Supporting Information

Chlorinated Paraffins in Car Tires recycled to Rubber Granulates and Playground Tiles

Brandsma, Sicco H.[1]*, Brits, Martin [1,2,3], Groenewoud, Quinn R.[1], van Velzen, Martin J.M.[1],

Leonards, Pim E.G.[1], De Boer, Jacob [1]

[1]Vrije Universiteit, Dept. Environment and Health, De Boelelaan 1085, 1081 HV, Amsterdam, the Netherlands, [2]National Metrology Institute of South Africa (NMISA), CSIR Campus, Meiring Naude Road, Pretoria 0040, South Africa, [3]Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, Lynnwood Road, Pretoria 0002, South Africa

*Corresponding author. +31 20 5989566; fax: +31 20 5989553; e-mail:sicco.brandsma@vu.nl

Solvents, standards and materials

The following eight commercial available CP standard mixtures were used for the deconvolution of the SCCP, MCCP and LCCP pattern in the rubber samples;

• Chlorinated paraffin C10-C13 51.5%Cl (SCCP 51.5%Cl)

• Chlorinated paraffin C10-C13 55.5%Cl (SCCP 55.5%Cl)

• Chlorinated paraffin C10-C13 63% Cl (SCCP 63%Cl)

• Chlorinated paraffin C14-C17 42% Cl (MCCP 42%Cl)

• Chlorinated paraffin C14-C17 52% Cl (MCCP 52%Cl)

• Chlorinated paraffin C14-C17 57% Cl (MCCP 57%Cl)

• Chlorinated paraffin C18-C20 36% Cl (LCCP 36%Cl)

• Chlorinated paraffin C18-C20 49% Cl (LCCP 49%Cl)

The concentration of the eight commercial CP standard mixtures was 100 ng/μL and purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All solvents and chemicals used were HPLC analysis grade. N-hexane, acetone, and dichloromethane (DCM) from Promochem (Wesel, Germany) and toluene from VWR Chemicals , acetonitrile (ACN) from Biosolve (Valkenswaard, The Netherlands). were used for cleaning, extraction cleanup and analysis. $^{13}C_{10}$-dechlorane plus was used as injection standard and was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Silicagel (70-230 μm) and sodium sulphate (99%) and sulfuric acid (95-97%) was also purchased from Sigma Aldrich (Zwijndrecht , The Netherlands).

Table S1. Information (brand, year and country) of the car tires and playground tiles analyzed in this study.

Sample code	Brand	Year	Country
CT1	Continental	2010	France
CT2	Kumho	2012	China
CT3	Continental	2012	Portugal
CT4	Dunlop	2014	Germany
CT5	Pirelli	2008	Turkey
CT6	Pirelli	2014	Brazil
CT7	Michelin	2006	Spain
CT8	Continental	2012	Romania
CT9	Goodyear	2011	Slovenia
CT10	Continental	2013	Czech

Sample code	Year purchased	Country
PGT1	2018	The Netherlands
PGT2	2018	The Netherlands
PGT3	2018	The Netherlands
PGT4	2018	The Netherlands
PGT5	2018	The Netherlands
PGT6	2018	Spain

Table S2. Instrumental parameters LC-APCI-qTOF-MS.

Instrument setting	Value
Ionisation source	APCI, negative mode
Eluent	Dichloromethane (10%, v/v) in acetonitrile
Run time	4 min
Isocratic flow	250 µL/min
Vaporizer temperature	300°C
Dry temperature	200°C
Ion energy	5.0 eV
Collision energy (CE)	2.0 eV
MS scan range	100-2000 m/z
End plate offset	500 V
Capillary	1000 V
Corona	6000 nA
Nebulizer (N_2)	2.0 L/min
Dry Gas	2.0 L/min

Table S3. Results of the spike experiments of the car tires (CT), rubber granulates (RG) and playground tiles (PGT).

	Amount spike ng	Measured spike ng	Recovery SCCPs	R^2	Amount spike ng	Measured spike ng	Recovery MCCPs	R^2	Amount spike ng	Measured spike ng	Recovery LCCPs	R^2
RG7	143	214	150%	0.97	700	849	121%	0.97	134	156	116%	0.99
RG6	143	151	106%	0.99	700	571	82%	0.98	134	91	68%	1.00
RG2	143	135	94%	0.93	700	589	84%	0.98	134	103	77%	1.00
PGT2	143	182	127%	0.99	700	705	101%	0.98	134	129	96%	1.00
PGT6	143	201	141%	0.81	700	797	114%	0.96	134	101	75%	0.99
PGT4	143	215	150%	0.99	700	925	132%	0.97	134	178	132%	1.00
CT8	143	210	147%	0.99	700	909	130%	0.96	134	202	151%	1.00
CT9	143	173	121%	0.99	700	682	97%	0.96	134	138	103%	1.00
CT5	143	181	127%	0.99	700	664	95%	0.97	134	133	99%	1.00
		Mean	129%			Mean	106%			Mean	102%	
		RSD	15%			RSD	18%			RSD	27%	

Table S4. CP levels in μg/g in the NIST SRM2585.

