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Two optimized methods for the quantification of anthropogenic and biogenic markers in aerosol samples using liquid chromatography mass spectrometry and gas chromatography mass spectrometry

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Table S1. List of compounds, solvents and gases with their characteristics used during the method development and analysis in the UPLC/ESI-IMSQTOFMS and GC-MS.

Compound name	CAS #	Molecular formula	Weight	Manufacturer	Purity (%)	Detection technique
Solvents						
Methanol ULC/MS-CC/SFC	67-56-1	CHO_3OH	32	Biosolve	99.99	UPLC
Acetonitrile ULC/MS-CC/SFC	75-05-8	C_2H_3N	41	Biosolve	99.99	UPLC
Formic acid ULC/MS-CC/SFC	64-18-6	CH_2O_2	46	Biosolve	99	UPLC
Water	-	H_2O	18	Millipore	Milli-Q	UPLC/GC
Acetonitrile HPLC	75-05-8	C_2H_3N	41	VWR chemical	99.95	GC
Cleaning material						
Neodisher LaboClean FLA	-	KOH	-	Dr. Weigert	-	-
Neodisher N	-	$H_3PO_4/C_6H_8O_7$	-	Dr. Weigert	-	-
Internal Standards and derivatisation reagent						
(1S)-(+)-camphor-10-sulfonic acid	5872-08-2	$C_{10}H_{16}O_4S$	232	Sigma Aldrich	98	UPLC
Heptanoic acid	111-14-8	$C_7H_{14}O_2$	130	Sigma Aldrich	99	GC
N,O-Bis(trimethylsilyl)trifluoroacetamide	25561-30-2	$C_8H_{18}F_3NOSi_2$	257	Sigma Aldrich	99	GC
Target organic compounds						
Cis-pinonic acid	61826-55-9	$C_{10}H_{16}O_3$	184	Sigma Aldrich	98	UPLC/GC
Pinic acid	28664-02-0	$C_9H_{14}O_4$	186	TRC (LGC Standards)	95	UPLC/GC
Norpinic acid	3211-59-4	$C_8H_{12}O_4$	172	Sigma Aldrich	>95	UPLC
Terebic acid	79-91-4	$C_7H_{10}O_4$	158	Sigma Aldrich	>95	UPLC
3-methyl-1,2,3-butanetricarboxylic acid	114701-91-6	$C_8H_{12}O_6$	204	TRC (LGC Standards)	98	UPLC
(1S,2S,3R,5S)-(+)- Pinanediol	18680-27-8	$C_{10}H_{18}O_2$	170	Sigma Aldrich	99	GC
1R-(+)-Nopinone	38651-65-9	$C_9H_{14}O$	138	Sigma Aldrich	98	GC
α-methylglyceric acid	21620-60-0	$C_4H_8O_4$	120	Wonderchem	95	GC
2-methylerythritol	58698-37-6	$C_5H_{12}O_4$	136	Sigma Aldrich	90	GC
4-nitrocathecol	3316-09-4	C_6H_5NO	155	Sigma Aldrich	97	UPLC/GC
Syringaldehyde	134-96-3	$C_9H_{10}O_4$	182	Sigma Aldrich	97	UPLC
4-methyl phthalic acid	4316-23-8	$C_9H_8O_4$	180	Sigma Aldrich	99	UPLC
Phthalic acid	88-99-3	$C_8H_6O_4$	166	Sigma Aldrich	99.5	UPLC/GC
2,3-dihydroxy-4-oxopentanoic acid	37520-06-2	$C_5H_8O_5$	148	TRC (LGC Standards)	98	GC
2,5-dihydroxy benzoic acid	490-79-9	$C_7H_6O_4$	154	Sigma Aldrich	98	UPLC
Succinic acid	14493-42-6	$C_4H_6O_4$	118	Sigma Aldrich	99	GC
Glycolic acid	79-14-1	$C_2H_4O_3$	76	Sigma Aldrich	99	GC
3-acetyl-benzoic acid	586-42-5	$C_9H_8O_3$	164	Sigma Aldrich	98	UPLC
Salicylic acid	69-72-7	$C_7H_6O_3$	138	Sigma Aldrich	99	UPLC
o-toluic acid	118-90-1	$C_8H_8O_2$	136	Acros organic	99	GC
4-nitrophenol	100-02-7	$C_6H_5NO_3$	139	Sigma Aldrich	100	UPLC
2-methyl-4-nitrophenol	99-53-6	$C_7H_7NO_3$	153	Sigma Aldrich	97	UPLC/GC
2-hydroxy-3methylbenzaldehyde	824-42-0	$C_8H_8O_2$	136	Sigma Aldrich	97	GC
Azelaic acid	123-99-9	$C_9H_{16}O_4$	188	Fluka Chemika	99	UPLC
Gases						
Helium	7440-59-7	He	4	Air Liquide	99.9	GC

