# 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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**Supplementary material:**

Figures S1 to S10

Table S1 and S2

**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 | Company | 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 |
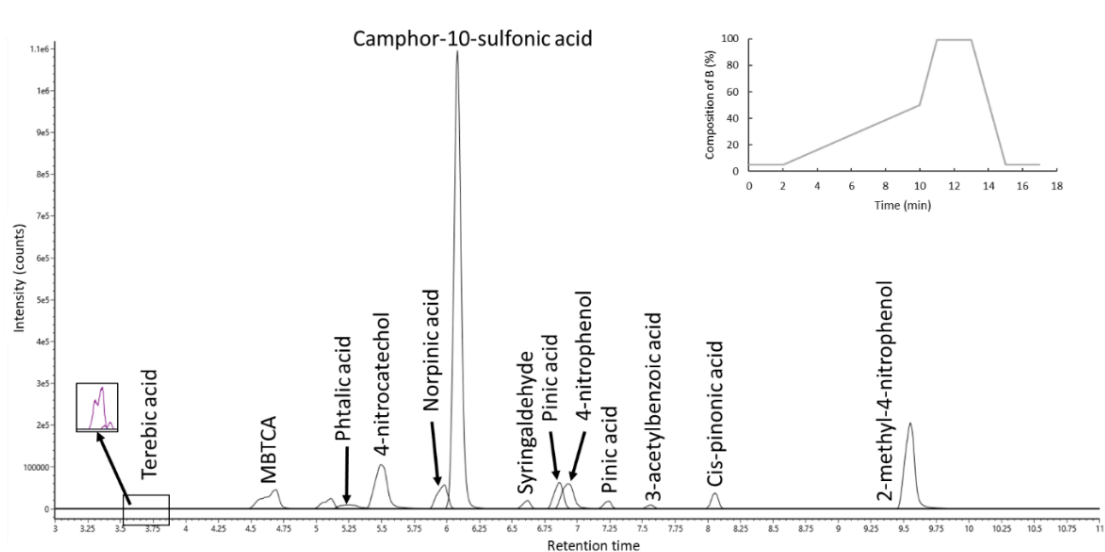
**Figure S1.** Overlap TIC chromatograms of individual compounds injected in the UPLC/ESI-IMS-QTOFMS using a 17 min elution method with methanol as organic solvent.
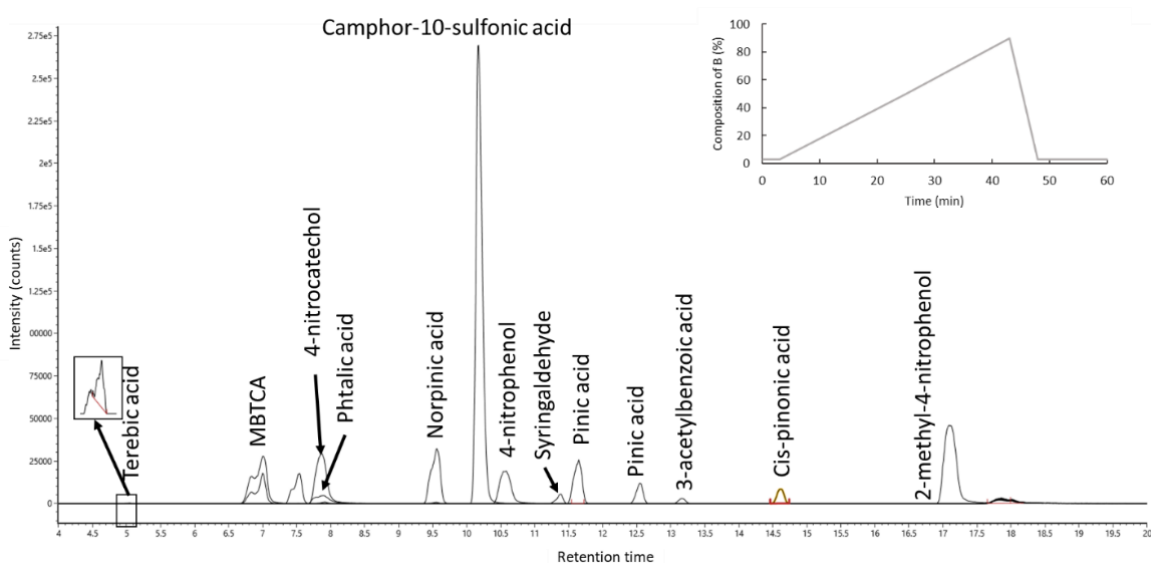
**Figure S2.** Overlap TIC chromatograms of individual compounds injected in the UPLC/ESI-IMS-QTOFMS using a 60 min elution method with methanol as organic solvent.