	∑SCCPs (μg/g)	R^2	%Cl	∑MCCPs (μg/g)	R^2	%Cl	∑LCCPs (μg/g)	R^2	%Cl
SRM1	7.4	0.90	59.2%	9.9	0.77	52.0%	17	0.01	42.5%
SRM2	7.0	0.90	59.2%	9.6	0.77	51.9%	16	0.01	42.6%
SRM3	7.0	0.99	59.2%	9.5	0.59	51.9%	16	0.01	42.6%
Mean	7.1			9.7			16		
Stdev	0.2			0.2			0.4		

Table S5. Concentrations in µg/g for the SCCPs, MCCPs and LCCPs and percentage contribution of the congener carbon chain lengths. Goodness of fit (R^2) below 0.5 are given in highlighted red with indicate that the reported values is tentative.

	C10 (%)	C11 (%)	C12 (%)	C13 (%)	∑SCCPs (µg/g)	R^2	C14 (%)	C15 (%)	C16 (%)	C17 (%)	∑MCCPs (µg/g)	R^2
RG1	7%	25%	33%	35%	4.8	**0.6**	45%	27%	17%	11%	45%	**0.8**
RG2	6%	23%	33%	37%	9.1	**0.2**	39%	33%	18%	10%	39%	**0.8**
RG3	7%	18%	31%	44%	2.2	**0.8**	46%	24%	18%	13%	46%	**0.9**
RG4.1	10%	33%	34%	22%	7.2	**0.1**	48%	27%	14%	10%	48%	**0.9**
RG4.2	10%	28%	30%	31%	6.1	**0.3**	44%	25%	17%	14%	44%	**0.9**
RG5	5%	20%	28%	47%	2.1	**0.8**	41%	23%	18%	17%	41%	**0.8**
RG6	6%	20%	26%	48%	2.3	**0.8**	39%	24%	20%	17%	39%	**0.7**
RG7	6%	20%	29%	46%	6.2	**0.8**	41%	25%	19%	14%	41%	**0.8**
RG8	6%	17%	22%	55%	7.8	**0.7**	40%	27%	18%	15%	40%	**0.8**
RG9	6%	21%	25%	48%	2.7	**0.8**	37%	27%	21%	16%	37%	**0.7**
PGT1	6%	18%	32%	44%	1.9	**0.8**	43%	25%	18%	14%	43%	**0.8**
PGT2	12%	31%	11%	46%	2.6	**0.6**	47%	27%	15%	11%	47%	**0.9**
PGT3	2%	14%	24%	60%	4.8	**0.7**	55%	24%	11%	9%	55%	**1.0**
PGT4	5%	24%	27%	45%	4.7	**0.8**	50%	25%	14%	11%	50%	**0.9**
PGT5.1	4%	18%	23%	55%	6.3	**0.5**	53%	26%	13%	9%	53%	**1.0**
PGT5.2	2%	8%	11%	79%	6.5	**0.4**	55%	27%	11%	6%	55%	**1.0**
PGT6	12%	21%	24%	43%	25	**0.8**	46%	23%	15%	16%	46%	**0.9**
CT1	15%	31%	28%	26%	0.8	**0.8**	45%	28%	17%	10%	45%	**0.9**
CT2.1	20%	36%	16%	28%	0.4	**0.5**	49%	30%	13%	8%	49%	**0.9**
CT2.2	19%	34%	21%	26%	0.5	**0.6**	38%	34%	19%	8%	38%	**0.8**
CT3	10%	30%	26%	34%	<0.2	**0.8**	44%	28%	18%	10%	44%	**0.8**
CT4	14%	26%	27%	32%	<0.2	**0.8**	45%	27%	18%	10%	45%	**0.9**
CT5	12%	24%	28%	35%	0.7	**0.8**	38%	29%	19%	14%	38%	**0.8**
CT6	16%	29%	23%	32%	0.3	**0.6**	42%	19%	19%	21%	42%	**0.8**
CT7	7%	26%	32%	35%	1.8	**0.8**	39%	32%	19%	10%	39%	**0.8**
CT8	4%	26%	28%	41%	0.6	**0.8**	39%	29%	19%	12%	39%	**0.8**
CT9	26%	26%	21%	27%	0.6	**0.4**	49%	28%	15%	9%	49%	**0.9**
CT10	0%	32%	35%	33%	0.3	**0.9**	41%	30%	19%	10%	41%	**0.8**

