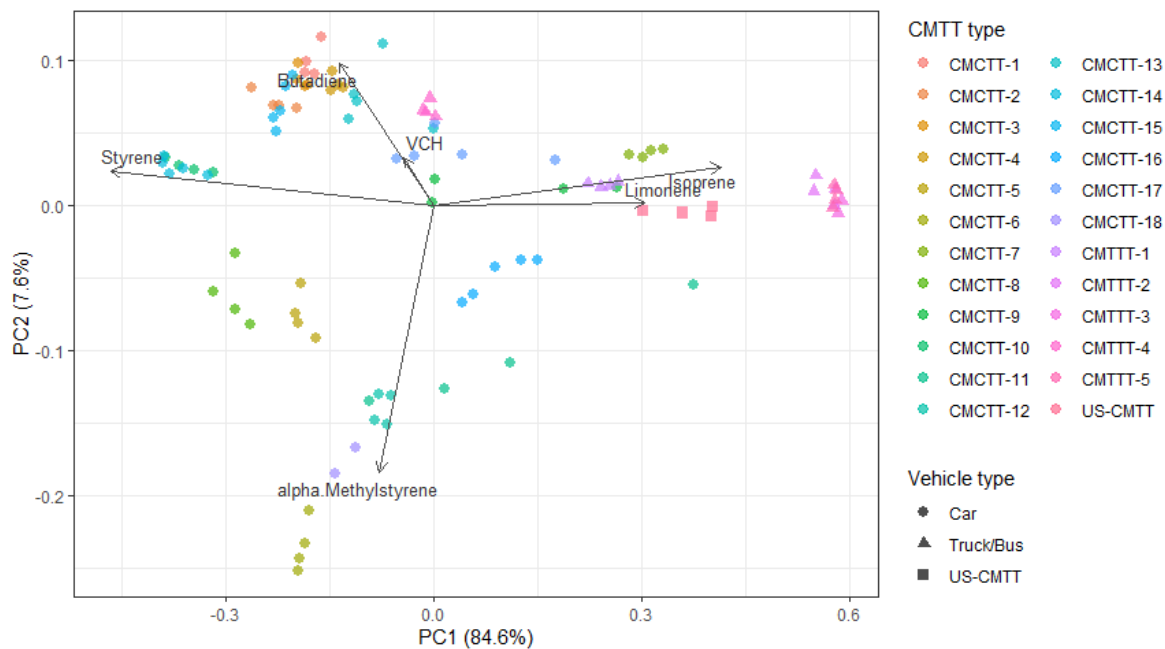


Figure S9. Biplot showing the scores of the measured CMTT samples in the plane spanned by the first two principal components (PC1 and PC2).

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S11 Pyrolysis marker signal vs. mass of CMTT

