Micropollutants in urban runoff from traffic areas: target and non-target screening on four contrasted sites

Johnny Gasperi, Julien Le Roux, Steven Deshayes, Sophie Ayrault, Louise Bordier, Lila Boudahmane, Hélène Budzinski, Emilie Caupos, Nadège Caubrière, Kelsey Flanagan, Martin Guillon, Nina Huynh , Pierre Labadie, Laurent Meffray, Pascale Neveu, Chandirane Partibane, Julien Paupardin, Mohamed Saad, Lucie Varnede and Marie-Christine Gromaire

Supplementary material

Table S1. Pollutants analyzed in runoff

Families	Methods	Individual compounds and abbreviations
INORGANICS 11 major elements	ICP - OES	Aluminum (Al), Barium (Ba), Calcium (Ca), Iron (Fe), Magnesium (Mg), Manganese (Mn), Phosphor (P), Potassium (K), Sodium (Na), Strontium (Sr), Titan (Ti)
15 trace elements	ICP-MS	Antimony (Sb), Silver (Ag), Arsenic (As), Cadmium (Cd), Cesium (Cs), Chromium (Cr), Cobalt (Co), Copper (Cu), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Rubidium (Rb), Selenium (Se), Vanadium (V), Zinc (Zn)
15 rare earth elements +	ICP-MS	Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Thulium (Tm), Erbium (Er), Ytterbium (Yb), Lutecium (Lu)
3 platinoids*		Platinum (Pt), Palladium (Pd), Rhodium (Rh)
HYDROCARBONS 16 PAH (US-EPA) + 2 methyl-PAH + coronene + Total hydrocarbon	GC-MS	Naphthalene (N), 1-methyl-naphtalene (1methyl-N), 2-methyl-naphtalene (2methyl-N), acenaphthylene (Acy), acenaphthene (Acen), fluorene (F), phenanthrene (P), anthracene (A), fluoranthene (Fluo), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(cd)pyrene (IcdP), dibenzo(ah)anthracene (DahA), benzo(ghi)perylene (BghiP), coronene (Cor)
Phthalates 15 compounds	GC-MS	dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DiBP), butylbenzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), di-n-octyl-phthalate (DNOP), di-2-butoxyethyl phthalate (DBEP), dinonyl phtalate (DNP), diisobutyl phthalate (DiBP), dimethoxyethyl phthalate (DMEP), di-n-pentyl phthalate (DnPP), diethoxyethyl phthalate (DEEP), dicyclohexyl phthalate (DCHP), di-4-methyl-2-pentyl phthalate (DMPP), di-n-hexyl phthalate (DNP)
PBDE 10 compounds	GC-MS	BDE 7, BDE 15, BDE 17, BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 209
AP et BPA 7 compounds BPA	LC-MS	Nonylphenols (NP), nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), octylphenol (OP), octylphenol monoethoxylate (OP1EO), octylphenol diethoxylate (OP2EO), nonylphenoxy acetic acid (NP1EC) Bisphenol A (BPA)
PFAS 18 compounds, i.e. - 8 carboxylic acids - 6 sulfonic acids - Sulfamide - 3 fluorotelomere sulfonates	LC-MS	perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoc acid (PFOA), perfluoronoanoic acid (PFNA), perfluorodecanoique acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA) perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluoroheptane sulfonic acid (PFHpS), perfluorooctane sulfonic acid, linear isomer (L-PFOS), perfluorooctane sulfonic acid, sum of branched isomer (Br-PFOS), perfluorodecane sulfonic acid (PFDS) Perfluorooctane sulfonamide (FOSA) 4:2 fluorotelomere sulfonate (4:2 FTSA), 6:2 fluorotelomere sulfonate (6:2 FTSA), 8:2 fluorotelomere sulfonate (8:2 FTSA)
Benzotriazoles* 4 compounds	LC-MSMS	1H-benzotriazole, 4-methyl-1H-benzotriazole, 5-methyl-1H-enzotriazole, 5,6-dimethyl-1H-benzotriazole

Oxygenated ethers* 3 compounds	GC-ECD	Methyl-tert-butyl ether (MTBE), ethyl-tert-butyl ether (ETBE), tert-amyl-methyl ether (TAME)
Organotins* 3 compounds	GC-MS	Tributyltin, dibutyltin, monobutyltin
Others 5 compounds	GC-MSMS CG-ECD LC-MSMS	Tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD), chloroalkanes* (C10-C13)*, benzophenone*, Linear alkylbenzene sulfonate (LAS)*

*These substances were researched in a very exploratory way, on a very small pool of samples.