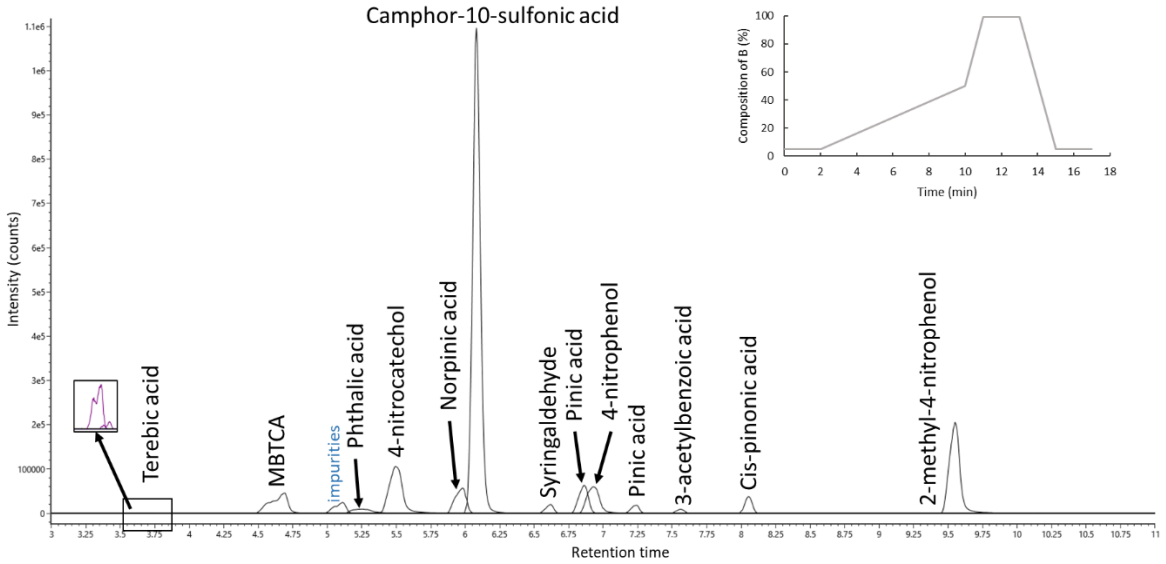

Figure S1. Overlap TIC chromatograms of individual compounds injected in the UPLC/ESI-IMS-QTOFMS using a 17 min elution method with methanol as organic solvent.

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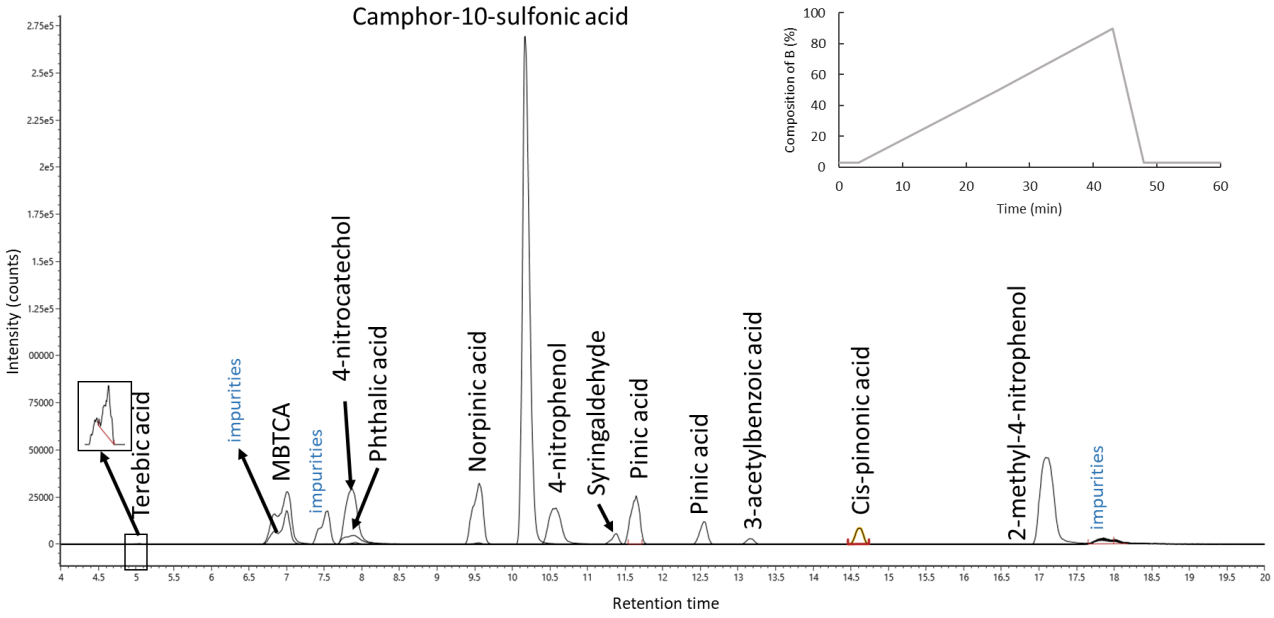

Figure S2. Overlap TIC chromatograms of individual compounds injected in the UPLC/ESI-IMS-QTOFMS using a 60 min elution method with methanol as organic solvent.