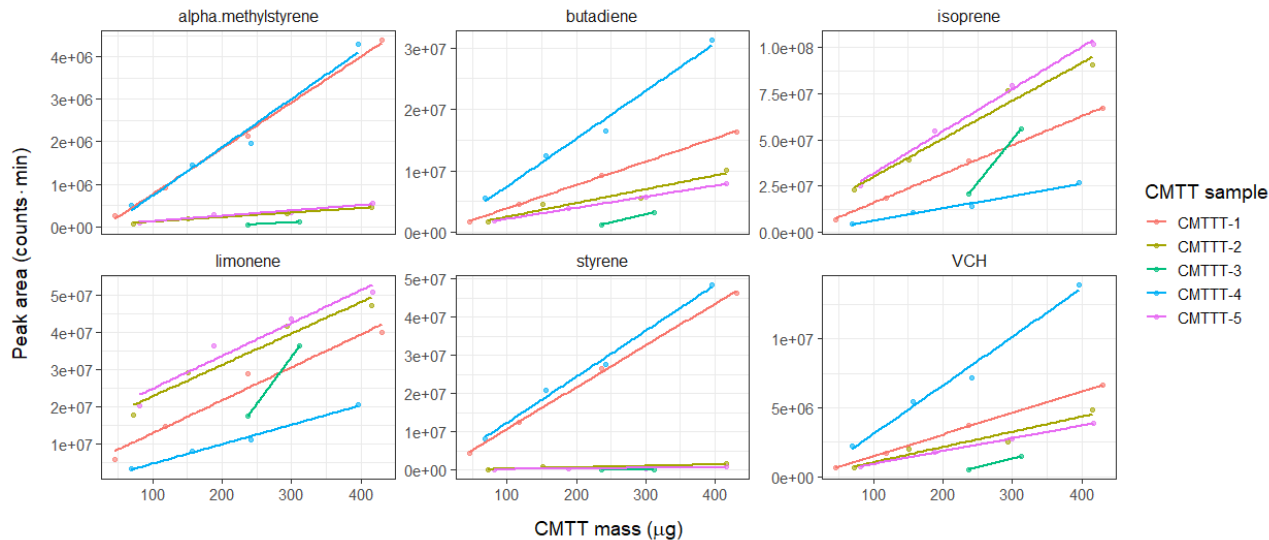
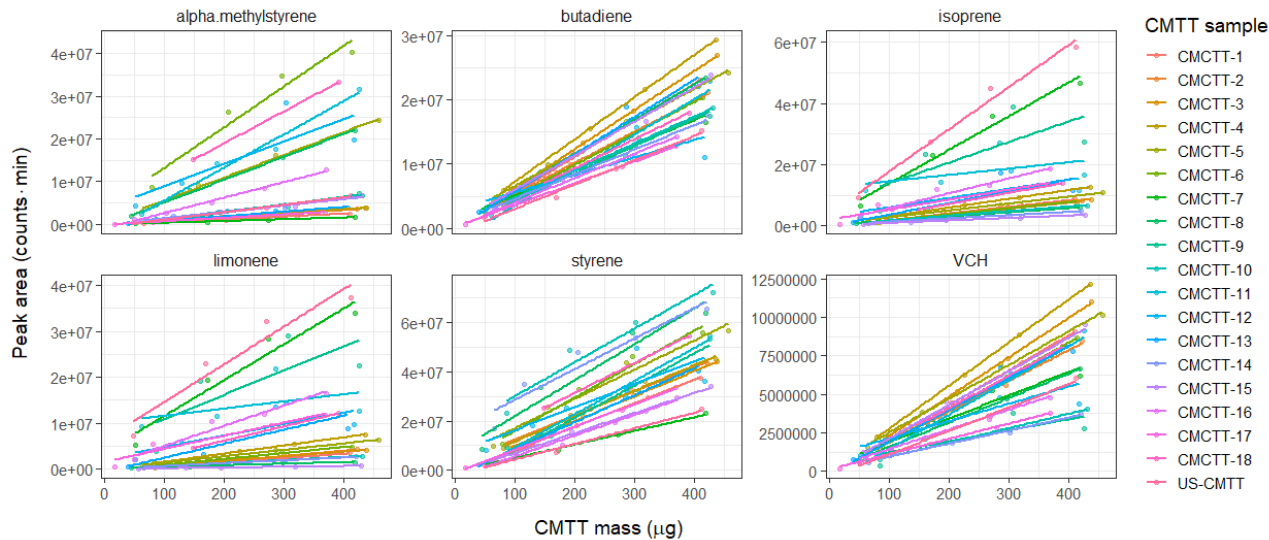