Table S2. Limit of quantification for inorganic elements - I

Nom	LQ	Uncertainties %
Al	D: 100 µg/l P: 54 µg/g	13.8
Ba	D: 0.2 µg/l P: 0.04 µg/g	6.2
Ca	D: 200 µg/l P: 8 µg/g	8.7
Fe	D: 50 µg/l P: 54 µg/g	10.9
Mg	D: 30 µg/l P: 54 µg/g	9.8
Mn	D: 1 µg/l P: 0.04 µg/g	6.4
Mo	D: 2 µg/l P: 0.02 µg/g	6.1
P	D: 100 µg/l P: 54 µg/g	6.9
K	D: 250 µg/l P: 11 µg/g	7.1
Na	D: 250 µg/l P: 28 µg/g	7.1
Sr	D: 2 µg/l P: 0.18 µg/g	5.7
Ti	D: 1 µg/l P: 0.005 µg/g	10.4

D: Dissolved fraction, P: Particulate fraction

Table S3. Limit of quantification for inorganic elements - II

Nom	LQ	Uncertainties %
Sb	D: 0.005 µg/l P: 0.03 µg/g	ND
Ag	D: 0.004 µg/l P: 0.005 µg/g	ND
As	D: 0.04µg/l P: 0.005 µg/g	13.4
Cd	D: 0.02 µg/l P: 0.005 µg/g	12.8
Cs	D: 0.05 µg/l P: 0.02 µg/g	ND
Cr	D: 0.5 µg/l P: 0.29 µg/g	7.4
Co	D: 2 µg/l P: 0.005 µg/g	7.6
Cu	D: 0.25µg/l P: 0.17 µg/g	17.3
Ni	D: 0.5 µg/l P: 0.005 µg/g	7.8
Pb	D: 0.1µg/l P: 0.02 µg/g	12.3
Rb	D: 0.05 µg/l P: 0.16 µg/g	ND
Se	D: 0.05µg/l P: -	ND
V	D: 0.015µg/l P: 0.14 µg/g	9.1
Zn	D: 1.8 µg/l P: 0.41 µg/g	7.2

D: dissolved fraction, P: Particulate fraction, ND: not determined

Table S4. Limit of quantification for inorganic elements - III

Nom	LQ	Uncertainties %
Y	D: 7.5 ng/l P: 3.10 ng/g	ND
La	D: 8 ng/l P: 0.05 ng/g	ND
Ce	D: 6 ng/l P: 0.05 ng/g	ND
Pr	D: 1 ng/l P: 5.65 ng/g	ND
Nd	D: 4 ng/l P: 7.28 ng/g	ND
Sm	D: 0.5 ng/l P: 5 ng/g	ND
Eu	D: 1 ng/l P: 8.26 ng/g	ND
Gd	D: 2 ng/l P: 8.59 ng/g	ND
Tb	D: 0.2 ng/l P: 4.62 ng/g	ND
Dy	D: 1 ng/l P: 3.26 ng/g	ND
Ho	D: 0.2 ng/l P: 5.11 ng/g	ND
Tm	D: 0.1ng/l P: 3.75 ng/g	ND
Er	D: 0.7 ng/l P: 7.17 ng/g	ND
Yb	D: 0.5 ng/l P: 2.23 ng/g	ND
Lu	D: 0.1 ng/l P: 3.64 ng/g	ND

D: dissolved fraction, P: Particulate fraction, ND: not determined

Table S5. Limit of quantification for organic elements – Total hydrocarbon and PAHs