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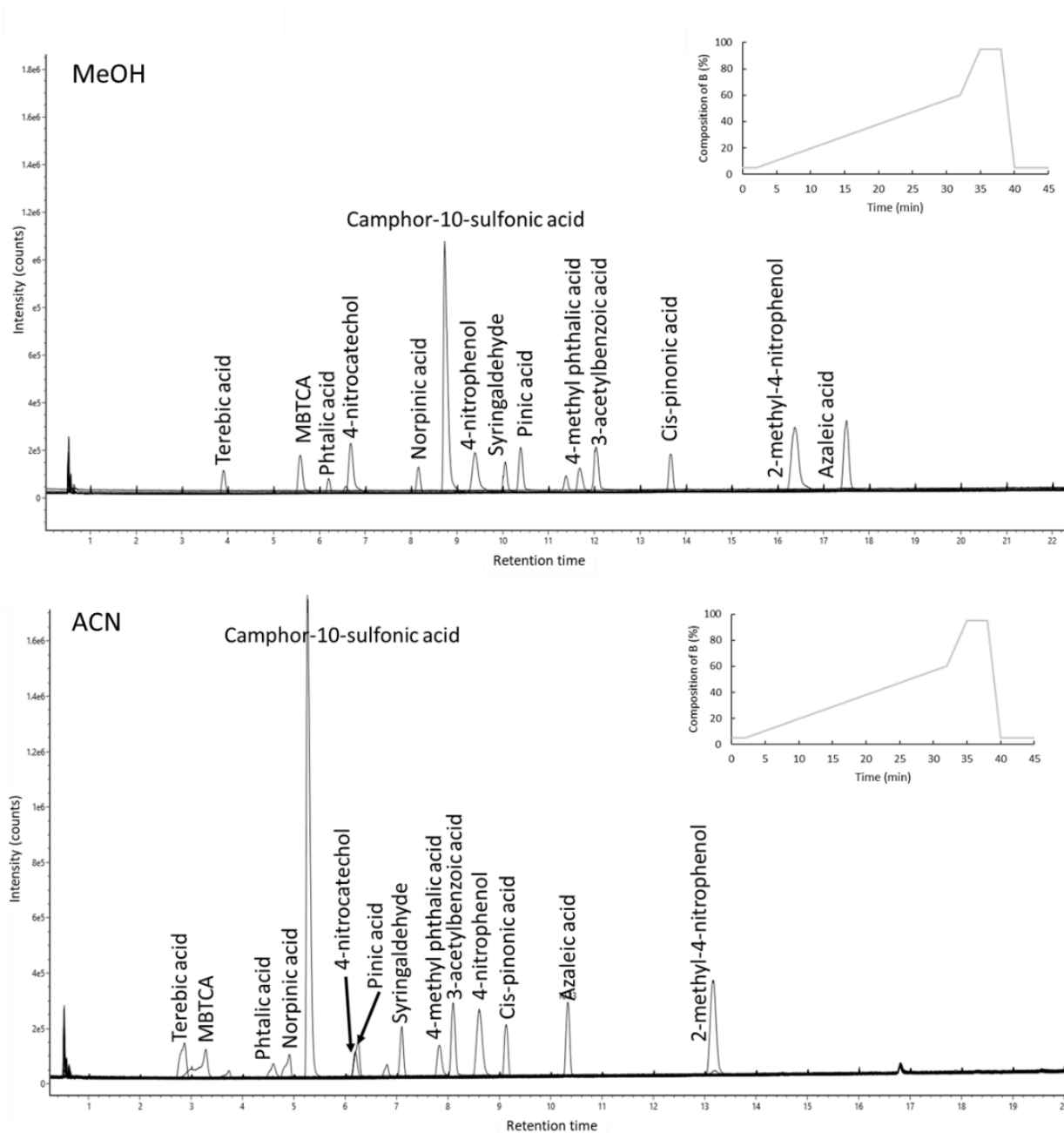


**Figure S3.** TIC chromatograms of a mixture of anthropogenic and biogenic standards injected in the UPLC/ESI-IMS-QTOFMS using a 45 min elution method with methanol (MeOH, top panel) and acetonitrile (ACN, bottom panel) as organic solvent.