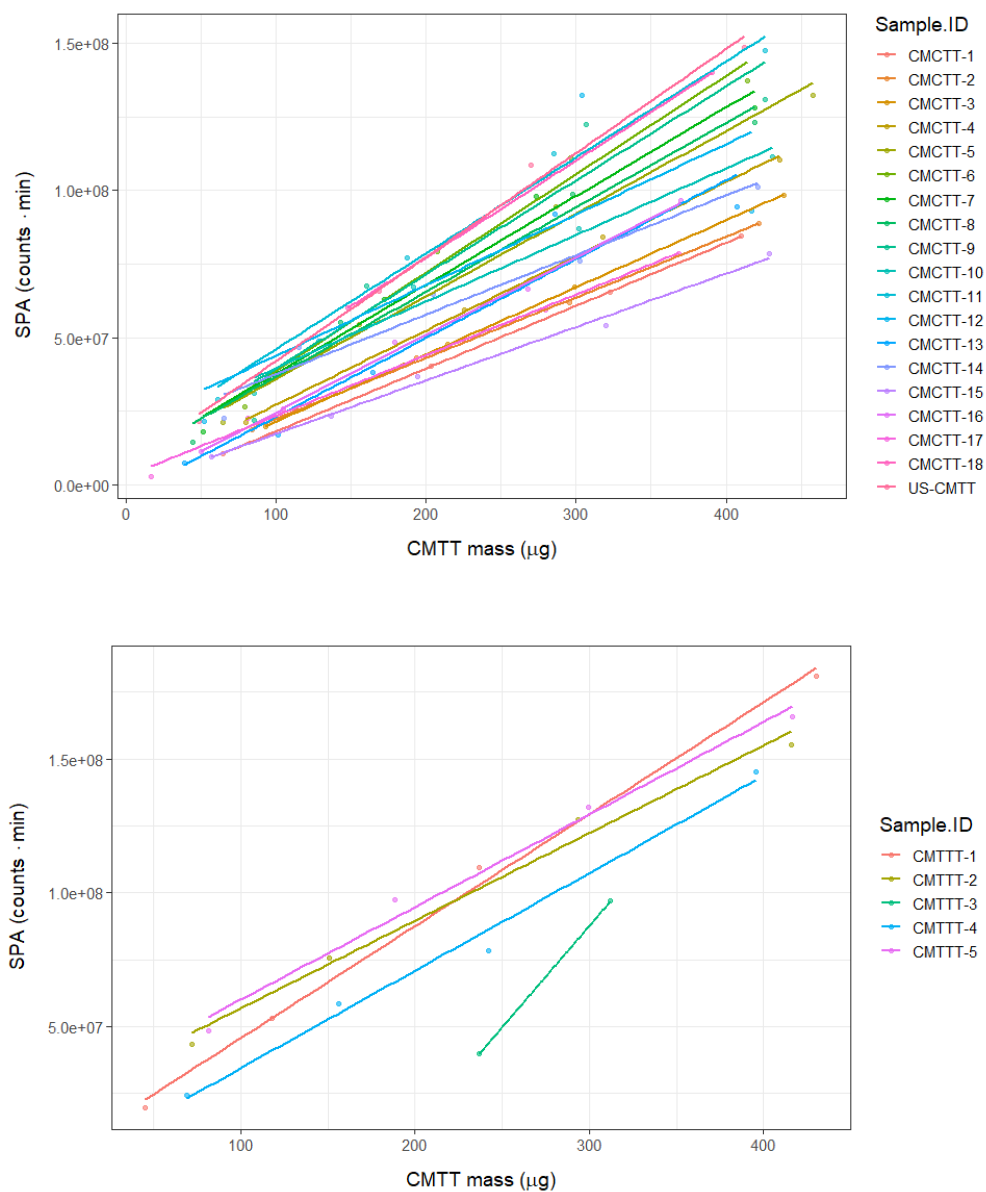