Nom	LQ	Uncertainties %
HT	T: 0.20 mg/L	40
N	D: 10 ng/l P: -	40
1M-N	D: 10 ng/l P: 152 ng/g	40
2M-N	D: 10 ng/l P: 30 ng/g	40
Acyl	D: 10 ng/l P: 30 ng/g	40
Acen	D: 10 ng/l P: 152 ng/g	40
F	D: 10 ng/l P: 104 ng/g	40
A	D: 10 ng/l P: 130 ng/g	40
Phe	D: 10 ng/l P: 130 ng/g	40
Pyr	D: 10 ng/l P: 130 ng/g	40
Fluo	D: 10 ng/l P: 130 ng/g	40
BaA	D: 10 ng/l P: 130 ng/g	40
Chry	D: 10 ng/l P: 130 ng/g	40
BaP	D: 10 ng/l P: 130 ng/g	40
BkB	D: 10 ng/l P: 130 ng/g	40
BbF	D: 10 ng/l P: 130 ng/g	40
BPer	D: 10 ng/l P: 130 ng/g	40
IP	D: 10 ng/l P: 130 ng/g	40
DahA	D: 10 ng/l P: 159 ng/g	40
Cor	D: 10 ng/l P: 30 ng/g	40

D: dissolved fraction, P: Particulate fraction

Table S6. Limit of quantification for organic elements – PBDE

Nom	LQ	Uncertainties %
BDE 7	D: 0.017 µg/l P: -	ND
BDE 15	D: 0.03 µg/l P: -	ND
BDE 17	D: 0.022 µg/l P: -	ND
BDE 28	D: 0.02 µg/l P: 2.2 µg/g	D: 8 P: 6
BDE 47	D: 0.041 µg/l P: 1 µg/g	D: 3 P: 4
BDE 99	D: 0.059 µg/l P: 1 µg/g	D: 18 P: 9
BDE 100	D: 0.046 µg/l P: 2.1 µg/g	D: 13 P: 4
BDE 153	D: 0.243 µg/l P: 1.9 µg/g	D: 19 P: 15
BDE 154	D: 0.09 µg/l P: 1.3 µg/g	D: 22 P: 9
BDE 209	D: - µg/l P: 403 µg/g	D: 4 P: 9

D: dissolved fraction, P: Particulate fraction, ND: non deterimined

Table S7. Limit of quantification for organic elements – AP, BPA, HBCD and TBBPA

Nom	LQ	Uncertainties %
OP	D: 21 ng/l P: 139 ng/g	D: 25 P: 48
OP1EO	D: 17 ng/l P: 113 ng/g	D: 25 P: 40
OP2EO	D: 6 ng/l P: 56 ng/g	D: 32 P: 19
NP	D: 5 ng/l P: 120 ng/g	D: 37 P: 44
NP1EO	D: 60 ng/l P: 419 ng/g	D: 91 P: 43
NP2EO	D: 31 ng/l P: 203 ng/g	D: 67 P: 56
NPEC1	D: - P: 107 ng/g	D: 29 P: 49
BPA	D: 17 ng/l P: 113 ng/g	D: 28 P: 25
TBBPA	D: 0.1 ng/l P: 0.20 ng/g	D: 7 P: 24
a-HBCD	D: 0.002 µg/l P: 5 ng/l	D: 8 P: 53
b-HBCD	D: 0.004 µg/l P: 5 ng/g	D: 12 P: 12
g-HBCD	D: 0.002 µg/l P: 5 ng/g	D: 60 P: 10

D: dissolved fraction, P: Particulate fraction

Table S8. Limit of quantification for organic elements - Phthalates

Nom	LQ	Uncertaincies %
DEP	D: 0.09 µg/l P: 189 ng/g	ND
BBP	D: 0.11 µg/l P: 210 ng/g	ND
DBP	D: 0.13 µg/l P: 180 ng/g	25*
DEHP	D: 0.13 µg/l P: 350 ng/g	35*
DIBP	D: 0.17 µg/l P: 520 ng/g	35*
DMP	D: 0.15 µg/l P: 250 ng/g	45*
DMEP	D: 0.01 µg/l P: 20 ng/g	ND
DMPP	D: 0.12 µg/l P: 240 ng/g	ND
DEEP	D: 0.10 µg/l P: 191 ng/g	ND
DPP	D: 0.09 µg/l P: 185 ng/g	ND
DNHP	D: 0.13 µg/l P: 258 ng/g	ND
DBEP	D: 0.10 µg/l P 197 ng/g	ND
DCHP	D: 0.12 µg/l P: 233	ND
DNOP	D: 0.08 µg/l P: 165 ng/g	ND
DNP	D: 0.08 µg/l P: 110 ng/g	32*