	C18 (%)	C19 (%)	C20 (%)	C21 (%)	C22 (%)	C23 (%)	C24 (%)	C25 (%)	C26 (%)	C27 (%)	C28 (%)	C29 (%)	C30 (%)	∑LCCPs	R^2
RG1	35%	14%	4%	4%	5%	7%	2%	8%	7%	6%	3%	4%	1%	35%	**0.8**
RG2	38%	13%	4%	3%	4%	6%	2%	8%	7%	6%	4%	2%	2%	38%	**0.8**
RG3	67%	18%	6%	0%	0%	2%	2%	3%	1%	2%	0%	0%	0%	67%	**0.9**
RG4.1	39%	8%	4%	3%	3%	6%	1%	9%	11%	8%	3%	2%	1%	39%	**0.6**
RG4.2	46%	15%	3%	1%	2%	5%	0%	7%	6%	5%	2%	4%	3%	46%	**0.7**
RG5	67%	21%	7%	1%	2%	2%	0%	0%	0%	1%	0%	0%	0%	67%	**1.0**
RG6	46%	13%	5%	2%	2%	6%	0%	7%	7%	5%	4%	2%	1%	46%	**0.9**
RG7	50%	18%	6%	2%	3%	5%	1%	4%	4%	3%	1%	2%	1%	50%	**1.0**
RG8	65%	22%	6%	2%	2%	1%	0%	1%	1%	0%	0%	0%	0%	65%	**0.9**
RG9	60%	23%	7%	3%	2%	1%	1%	1%	1%	0%	1%	0%	0%	60%	**1.0**
PGT1	67%	26%	6%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	67%	**1.0**
PGT2	25%	7%	3%	1%	3%	7%	2%	11%	10%	12%	11%	6%	0%	25%	**0.5**
PGT3	48%	11%	10%	6%	10%	7%	0%	3%	4%	1%	0%	0%	0%	48%	**0.8**
PGT4	48%	19%	8%	3%	2%	5%	3%	4%	8%	0%	0%	0%	0%	48%	**0.8**
PGT5.1	73%	16%	8%	0%	0%	0%	0%	0%	3%	0%	0%	0%	0%	73%	**0.9**
PGT5.2	79%	12%	0%	0%	0%	0%	0%	2%	3%	0%	4%	0%	0%	79%	**0.9**
PGT6	24%	23%	21%	14%	10%	6%	0%	2%	1%	0%	0%	0%	0%	24%	**0.5**
CT1	70%	16%	9%	5%	0%	0%	0%	0%	0%	0%	0%	0%	0%	70%	**0.9**
CT2.1	44%	18%	16%	16%	0%	6%	0%	0%	0%	0%	0%	0%	0%	44%	**0.7**
CT2.2	15%	12%	15%	16%	18%	11%	1%	6%	5%	0%	0%	0%	0%	15%	**0.2**
CT3	77%	6%	8%	3%	5%	0%	0%	0%	0%	0%	0%	0%	0%	77%	**0.9**
CT4	78%	12%	3%	7%	0%	0%	0%	0%	0%	0%	0%	0%	0%	78%	**0.8**
CT5	56%	24%	6%	3%	4%	2%	1%	2%	1%	0%	1%	0%	0%	56%	**0.9**
CT6	6%	4%	5%	8%	9%	11%	3%	15%	15%	12%	8%	4%	1%	6%	**<0.1**
CT7	58%	25%	8%	2%	2%	1%	0%	1%	1%	1%	0%	0%	0%	58%	**0.8**
CT8	38%	16%	14%	8%	10%	6%	2%	3%	3%	0%	1%	0%	0%	38%	**0.1**
CT9	8%	2%	6%	2%	6%	1%	6%	10%	13%	11%	11%	12%	11%	8%	**<0.1**
CT10	79%	4%	10%	0%	7%	0%	0%	0%	0%	0%	0%	0%	0%	79%	**<0.1**

Table S6. Calculated chlorination degrees for the eight technical CP mixtures.

