Road Runoff characterization: ecotoxicological assessment combined with (non-)target screenings of micropollutants for the identification of relevant toxicants in the dissolved phase

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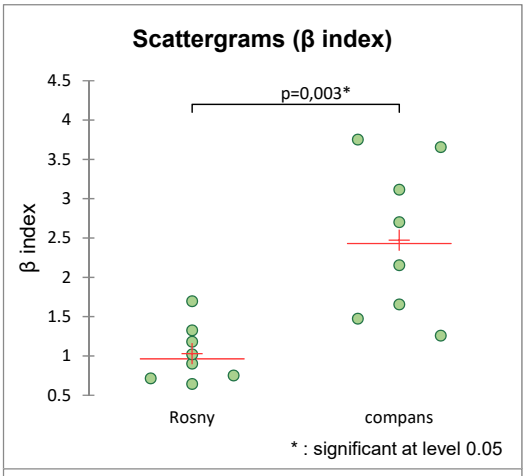
Supplementary material


Scattergrams (β index)
p=0,003*
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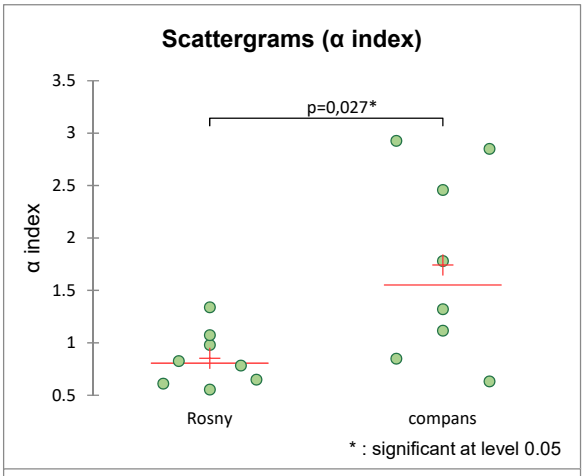
4
3.5
3
2.5
2
1.5
1
0.5
Rosny
compans
* : significant at level 0.05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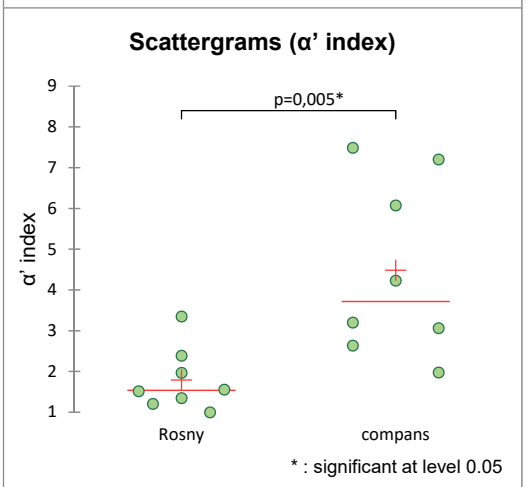
2.5
2
1.5
1
0.5
Rosny
compans
* : significant at level 0.05


Scattergrams (α' index)
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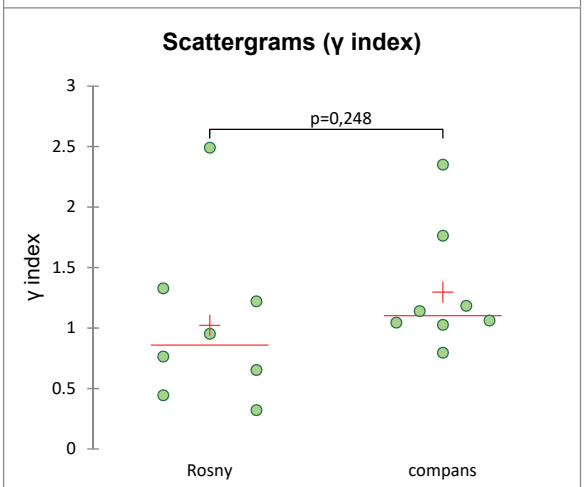
8
7
6
5
4
3
2
1
Rosny
compans
* : significant at level 0.05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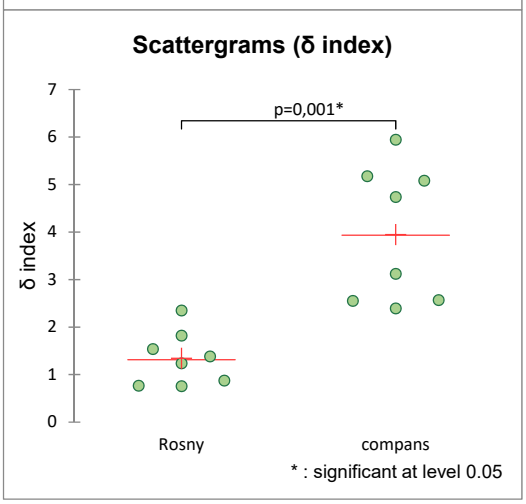
2
1.5
1
0.5
0
Rosny
compans