D: dissolved fraction, P: Particulate fraction, ND: non deterimined

Table S9. Limit of quantification for organic elements - PFAS

Nom	LQ	Uncertaincies %
PFOS	D: 0.69 ng/l P: 0.46 ng/g	D: 12 P: 13
PFOA	D: 0.69 ng/l P: 0.97 ng/g	D: 15 P: 15
PFPA	D: 0.92 ng/l P: 0.83 ng/g	D: 9 P: 7
PFHpA	D: 0.69 ng/l P: 0.28 ng/g	D: 6 P: 5
PFDA	D: 0.69 ng/l P: 0.23 ng/g	D: 20 P: 22
PFUA	D: 0.92 ng/l P: 0.94 ng/g	D: 12 P: 9
PFDoA	D: 0.92 ng/l P: 2.02 ng/g	D: 15 P: 14
PFHxA	D: 0.69 ng/l P: 0.38 ng/g	D: 15 P: 13
PFNA	D: 0.69 ng/l P: 0.45 ng/g	D: 10 P: 9
PFBS	D: 0.23 ng/l P: 0.98 ng/g	D: 13 P: 14
PFHxS	D: 0.46 ng/l P: 0.63 ng/g	D: 11 P: 12
PFHpS	D: 0.46 ng/l P: 0.63 ng/g	D: 9 P: 7
PFDS	D: 0.69 ng/l P: 0.23 ng/g	D: 6 P: 5
FOSA	D: 0.23 ng/l P: 0.23 ng/g	D: 3 P: 1
4:2 FTSA	D: 0.23 ng/l P: 0.46 ng/g	D: 7 P: 7
6:2 FTSA	D: 0.46 ng/l P: 0.46 ng/g	D: 7 P: 5
8:2 FTSA	D: 0.46 ng/l P: 0.46 ng/g	D: 19 P: 22

D: dissolved fraction, P: Particulate fraction

Table S10. Limit of quantification for organic elements – Other molecules

Nom	LQ	Uncertainties %
TBT	D: 0.02 µg/l	14
DBT	D: 0.02 µg/l	15
MBT	D: 0.02 µg/l	23
SCCP	D: 50 µg/l	ND
MTBE	D: 0.5 µg/l	ND
ETBE	D: 0.5 µg/l	ND
TAME	D: 1 µg/l	ND
Benzophénone	D: 1 µg/l	ND
LAS	D: 10 µg/l	ND
1H-Benzotriazole	D: 0.01 µg/l	ND
4-Methyl-1H-benzotriazole	D: 0.01 µg/l	ND
5-Methyl-1H-benzotriazole	D: 0.01 µg/l	ND
5,6-Dimethyl-1H-benzotriazole	D: 0.01 µg/l	ND

D: dissolved fraction, P: Particulate fraction, ND: non deterimined

Table S11. 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]
$C_{12}H_{23}NOS$	+H	252.1411	16.3	152.96	8	99.97	prosulfocarb	V
$C_{16}H_{25}N_5O_3$	+H	336.2025	3.22	177.38	-0.9	97.25	7-hexyl-3-methyl-8-(morpholin-4-yl)-3,7-dihydro-1H-purine-2,6-dione	V
$C_9H_{14}O_2$	+Na	177.0879	9.11	126.11	-4.3	87.23	4-oxo-2-nonenal	V
$C_{18}H_{38}O_{10}$	+H	415.2536	5.05	181.51	-0.5	98.44	Nonaethylene glycol (along with other PEGs*)	P
$C_{20}H_{38}O_{12}$	+Na	493.2255	7.12	197.93	-0.1	96.62	Octaoxaoctacosane-1,28-dioic acid	P
$C_{14}H_{26}N_2O_2$	+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
$C_{14}H_{30}O_8$	+Na	349.1827	4.31	162.93	-2	97.21	Heptaethylene glycol - and following PEGs until $C_{32}H_{66}O_{17}$ (PEG16)	C & P
$C_6H_9F_3O_3$	+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)-3-decanol	R

[1] The I-fit confidence percentage is a score giving the confidence of the proposed formula regarding isotopes measured for the feature. [2] P = Paris, C = Compans, R = Rosny-sous-Bois, V = Villeneuve-le-Roi.
* PEG: Polyethylene glycols.