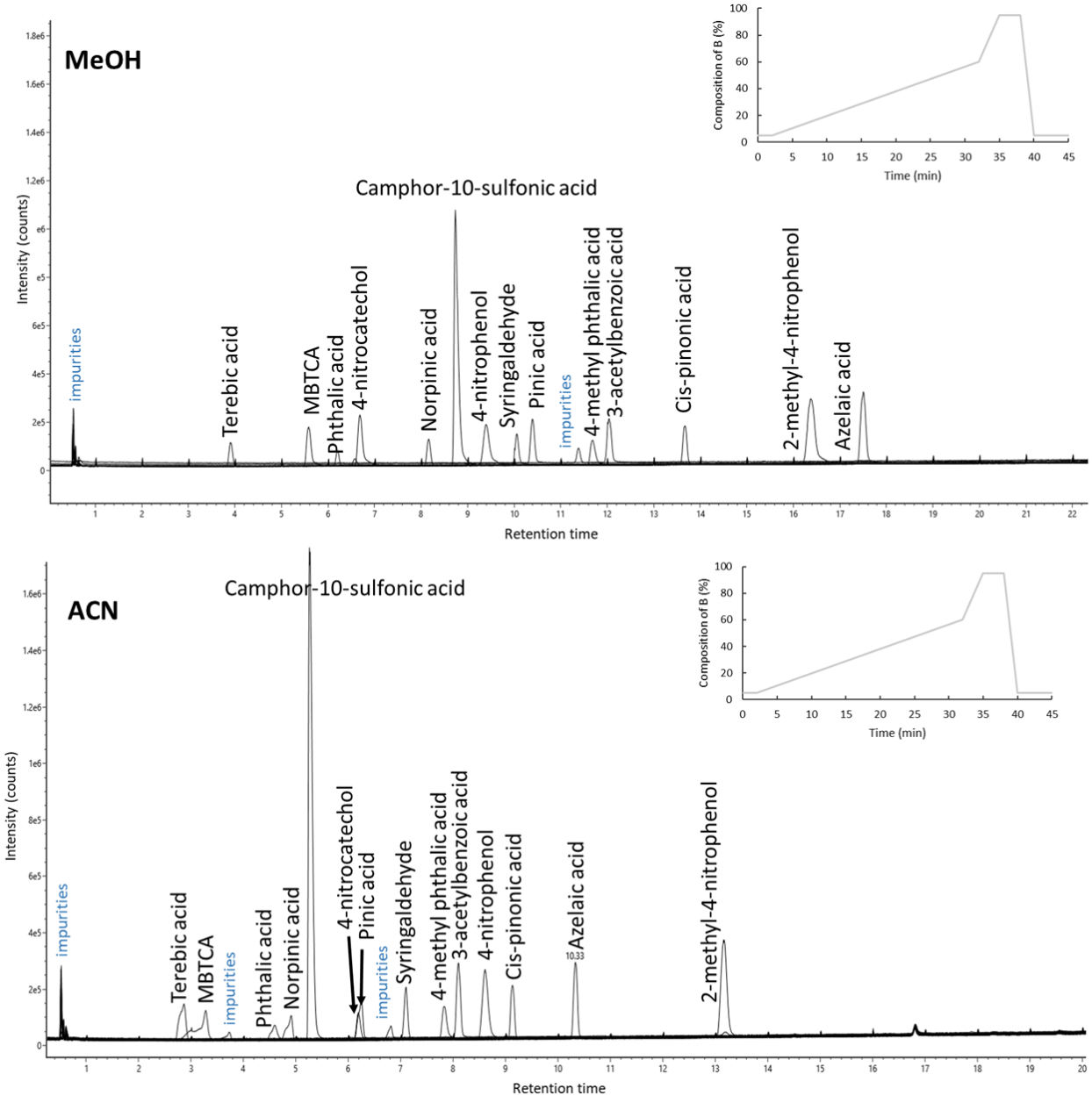

Figure S3. TIC chromatograms of a mixture of anthropogenic and biogenic standards injected in the UPLC/ESI-IMS-QTOFMS using a 45 min elution method with methanol (MeOH, top panel) and acetonitrile (ACN, bottom panel) as organic solvent.