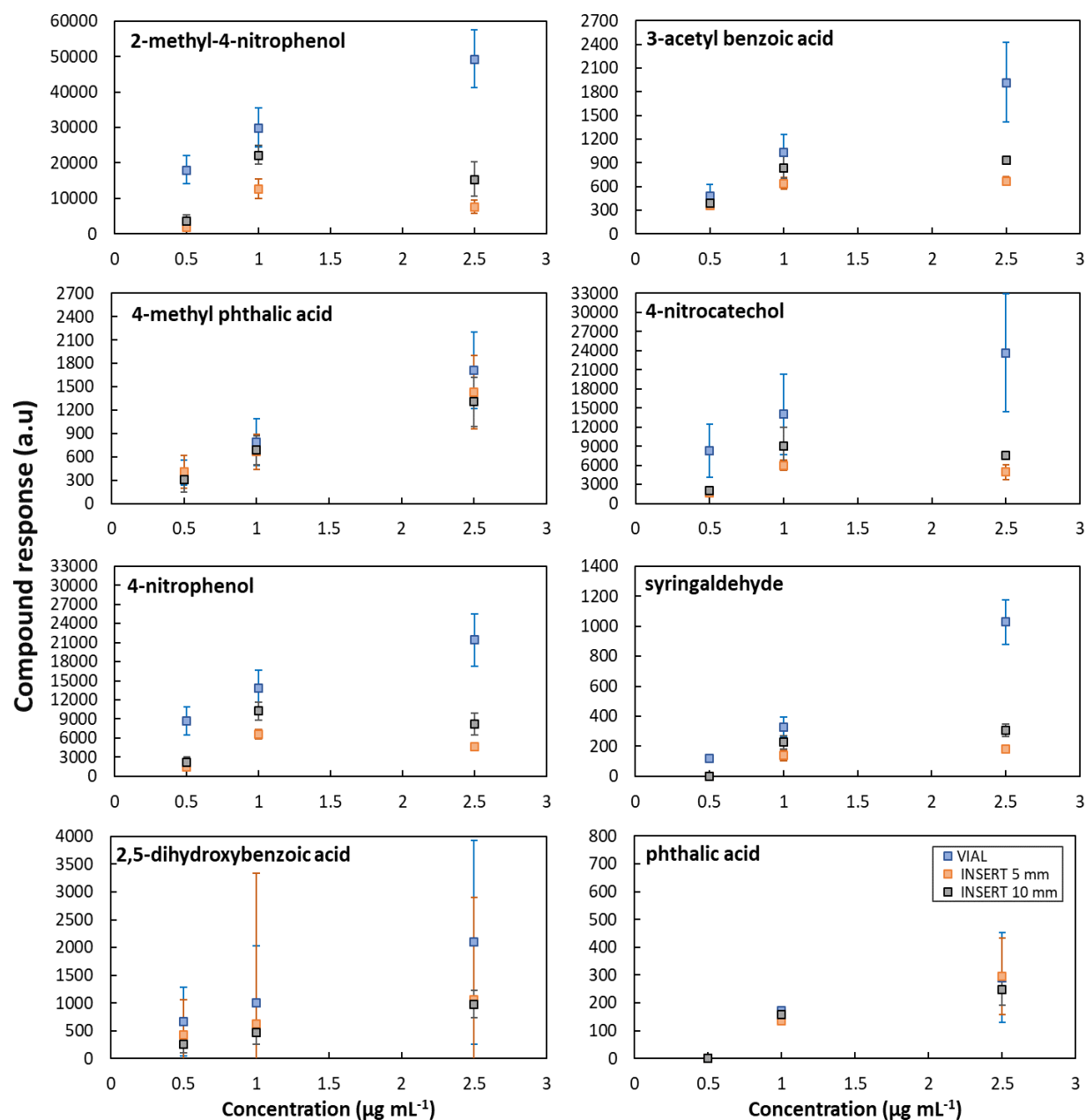



**Figure S4.** Comparison of the variability of compound responses in arbitrary units for samples injected in UPLC/ESI-IMS-QTOFMS from vials without inserts (vials) and vials with inserts (inserts), both of them without filter extraction. The needle position was tested at 5 and 10 mm from the