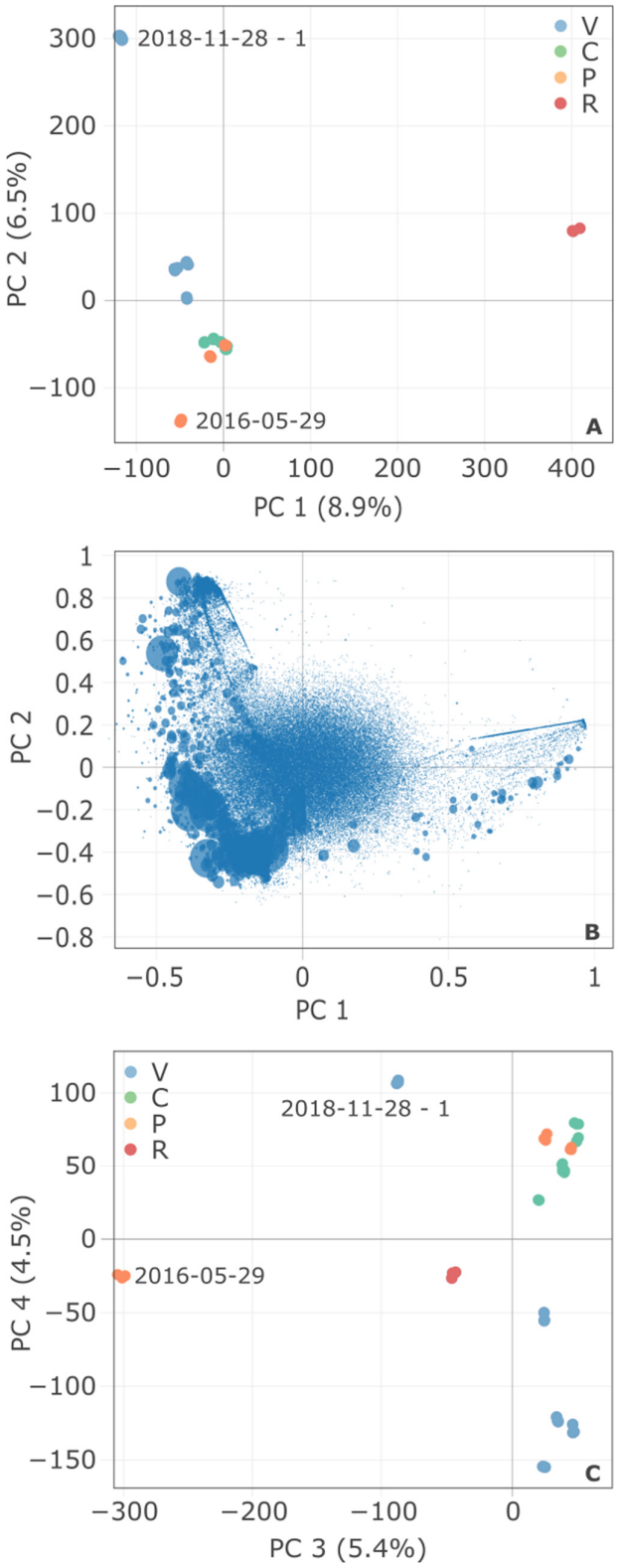

Figure S1. Principal component analysis of HRMS features. (A) Scores plot of first two principal components (PC1 and PC2) showing samples with selected sampling dates for the four sites; (B) Loadings plot showing all features detected in the samples, with the size of bubbles proportional to

the highest intensity of a given feature among all samples; (C) Scores plot of third and fourth principal components (PC3 and PC4).