Scattergrams (δ index)
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δ index
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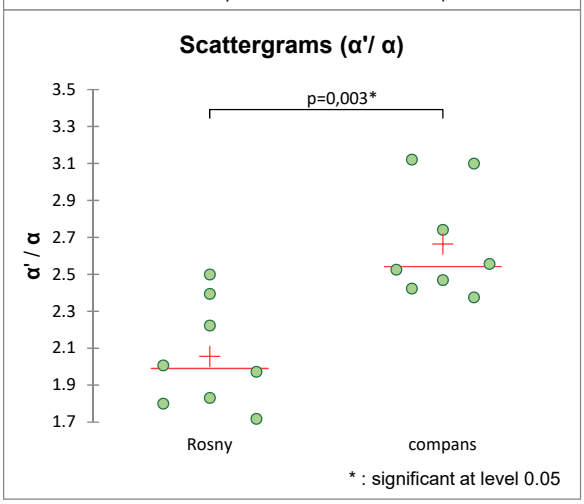
6
5
4
3
2
1
0
Rosny
compans
* : significant at level 0.05


Scattergrams (α'/ α)
p=0,003*
α' / α
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
Rosny
compans
* : significant at level 0.05

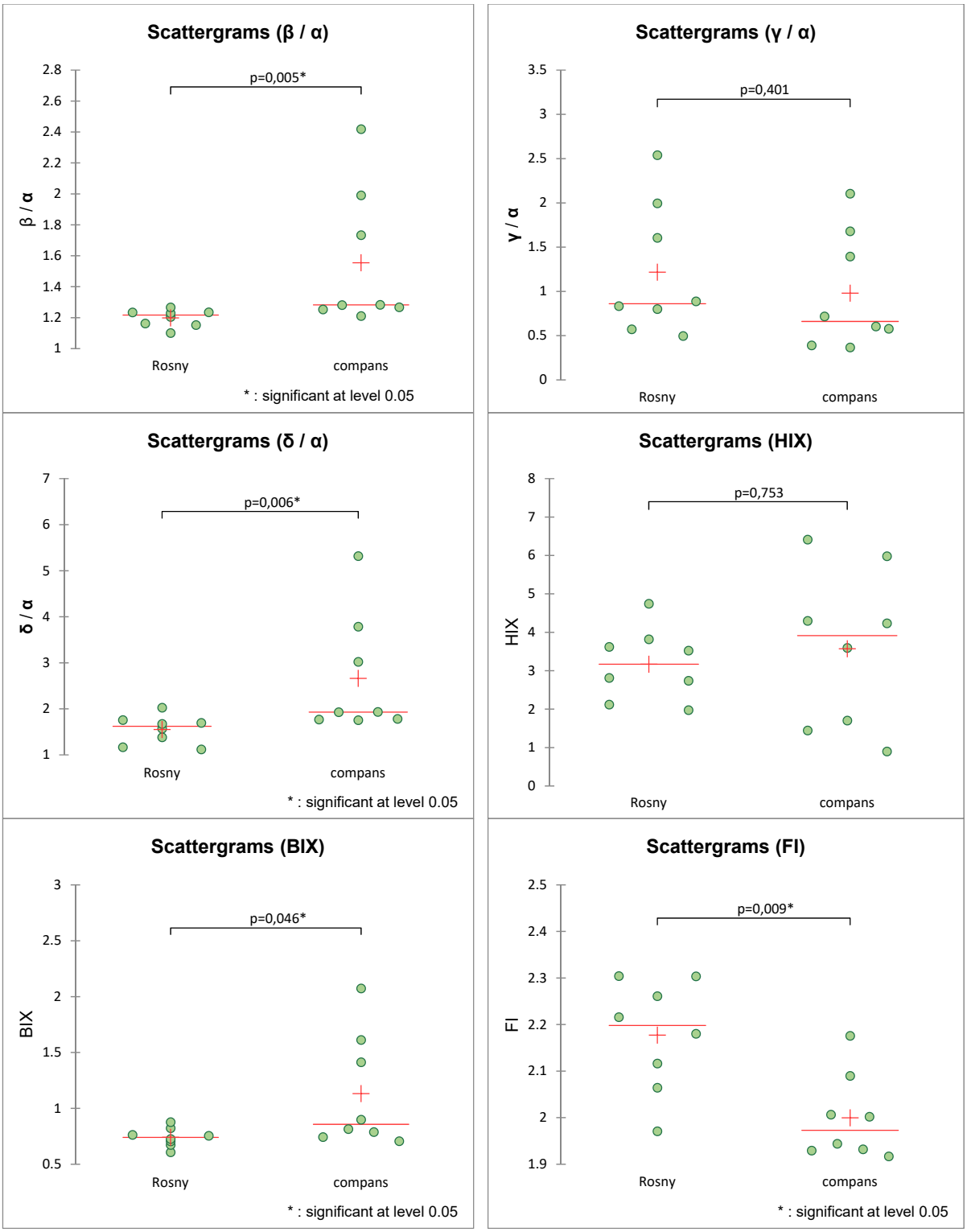


Figure S1. 3D fluorescence indexes for all road runoff samples collected from the two sites. α, α', β indexes related to humic-like components and γ and δ indexes related to protein-like components were obtained at specific pairs of Ex/Em (excitation/emission) wavelengths from measured excitation-emission matrices [44]. HIX = humification index, BIX = biological index, FI = fluorescence index.