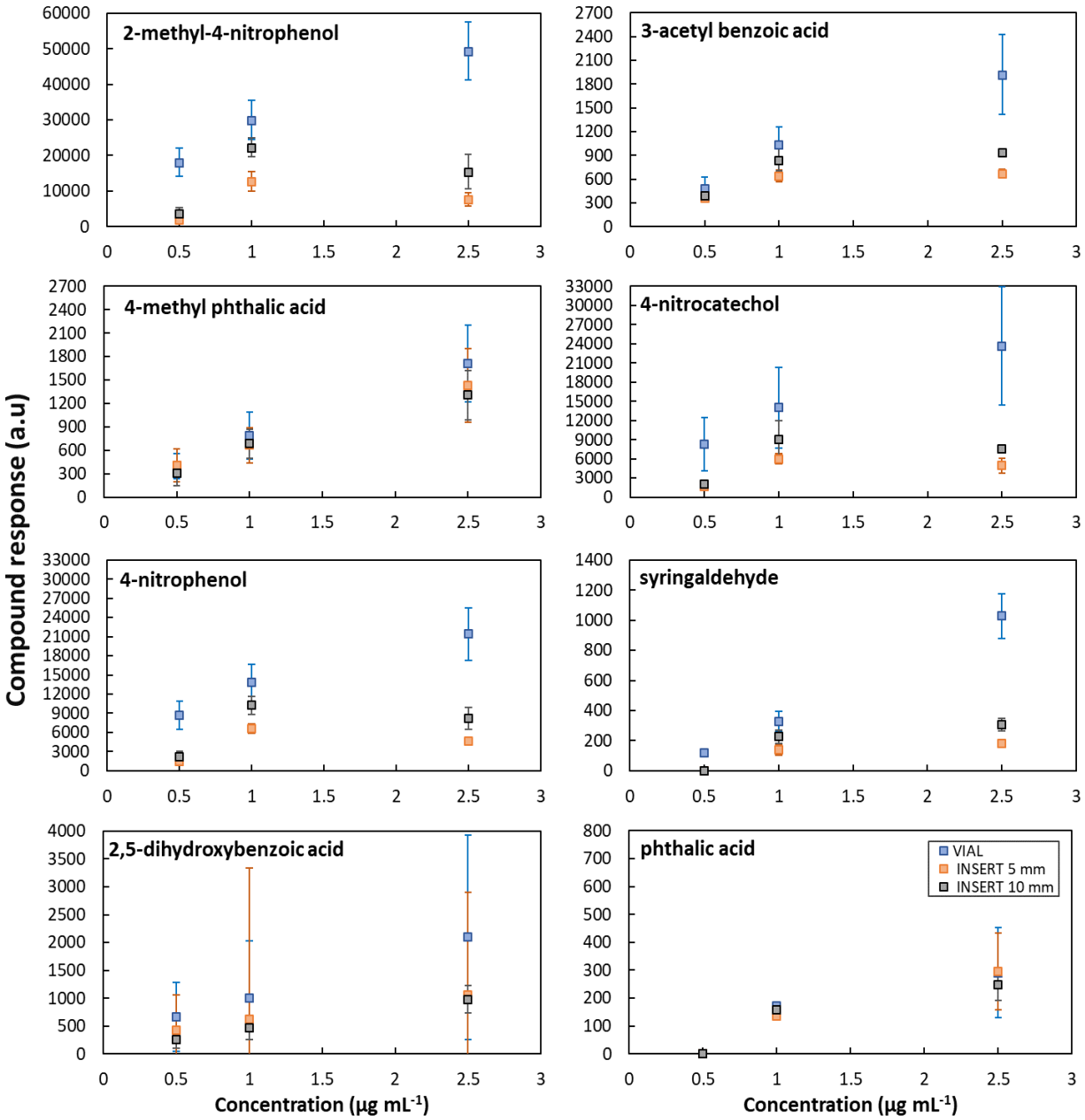

Figure S4. Comparison of the variability of compound responses in arbitrary units for samples injected in UPLC/ESI-IMS-QTOFMS from vials without inserts (vials) and vials with inserts (inserts), both without filter extraction. The needle position was tested at 5 and 10 mm from the insert bottom.

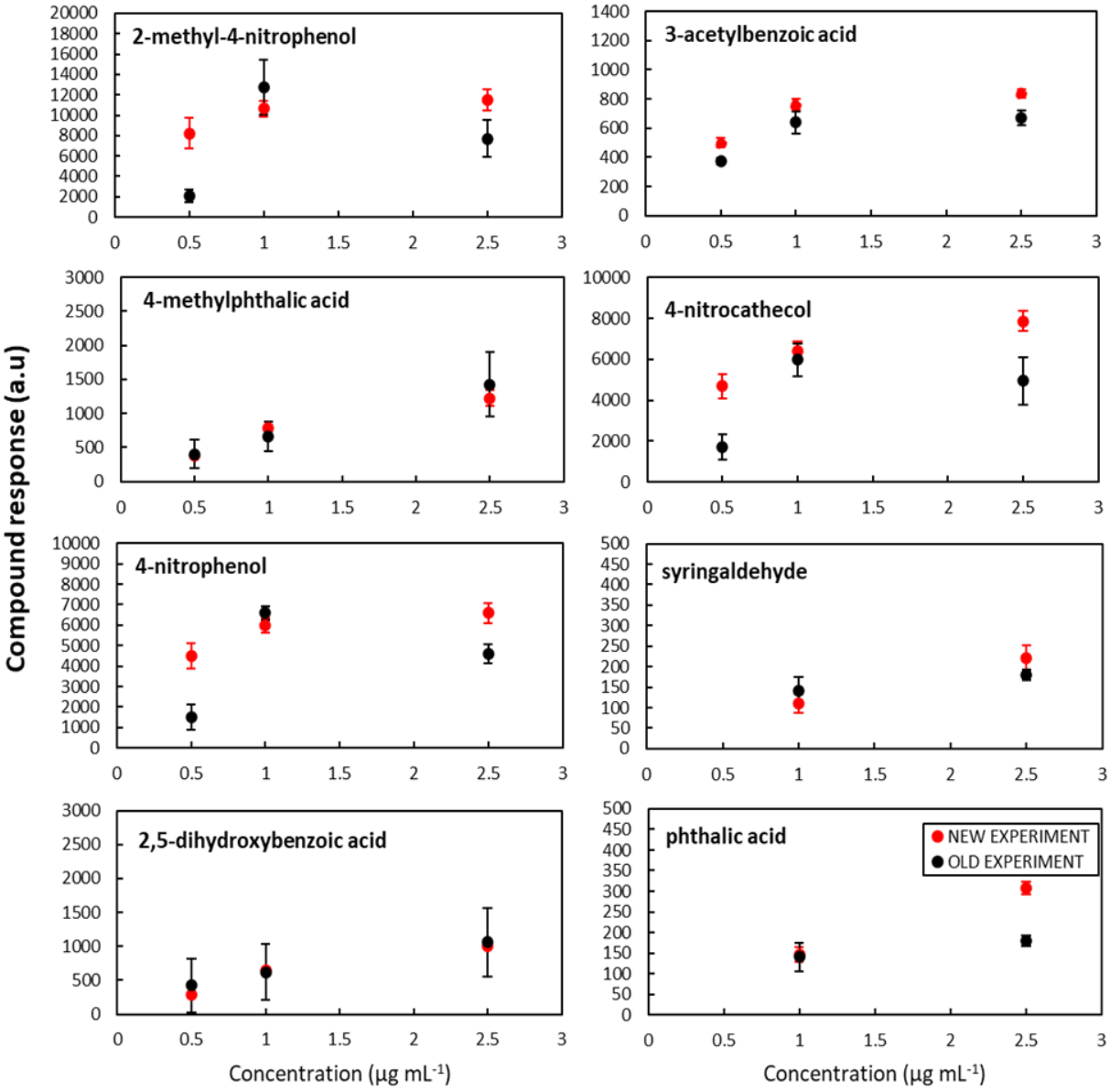

Figure S5. Comparison of the variability of compound responses in arbitrary units for samples injected in UPLC/ESI-IMS-QTOFMS from vials during different dates, labelled as new (14/03/2023) and old (03/03/2023), both without filter extraction.