Figure S10. Measured peak areas for the six pyrolysis markers against the mass of CMTT from passenger car tires and the US-CMTT mixture (top) and from truck tires (bottom). Note that for CMTTT-3 only measurements for two sample masses are available. Coefficients of determination (r^2) were mostly > 0.90 .

Marker	Car	Truck/Bus	All
VCH	0.70	0.34	0.61
α -methylstyrene	0.20	0.23	0.17
butadiene	0.86	0.31	0.71
isoprene	0.19	0.57	0.13
limonene	0.13	0.56	0.12
styrene	0.67	0.13	0.49

Table S2: The coefficients of determination (r^2) from linear regressions of the six pyrolysis markers against the mass of all CMTT samples from used tires and against the CMTT mass from used tires separated by vehicle category.

S12 Sum of peak area (SPA) vs. mass of CMTT



205 **Figure S11.** Dependence of the sum of peak areas (SPA) of all six pyrolysis markers and the mass of cryo-milled tire tread CMTT from passenger car tires and the US-CMTT mixture (top) and from truck tires (bottom). Note that for CMTTT-3 only measurements for two sample masses are available. All coefficients of determination were $r^2 > 0.90$ with the only exception of CMCTT-12 $r^2 = 0.66$.

Linear regression analysis of CMCTT-6						
Calibration measurements						
Marker	CMTT	$a'_{i,c}$	$p\text{-value } a'_{i,c}$	$b_{i,c}$	$p\text{-value } b_{i,c}$	r^2
Butadiene	CMCTT-6	49097	0.000	42490	0.837	1.000
Isoprene	CMCTT-6	19781	0.004	-338229	0.432	0.992
Limonene	CMCTT-6	12953	0.012	-438368	0.392	0.975
Styrene	CMCTT-6	136072	0.014	2360051	0.656	0.972
VCH	CMCTT-6	21550	0.000	-263429	0.002	1.000
α -Methylstyrene	CMCTT-6	95237	0.026	3705556	0.485	0.948
External control 1 (on day of analysis of samples DUET A and DUE A)						
Marker	CMTT	$a'_{i,s}$	$p\text{-value } a'_{i,s}$	$b_{i,s}$	$p\text{-value } b_{i,s}$	r^2
Butadiene	CMCTT-6	31852	0.000	1276718	0.084	0.971
Isoprene	CMCTT-6	7592	0.001	106914	0.613	0.940
Limonene	CMCTT-6	9599	0.001	-6399	0.978	0.952
Styrene	CMCTT-6	97276	0.005	7885991	0.087	0.890
VCH	CMCTT-6	17963	0.000	307649	0.221	0.987
α -Methylstyrene	CMCTT-6	73334	0.007	7384544	0.063	0.871
External control 2 (on day of analysis of samples DUET B and DUE B)						
Marker	CMTT	$a'_{i,s}$	$p\text{-value } a'_{i,s}$	$b_{i,s}$	$p\text{-value } b_{i,s}$	r^2
Butadiene	CMCTT-6	117674	0.000	266388	0.586	0.999
Isoprene	CMCTT-6	21520	0.038	734028	0.501	0.926
Limonene	CMCTT-6	22293	0.026	449417	0.616	0.949
Styrene	CMCTT-6	230321	0.026	7227745	0.459	0.948
VCH	CMCTT-6	52023	0.000	-234536	0.308	0.999
α -Methylstyrene	CMCTT-6	155424	0.050	9626703	0.329	0.903

Table S3. Slopes $a'_{i,c}$, and $a'_{i,s}$, as well as the intercept $b_{i,c}$ and $b_{i,s}$ as well as the corresponding p-values, and coefficient of determination (r^2) for the linear regressions of measurements of CMCTT-6 for method calibration and as external controls with the measurement of the atmospheric deposition samples DUET A, DUE A, DUET B, and DUE B.

215

S14 Principal component analysis of CMTT sample data

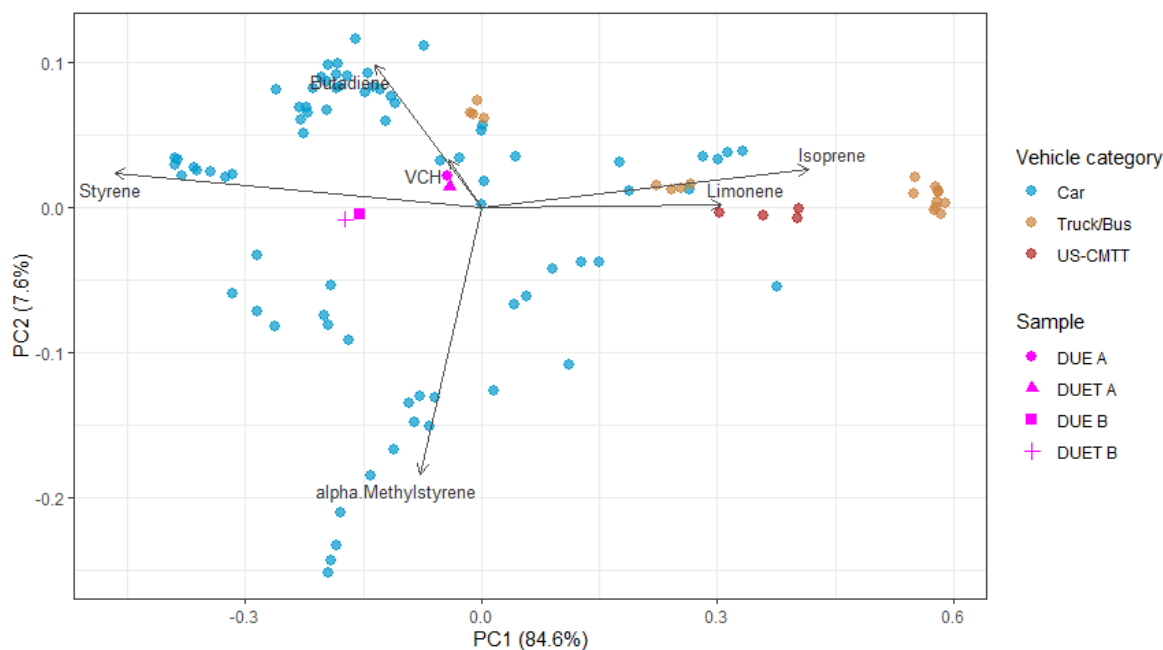


Figure S12. Same as Figure S9 except that the CMTT samples are grouped by vehicle category. In addition, the scores of the atmospheric deposition samples are shown.