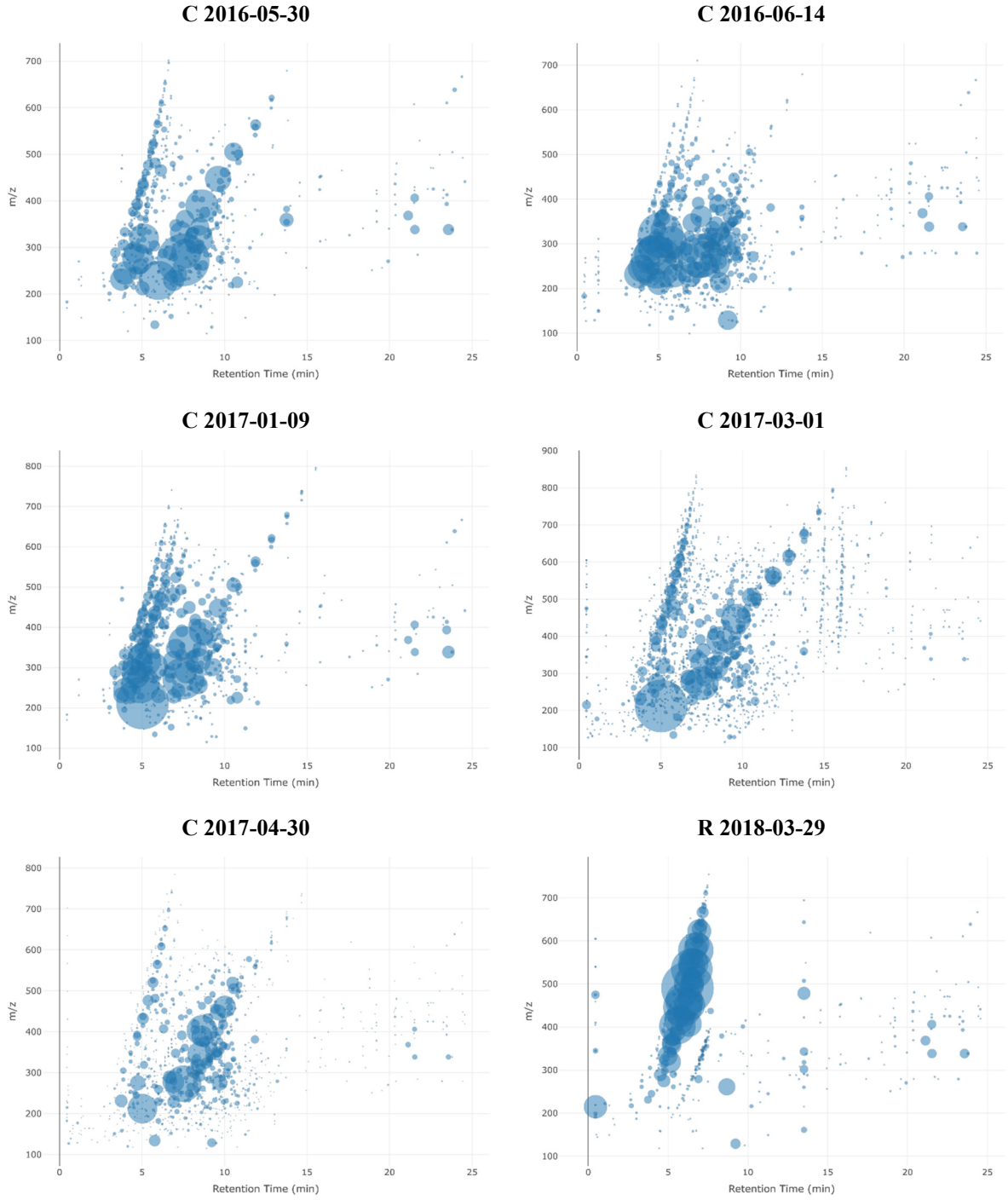


Figure S2. HRMS fingerprints of road runoff samples (C = Compans, R = Rosny-sous-Bois). The size of bubbles is proportional to the intensity of the feature, and intensities are normalized by the highest intensity of each sample (i.e., all fingerprints get the same range of intensities).