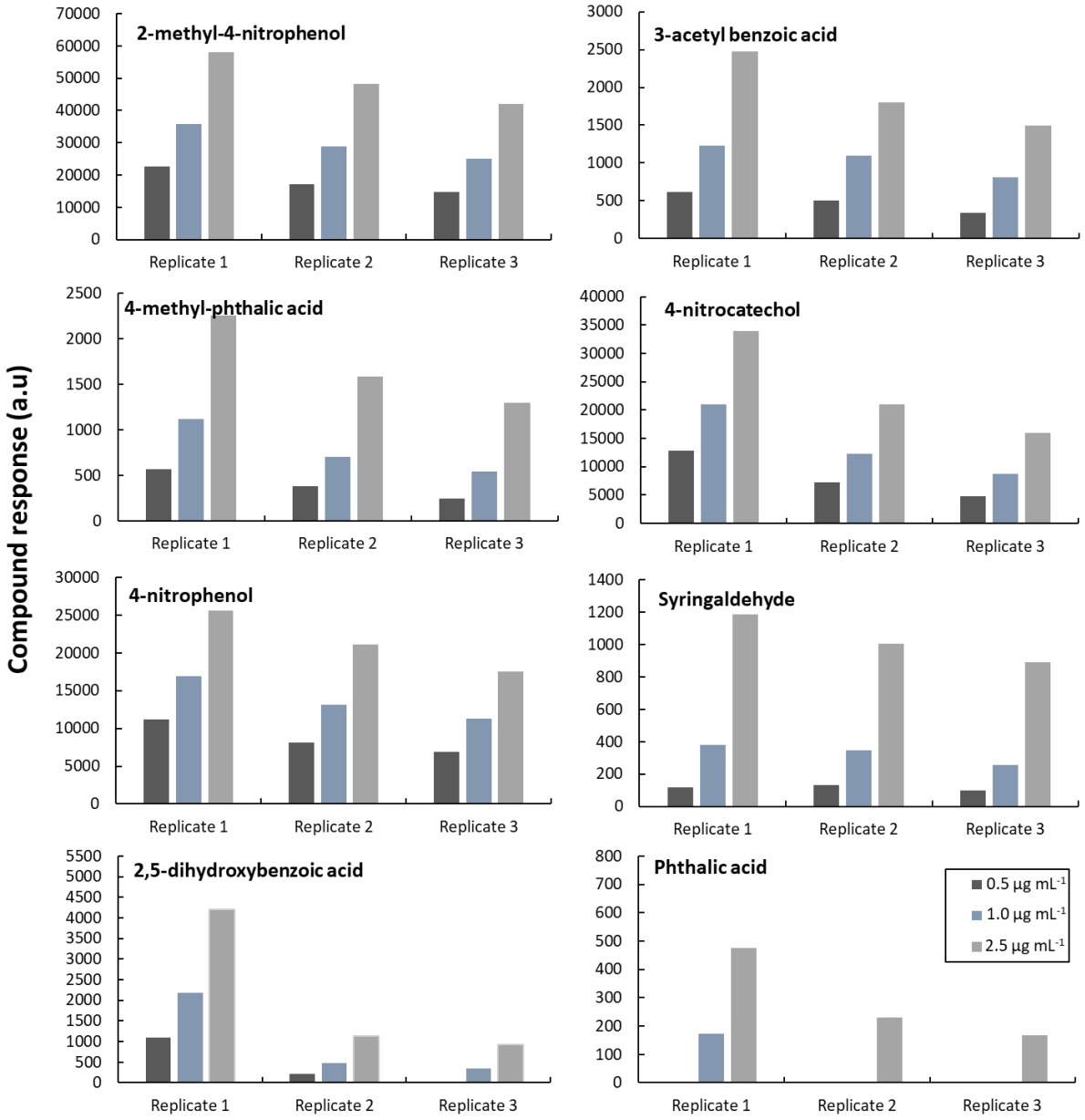

Figure S6. Example of signal loss from different compounds analyzed by non-consecutive replicates at 8 h time span between injections at three concentrations.

Table S2. Stability test performed for the target anthropogenic markers in 50/50 ultrapure water/acetonitrile. Percentage values represent the variability between injections performed by consecutive triplicates.

Compound name	1.5 µg mL^{-1}	2.5 µg mL^{-1}
2-methyl-4-nitrophenol	6.1%	4.3%
3-acetylbenzoic acid	2.6%	4.3%
4-methylphthalic acid	2.8%	9.2%
4-nitrocatechol	6.0%	5.0%
4-nitrophenol	6.2%	3.3%
Syringaldehyde	6.8%	11.9%
2,5-dihydroxybenzoic acid	1.9%	15.5%
Phthalic acid	2.9%	6.8%

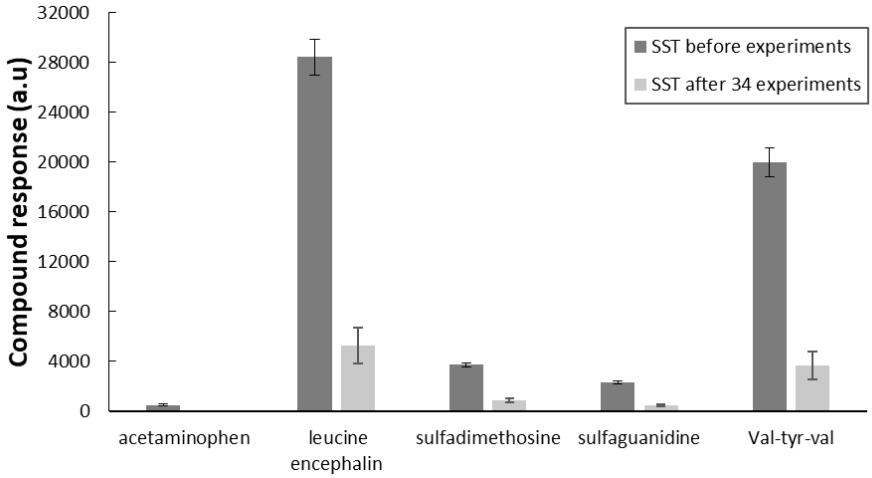

Figure S7. Response in arbitrary units for a control solution at the beginning of the experiments and after injecting a sequence of 34 injections (approx. 25 h).