insert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

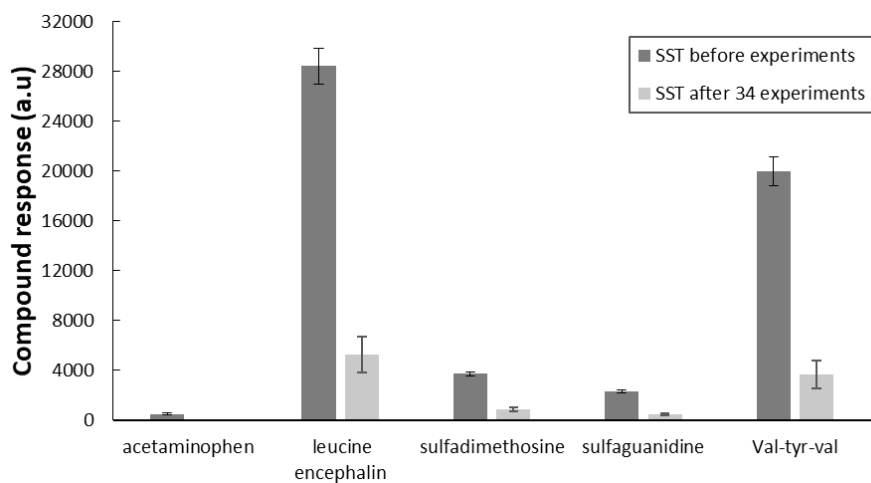



**Figure S5.** Response in arbitrary units for a control solution at the beginning of the experiments and after injecting a sequence of 34 injections (approx. 25 h).

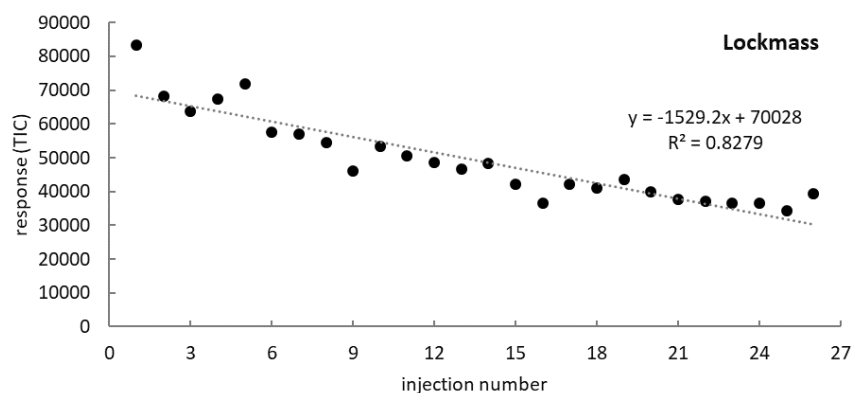
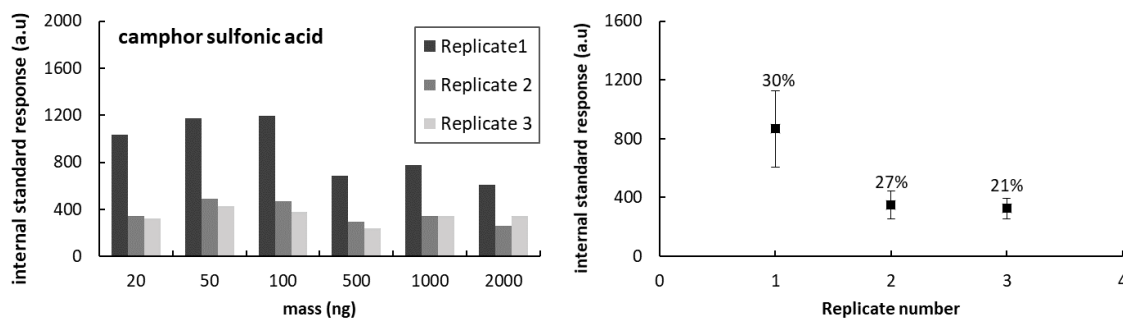