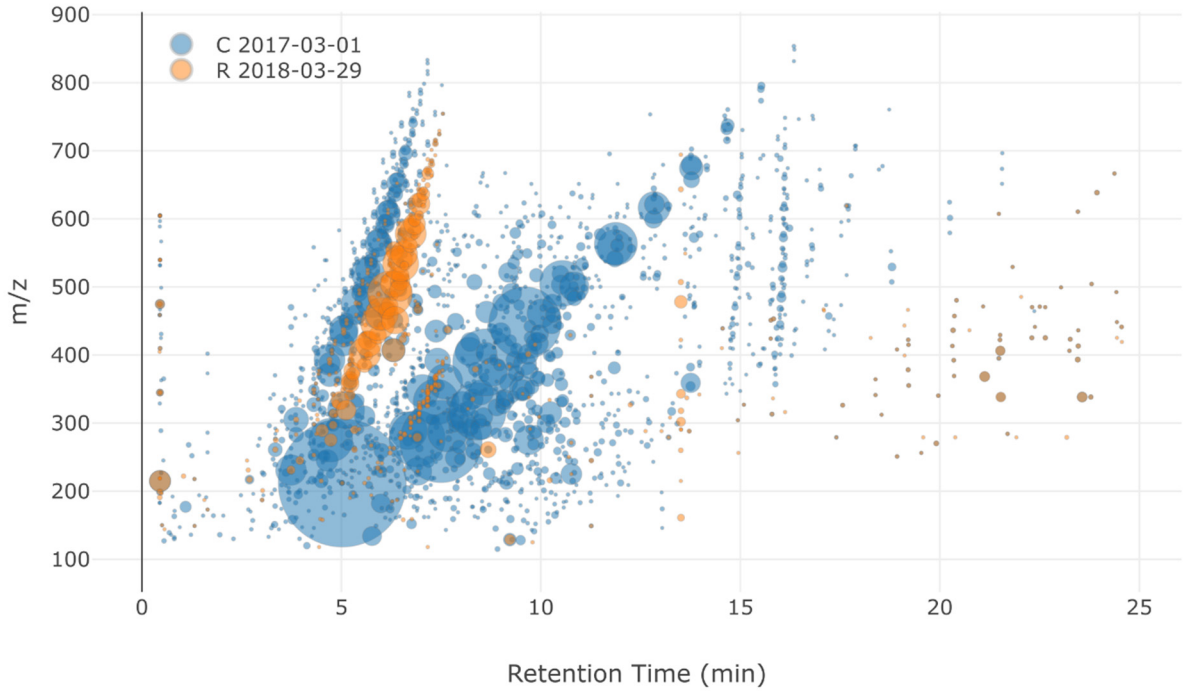


Figure S3. HRMS fingerprints of road runoff samples (C = Compans, R = Rosny-sous-Bois): comparison between C 2017-03-01 and R 2018-03-29 samples. The size of bubbles is proportional to the intensity of the feature.

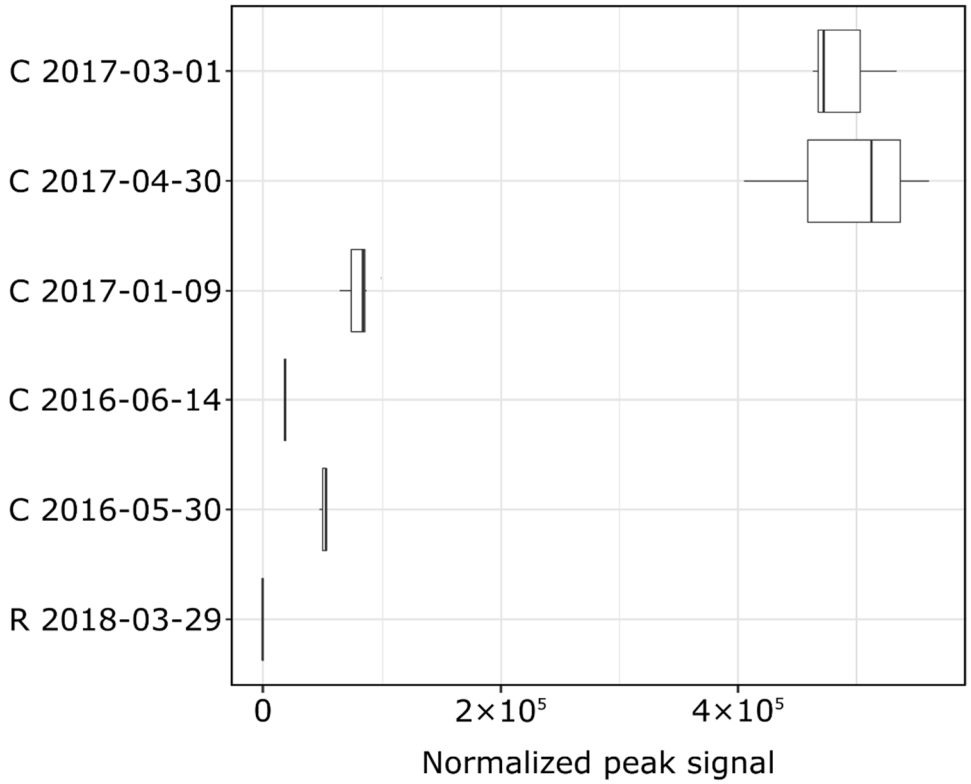


Figure S4. Boxplots representing the intensities of benzotriazole in each sample (triplicate injections in ESI+ mode). C = Compans; R = Rosny.