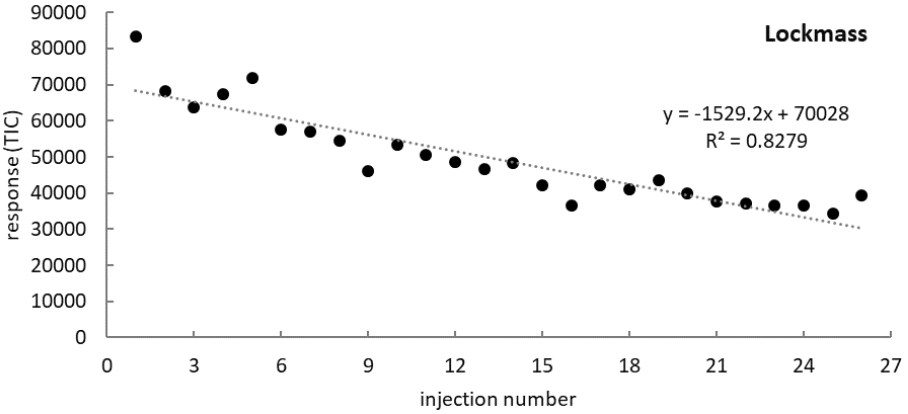

Figure S8. LockMass (Leucine-Enkephalin solution) evaluation of the summed response in arbitrary units for individual infusions of 45 min in a sequence of 25 injections (transition time approx. 19 h).

Table S3. Compound response in arbitrary units at different values of cone gas flow (50, 100, 150 L h^{-1}) used for the identification of anthropogenic compounds.

Component name	Response at 50 L h^{-1}	Response at 100 L h^{-1}	Response at 150 L h^{-1}
4-nitrocatechol	30433	32143	34787
Syringaldehyde	1395	1452	1645
4-methylphthalic acid	4010	3875	3856
Phthalic acid	1193	1118	1142
2,5-dihydroxybenzoic acid	3742	3818	3765
3-acetylbenzoic acid	3234	3181	3260
2-methyl-4-nitrophenol	49818	53639	55575
4-nitrophenol	24418	24791	26406

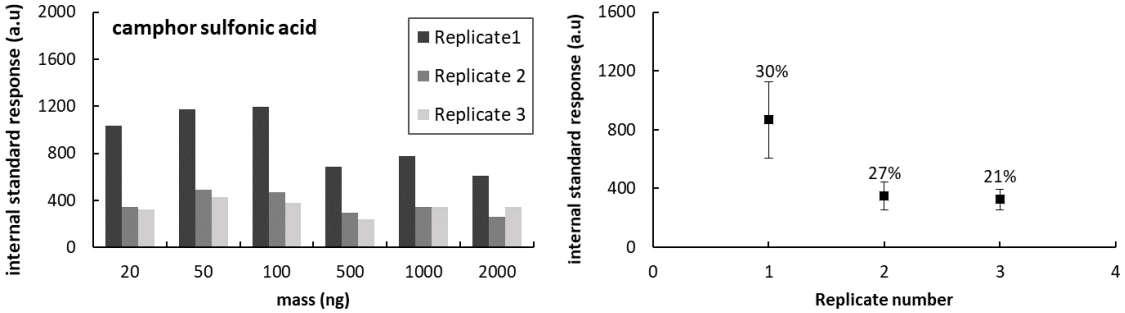

Figure S9. Analysis of the replicate's variability of internal standard response in arbitrary units. Transition time between replicates is 14 hours approximately. In the right, the squares show the mean response value with their standard deviation and the percentage shows the variability calculated considering measurements from the left.