	Calculated Cl-degree
SCCP (51.5% Cl)	55.2% Cl
SCCP (55.5% Cl)	58.4% Cl
SCCP (63% Cl)	63.4% Cl
MCCP (42% Cl)	48.7% Cl
MCCP (52% Cl)	54.1% Cl
MCCP (57% Cl)	57.4% Cl
LCCP (36% Cl)	41.3% Cl
LCCP (49% Cl)	49.9% Cl

Figure S1. Measured and reconstructed CP pattern in rubber granulate (RG7) for the SCCPs, in the playground tile (PGT4) for the MCCPs and in the car tire (CT5) for the LCCPs. The goodness of fit (R2) of the deconvolution is given in the figure.
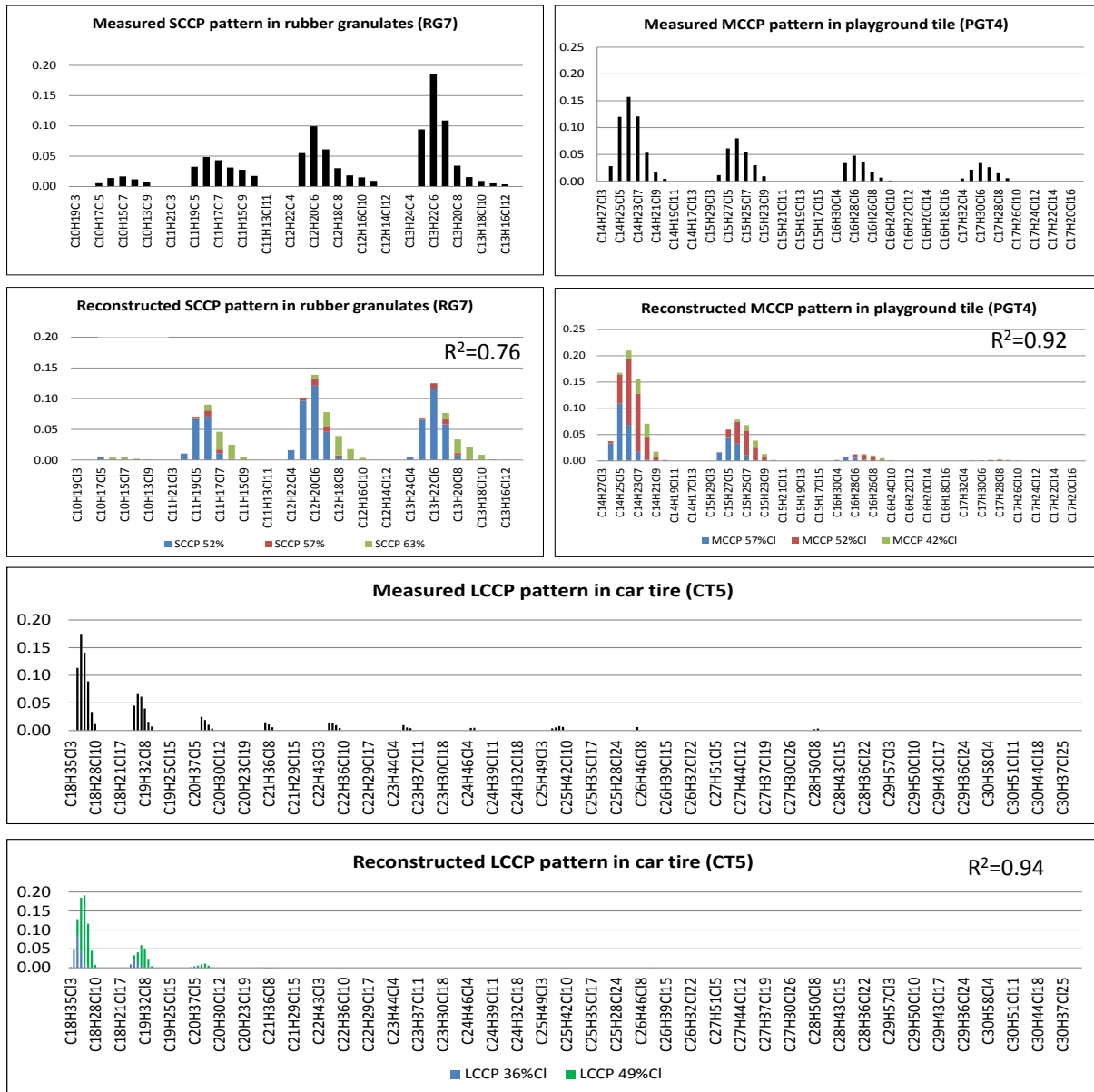
Figure S2. Measured SCCP pattern in playground tile sample PGT6, including the presence of C_9.