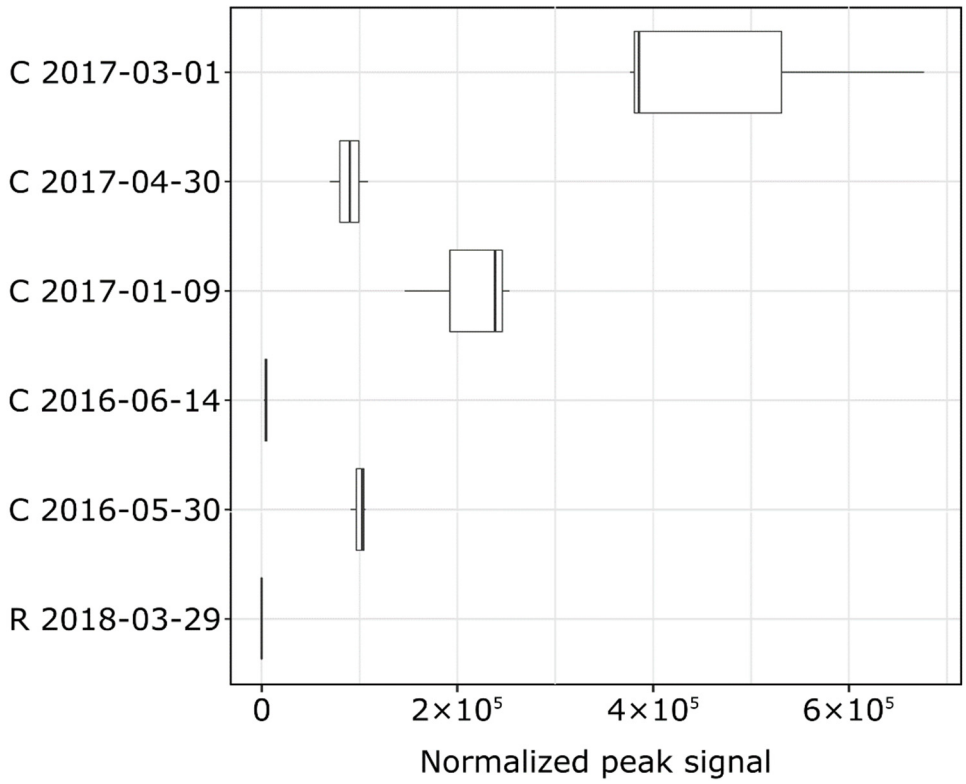


Figure S5. Boxplots representing the intensities of 1,3-benzothiazole-2-sulfonic acid in each sample (triplicate injections in ESI- mode). C = Compans; R = Rosny.