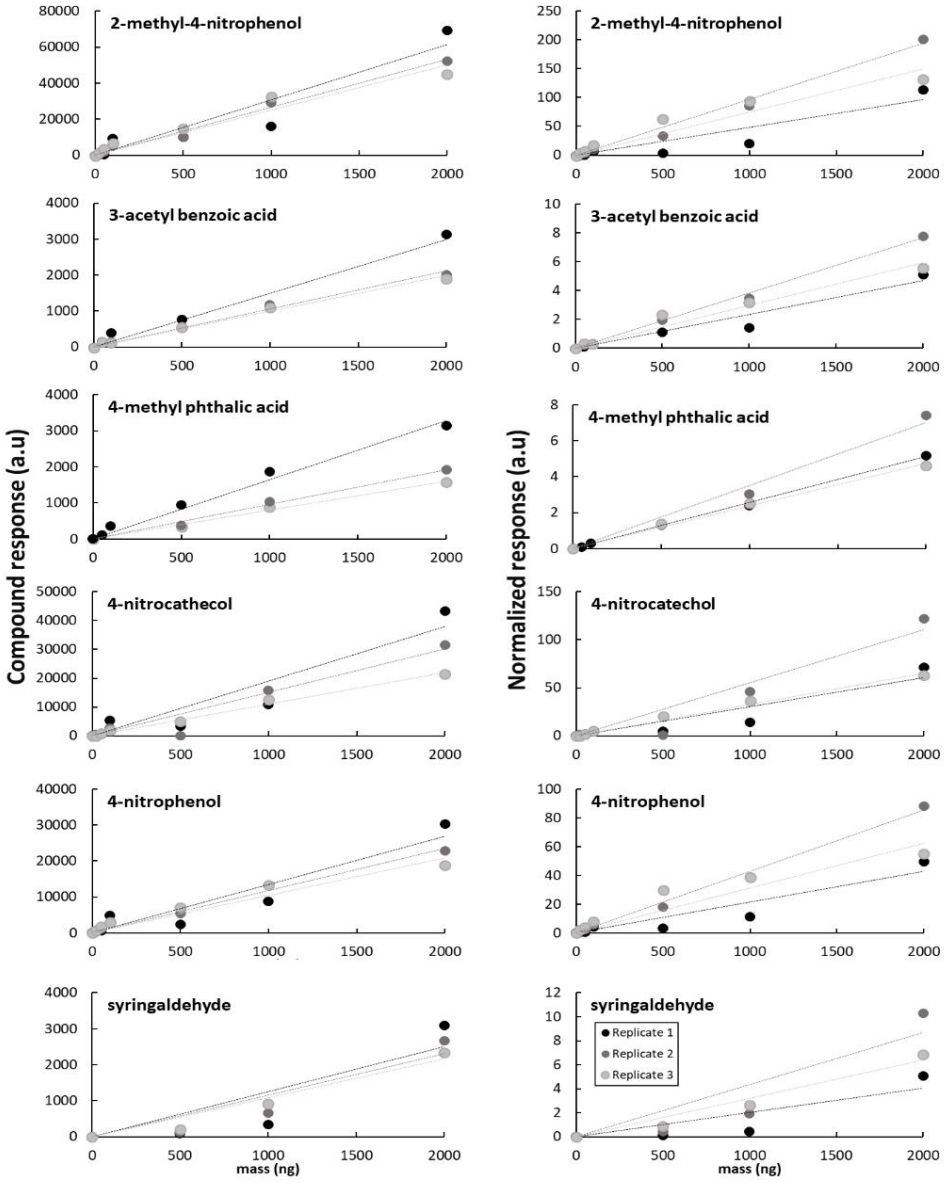

Figure S10. Calibration curves observed for the compound direct response (left) and response normalized to the internal standard camphor sulfonic acid (right).

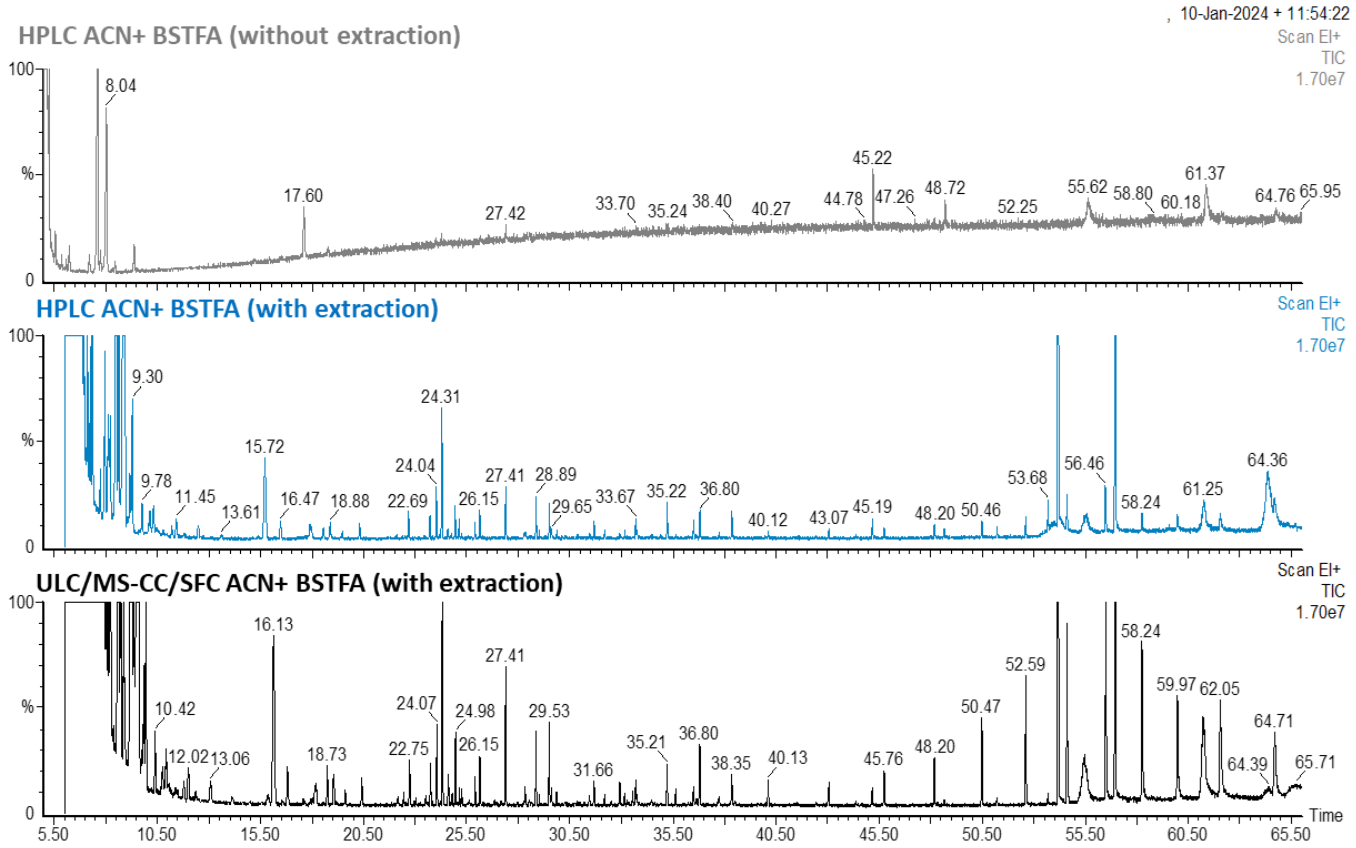

Figure S11. Comparison of chromatograms obtained with GC-MS to assess the influence of different solvent levels used for filter extraction in the presence of the derivatization reagent BSTFA with and without heating. The top panel shows a blank chromatogram of acetonitrile HPLC grade and BSTFA directly injected, the middle panel shows a blank chromatogram of acetonitrile HPLC grade and BSTFA that underwent heating (according to the derivatization protocol), and the bottom panel shows a blank chromatogram of acetonitrile ULC/MS-CC/SFC grade (higher purity grade compared to HPLC) and BSTFA that underwent heating (according to the derivatization protocol).