**Figure S6.** LockMass (Leucine-Enkephalin solution) evaluation of the summed response in arbitrary units for individual infusions of 45 min in a sequence of 25 injections (transition time approx. 19 h).

**Table S2.** 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 |

50 **Figure S7.** Analysis of the replicates 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.

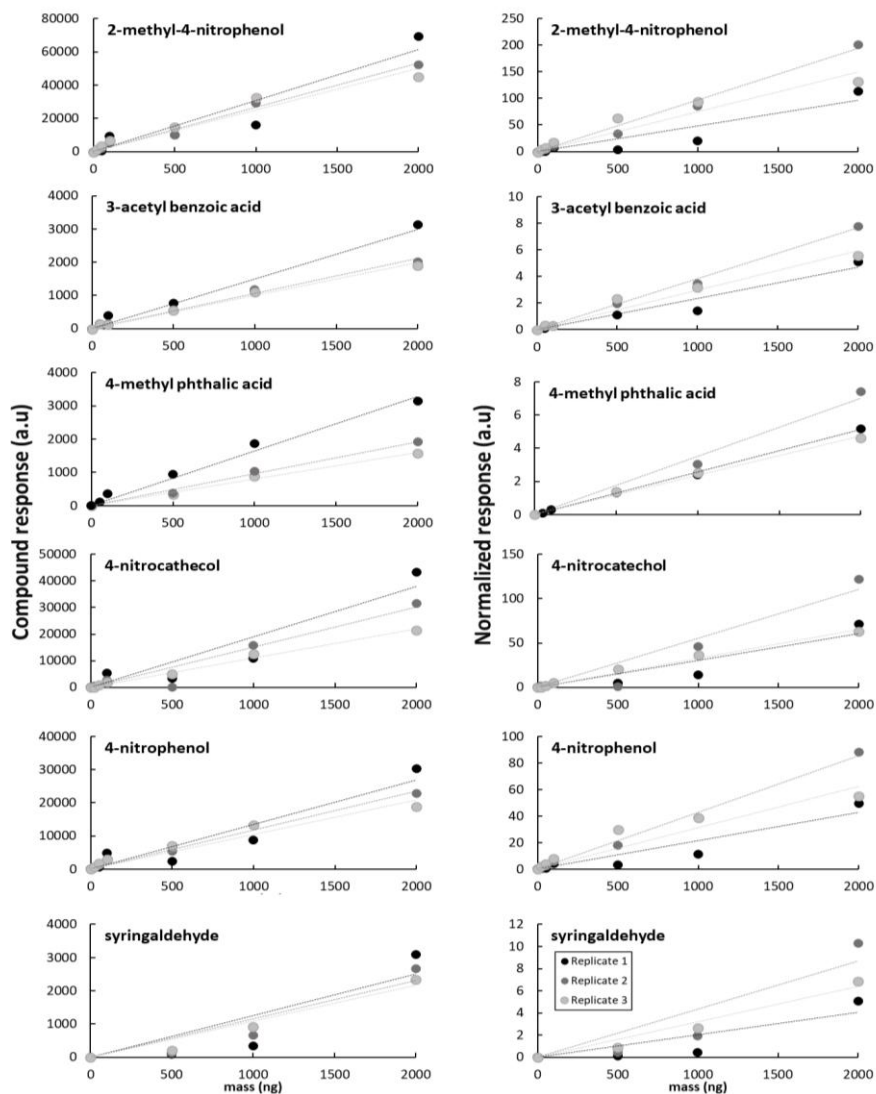



**Figure S8.** Calibration curves observed for the compound direct response (left) and response normalized to the internal standard

55 camphor sulfonic acid (right).