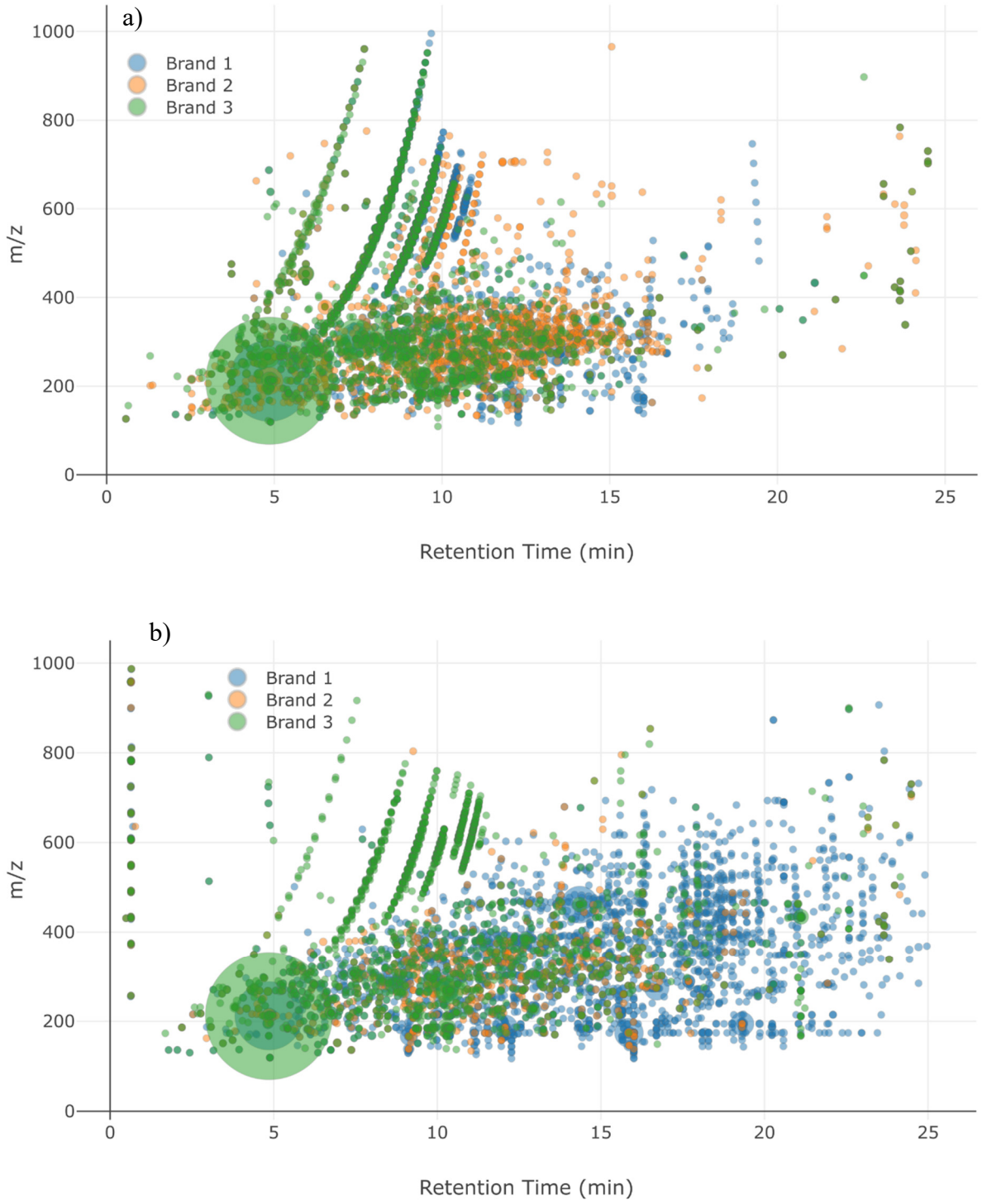


Figure S6. HRMS fingerprints of tire leachates (features with intensity values higher than 6000), obtained with **a**) simulated rainwater and **b**) methanol. The size of bubbles is proportional to the area of the feature.

Table S1. Specific features tentatively identified by non-target screening at each site.

Molecular formula	Adduct	Observed m/z	Observed RT (min)	Observed CCS (Å²)	Mass error (ppm)	I-fit confidence (%) [1]	Possible structure	Site [2]
$C_9H_{19}NO_4S$	-H	236.0963	7.81	158.08	0.5	99.99	-	C
$C_9H_{12}O_3S$	-H	199.0437	6.11	147.55	0.3	99.99	-	C
$C_7H_5NO_3S_2$	-H	213.9642	4.36	139.23	1.7	99.99	1,3-benzothiazole-2-sulfonic acid	C
$C_{12}H_{23}N$	+H	182.1897	5.98	142.21	-3.3	99.99	Dicyclohexylamine	C
$C_{13}H_{13}N_3$	+H	212.1178	5.02	143.5	-1.4	99.99	1,3-diphenylguanidine	C
$C_{14}H_{26}N_2O_2$	+H	277.1904	6.89	164.2	-2.5	99.94	4-[(2,2-Dimethylpropanoyl)amino]-N,N-diethylbenzamide	C
$C_{12}H_{26}O_5$	+Na	273.1667	7.43	153.41	-2.2	99.91	Tetrapropylene glycol	C
$C_{12}H_{24}O_6$	+Na	287.146	7.65	155.82	-1.9	99.59	(18-Crown-6) (no fragments)	C
$C_{14}H_{30}O_8$	+Na	349.1827	4.31	162.93	-2	97.21	Heptaethylene glycol	C
$C_{16}H_{34}O_9$	+Na	393.2093	4.70	172.47	-0.7	97.52	Octaethylene glycol	C
$C_{18}H_{38}O_{10}$	+Na	437.2353	5.05	182.48	-0.3	99.22	Nonaeethylene glycol	C
$C_{20}H_{42}O_{11}$	+Na	481.2616	5.37	191.95	-0.7	90.97	Decaethylene glycol	C
$C_{22}H_{46}O_{12}$	+Na	525.2876	5.66	203.20	-1	99.65	Undecaethylene glycol	C
$C_{24}H_{50}O_{13}$	+Na	569.3139	5.92	213.33	-0.9	95.33	Dodecaethylene glycol	C
$C_{26}H_{54}O_{14}$	+Na	613.3405	6.17	223.38	-0.1	95.23	PEG13	C
$C_{28}H_{58}O_{15}$	+Na	657.3668	6.39	233.01	0.1	99.59	PEG14	C
$C_{30}H_{62}O_{16}$	+Na	701.3935	6.59	243.83	0.9	0.61	PEG15	C
$C_{32}H_{66}O_{17}$	+Na	745.4206	6.79	253.21	1.9	0	PEG16	C
$C_{13}H_{31}N_5O_4$	+Na	344.2275	4.31	170.46	2.1	86.13	-	C
$C_{15}H_{35}N_5O_5$	+Na	388.2538	4.70	179.11	2.2	87.16	-	C
$C_{17}H_{39}N_5O_6$	+Na	432.2801	5.05	188.00	2.1	94.85	-	C
$C_{19}H_{43}N_5O_7$	+Na	476.3061	5.37	197.14	1.5	99.43	-	C