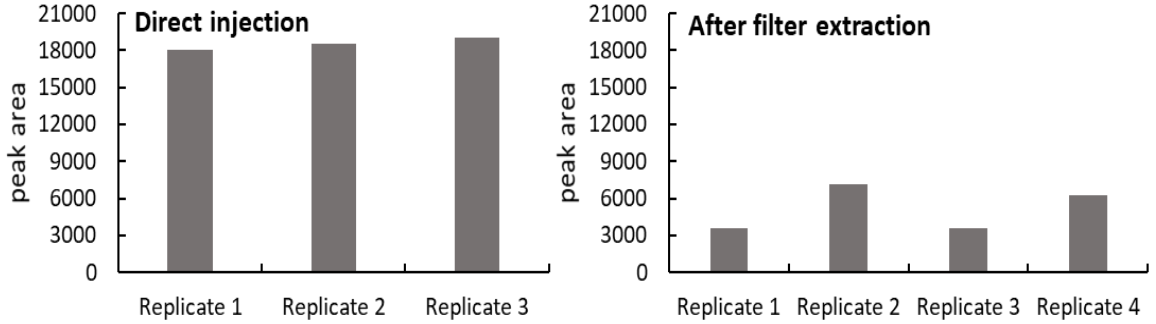

Figure S12. Heptanoic acid repeatability evaluation by GC-MS from a solution directly injected (left) and after extraction on filter (right).

Table S4. LOD comparison of some markers observed in this study with those previously reported in the literature associated with the analysis of aerosol samples.

Compound name	This study LOD	Literature LOD	Reference	Technique
cis-pinonic acid[b]	240 ng	6.7 ng 2.2-7.5 ng	Chiappini et al. (2006) Albinet et al. (2019)	SFE-GC-MS GC-MS
Pinic acid[b]	380 ng	1.2 ng 6.3-7.6 ng	Chiappini et al. (2006) Albinet et al. (2019)	SFE-GC-MS GC-MS
Norpinic acid[a]	190 ng mL^{-1}	1.5 ng mL^{-1}	Amarandei et al. (2023)	LC-MS
Terebic acid[a]	240 ng mL^{-1}	5.7 ng mL^{-1} 0.7 ng mL^{-1}	King et al. (2019) Amarandei et al. (2023)	LC-Orbitrap LC-MS
MBTCA[a]	255 ng mL^{-1}	2.7 ng mL^{-1} 0.9 ng mL^{-1}	King et al. (2019) Amarandei et al. (2023)	LC-Orbitrap LC-MS
(1S,2S,3R,5S)-(+)-Pinanediol[b]	400 ng			
1R-(+)-Nopinone[b]	37 ng			
α-methylglyceric acid[b]	560 ng	1.1-2.6 ng	Albinet et al. (2019)	GC-MS
2-methylerytritol[b]	0.1 ng	1.1-4.2 ng	Albinet et al. (2019)	GC-MS
4-nitrocatechol[a]	160 ng mL^{-1}	1.0 ng mL^{-1}	Ikemori et al. (2019)	LC-MS/MS
Syringaldehyde[a]	707 ng mL^{-1}	45.5 ng mL^{-1}	Hoffmann et al. (2007)	LC-MS
4-methyl-phthalic acid[a]	150 ng mL^{-1}	0.6 ng mL^{-1}	Ikemori et al. (2019)	GC-MS
Phthalic acid[a]	44 ng or 220 ng mL^{-1}	20 ng 8.9 ng mL^{-1}	Albinet et al. (2019) Amarandei et al. (2023)	LC-MS/MS LC-MS
DHOPA[b]	250 ng or 1000 ng mL^{-1}	1.0 ng mL^{-1} 3.7-11.0 ng	Ikemori et al. (2019) Albinet et al. (2019)	GC-MS GC-MS
2,5-dihydroxy benzoic acid[a]	260 ng mL^{-1}			
Succinic acid[b]	320 ng	1.0-1.3 ng	Albinet et al. (2019)	GC-MS
Glycolic acid[b]	370 ng	1.6 ng	Kitanovski et al. (2011)	LC-MS
3-acetyl-benzoic acid[a]	180 ng mL^{-1}			
Salicylic acid[a]	115 ng mL^{-1}	10.2 ng mL^{-1}	King et al. (2019)	LC-Orbitrap
o-toluic acid[b]	200 ng			
4-Nitrophenol[a]	17 ng mL^{-1}	27.8 ng mL^{-1} 1.2 ng mL^{-1} 0.26 ng mL^{-1}	 Amarandei et al. (2023)	LC-MS LC-MS/MS LC-MS
2-methyl-4-nitrophenol[a]	22 ng mL^{-1}	22 ng mL^{-1} 0.64 ng mL^{-1}	Hoffmann et al. (2007) Ikemori et al. (2019)	LC-MS LC-MS/MS
2-hydroxy-3-methylbenzaldehyde[b]	280 ng			

[a] when measurements were performed using UPLC/ESI-IMS-QTOFMS, [b] when measurements were performed using GC-MS.

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