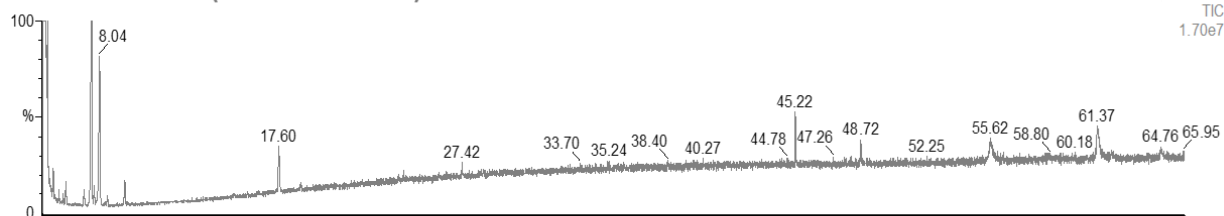
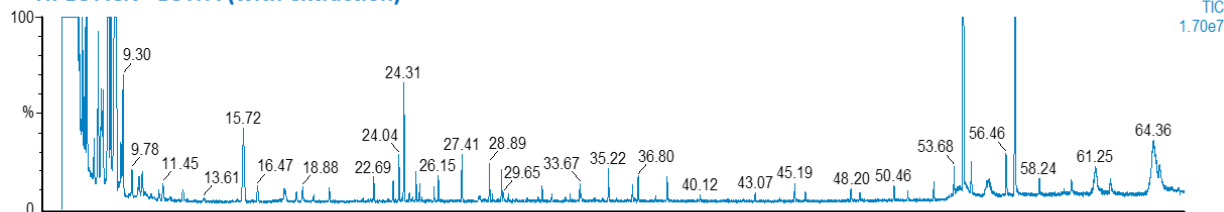
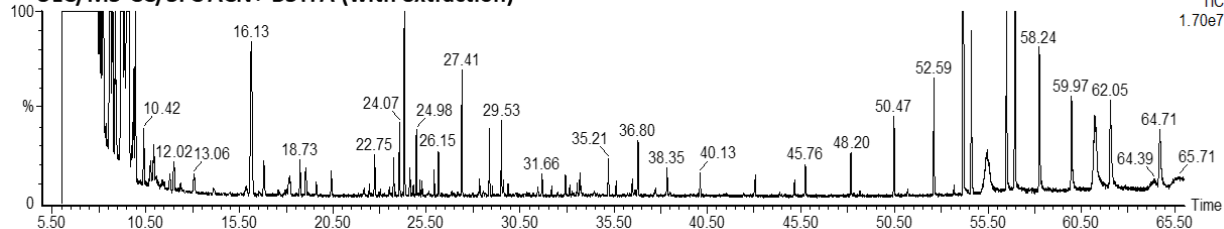



**Figure S9.** Chromatograms comparison of the influence of different solvent levels used for filter extraction in the presence of the derivatization reagent BSTFA with and without heating.

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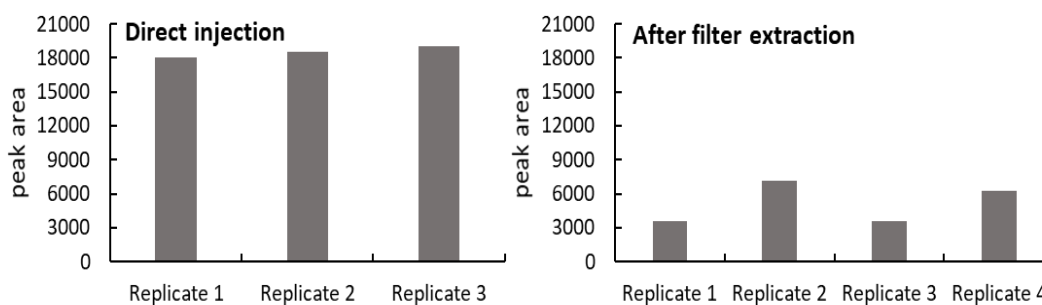
**Figure S10.** Heptanoic acid repeatability evaluation by GC-MS from a solution directly injected (left) and after extraction on filter (right).