$C_{21}H_{47}N_5O_8$	+Na	520.3324	5.66	205.99	1.5	95.87	-	C
$C_{23}H_{51}N_5O_9$	+Na	564.3585	5.92	215.25	1.1	97.83	-	C
$C_{25}H_{55}N_5O_{10}$	+Na	608.3851	6.16	225.5	1.6	55.14	-	C
$C_{27}H_{59}N_5O_{11}$	+Na	652.4115	6.39	235.04	1.9	78.51	-	C
$C_{29}H_{63}N_5O_{12}$	+Na	696.4379	6.59	246.28	2.1	91.27	-	C
$C_{31}H_{67}N_5O_{13}$	+Na	740.4649	6.79	255.73	-0.5	NA (formula not proposed)	-	C
$C_{33}H_{71}N_5O_{14}$	+Na	784.4906	6.97	265.71	2.1	0.08	-	C
-	+Na	563.3766	11.80	218.06	-	-	-	C
$C_{28}H_{59}FN_4O_8$	+Na	621.4189	12.80	231.15	-3.3	97.2	-	C
-	+Na	679.4607	13.78	245.63	-	-	-	C
-	+Na	737.5031	14.70	260.70	-	-	-	C
-	+Na	795.5445	15.57	273.57	-	-	-	C
$C_{17}H_{36}N_4O_3$	+Na	367.2685	8.60	178.70	1.5	78.46	-	C
$C_{20}H_{42}N_4O_4$	+Na	425.3106	9.71	192.36	1.9	34.5	-	C
$C_{23}H_{48}N_4O_5$	+Na	483.3525	10.82	205.17	1.7	3.3	-	C
$C_{22}H_{50}F_4N_8O$ ($C_{26}H_{54}N_4O_6$)	+Na	541.3947	11.85	217.17	2.2	86.1	-	C
$C_{29}H_{60}N_4O_7$	+Na	599.4369	12.81	230.30	2.5	0.9	-	C
-	+Na	657.4789	13.77	244.12	-	-	-	C
$C_6H_9F_3O_3$	+H	187.0568	1.57	124.71	-4.4	96.29	Ethyl 4,4,4-trifluoro-3-hydroxybutanoate	R
$C_{12}H_{24}F_2O_2$	+Na	261.1635	5.34	153.73	-0.74	99.99	1-(2,2-Difluoroethoxy)-	R

							3-decanol	
$C_{22}H_{46}N_4O_8$	+Na	517.3219	6.49	209.37	2.3	51.21	-	R
$C_9H_{20}O_5$	+Na	213.12	3.75	138.49	-1.2	99.99	Tetraethylene Glycol Monomethyl Ether	R
$C_{11}H_{24}O_6$	+Na	275.1462	4.32	146.51	-1.3	99.99	Pentaethylene Glycol Monomethyl Ether	R
$C_{13}H_{28}O_7$	+Na	319.1725	4.80	154.71	-0.6	99.92	Hexaethylene Glycol Monomethyl Ether	R
$C_{15}H_{32}O_8$	+Na	363.1984	5.23	164.85	-1.5	99.56	Heptaethylene Glycol Monomethyl Ether	R
$C_{17}H_{36}O_9$	+Na	407.2250	5.59	174.78	-0.4	98.38	Octaethylene Glycol Monomethyl Ether	R
$C_{19}H_{40}O_{10}$	+Na	451.2516	5.93	186.25	0.6	97.00	Nonaethylene Glycol Monomethyl Ether	R
$C_{21}H_{44}O_{11}$	+Na	495.2775	6.23	198.07	-0.8	97.78	Decaethylene Glycol Monomethyl Ether	R
$C_{23}H_{48}O_{12}$	+Na	539.3038	6.49	209.20	-0.1	32.84	Undecaethylene Glycol Monomethyl Ether	R
$C_{25}H_{52}O_{13}$	+Na	583.3295	6.74	218.75	-0.9	94.11	Dodecaethylene Glycol Monomethyl Ether	R
$C_{27}H_{56}O_{14}$	+Na	627.3566	6.96	228.69	0.6	93.44	mPEG13-OH	R
$C_{29}H_{60}O_{15}$	+Na	671.3830	7.17	238.75	0.8	0.1	mPEG14-OH	R
$C_{31}H_{64}O_{16}$	+Na	715.4092	7.36	249.55	1.6	0.8	mPEG15-OH	R
$C_{10}H_{20}N_4O_3$	+Na	267.1433	4.39	148.82	2.5	94.2	-	R
$C_{12}H_{24}N_4O_4$	+Na	311.1696	4.89	158.71	2.1	79.7	-	R
$C_{14}H_{28}N_4O_5$	+Na	355.1956	5.31	165.48	1.2	96.7	-	R
$C_{16}H_{32}N_4O_6$	+Na	399.2223	5.69	176.04	1.9	78.7	-	R
$C_{18}H_{36}N_4O_7$	+Na	443.2486	6.03	188.4	2.4	69.0	-	R
$C_{20}H_{40}N_4O_8$	+Na	487.2746	6.32	199.76	1.8	96.6	-	R

$C_{22}H_{44}N_4O_9$	+Na	531.3012	6.59	209.36	2.2	90.9	-	R
$C_{24}H_{48}N_4O_{10}$	+Na	575.3276	6.84	218.72	2.5	40.9	-	R
$C_{26}H_{52}N_4O_{11}$	+Na	619.3533	7.06	228.16	-2.8	32.2	-	R
$C_{10}H_{25}N_5O_2$	+Na	270.1907	4.32	154.65	2.5	99.99	-	R
$C_{12}H_{29}N_5O_3$	+Na	314.2170	4.81	163.3	2.4	98.65	-	R
$C_{14}H_{33}N_5O_4$	+Na	358.2430	5.20	173.24	1.7	93.3	-	R
$C_{16}H_{35}N_5O_5$	+Na	402.2696	5.60	181.29	2.4	58.5	-	R
$C_{18}H_{41}N_5O_6$	+Na	446.2963	5.93	191.06	3.3	42.48	-	R
$C_{20}H_{45}N_5O_7$	+Na	490.3321	6.23	200.39	2.1	79.17	-	R
$C_{22}H_{49}N_5O_8$	+Na	534.3485	6.49	210.52	2.2	66.4	-	R
$C_{24}H_{53}N_5O_9$	+Na	578.3743	6.74	220.73	1.4	59.01	-	R
$C_{26}H_{57}N_5O_{10}$	+Na	622.4012	6.96	231.44	2.3	22.6	-	R
$C_{28}H_{61}N_5O_{11}$	+Na	666.4274	7.17	241.66	2.2	97.4	-	R
$C_{30}H_{65}N_5O_{12}$	+Na	710.4535	7.36	252.33	1.9	1.6	-	R

[1] *The I-fit confidence percentage is a score giving the confidence of the proposed formula regarding isotopes measured for the feature.*
[2] *C: Compans, R: Rosny.*

Table S2. Features tentatively identified by non-target screening in the tire leachates

Molecular formula	Adduct	Observed m/z	Observed RT (min)	Observed CCS (Å²)	Mass error (ppm)	I-fit confidence (%) [1]	Possible structure	Also detected in site C
$C_{13}H_{13}N_3$	+H	212.1178	5.02	143.50	-1.4	99.99	1,3-diphenylguanidine	x
$C_{18}H_{24}N_2$	+H	269.2001	10.37	219.83	-4.1	97.42	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	x
$C_{12}H_{15}N$	+H	174.1271	12.28	170.54	-3.5	99.99	2-Phenylhexanenitrile	
$C_{13}H_{12}N_2O$	+H	213.1015	9.34	186.56	-2.5	99.40	4-[(2-Phenylhydrazono)methyl]phenol	x
$C_{13}H_{19}N_3$	+H	218.1645	6.72	192.91	-3.2	99.55	4-(4-Cyclopropyl-1-piperazinyl)aniline	x
$C_{13}H_{18}N_2O$	+H	219.1486	10.57	191.49	-2.1	99.92	2-Amino-N-cyclohexylbenzamide	x
$C_{13}H_{10}N_2S$	+H	227.0631	12.98	183.20	-1.2	99.45	2-mercapto-6-methyl-4-phenylnicotinonitrile	x
$C_{18}H_{25}NO$	+H	272.2002	13.54	215.49	-2.6	97.99	(E)-8-(1H-Indol-1-yl)-2,6-dimethyloct-7-en-2-ol	
$C_{19}H_{23}N_3$	+H	294.1956	9.83	222.56	-2.9	99.87	N-Cyclohexyl-N'-(4-(dimethylamino) naphthyl)carbodiimide	x
$C_{19}H_{19}N_3O$	+H	306.1599	7.45	219.82	-2.1	99.98	[2-(1H-Benzimidazol-2-yl)phenyl](1-piperidinyl)methanone	
$C_{19}H_{14}N_2OS_2$	+H	351.0611	14.55	229.08	-1.5	70.30	Ethanone, 2-(1-phenyl-2-benzimidazolylthio)-1-(2-thienyl)-	
$C_{24}H_{27}NO_3$	+H	378.2059	6.47	233.89	-1.2	96.56	-	