

Supplementary material

Seasonal differences of urban organic aerosol composition – an ultra-high resolution mass spectrometry study

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Compound identification using MS/MS

Accurate mass measurements combined with MS/MS fragmentation experiments of selected ions were used to assign possible molecular structures to individual species. Mass fragments are listed in decreasing intensity.

The most abundant ion at m/z 212.07476, $C_{10}H_{14}NO_2S^-$

In negative polarity at 30 eV this ion produces the following ions: m/z 156.2 ($C_6H_6NO_2S^-$): neutral loss of 56 Da, i.e. C_4H_8 showing a cleavage of N–C bond; m/z 133.99 ($C_4H_8NO_2S^-$): neutral loss of 78 Da, i.e. C_6H_6 as a benzene ring, due to direct cleavage of C–S bond; m/z 148 ($C_{10}H_{14}N^-$): neutral loss of 64 Da, i.e. SO_2 probably via a rearrangement process, which is a typical fragmentation of benzenesulfonamides^[1,2]; m/z 146 ($C_{10}H_{12}N^-$): neutral loss of 66 Da, which correspond to the loss of H_2SO_2 ; m/z 92 ($C_6H_6N^-$): neutral loss of 120 Da, i.e. $SO_2 + C_4H_8$; m/z 65 (HSO_2 loss of 149 Da), m/z 104 (C_7H_6N loss of 108 Da, $SO_2 + C_3H_8$), m/z 141 ($C_6H_5SO_2$ loss of 71 Da, as C_4H_9N).

The component was identified as *n*-butylbenzenesulfonamide ($C_{10}H_{14}NO_2S^-$) by comparison with the MS/MS fragments observed of a standard under the same conditions. In addition we quantified its concentration it using LC-ESI-UHRMS, up to ~ 4.5 ng L⁻¹.

LC conditions: column hypersil GOLD, Thermo Fisher Scientific, dimensions 50 × 2.1 mm, particle size 1.9 μm, pore size 175 Å. Mobile phase acetonitrile/water gradient from 20 to 80 in 20 min, sample volume 10 μL, flow rate 200 μL min⁻¹, the peak corresponding to *n*-butylbenzenesulfonamide has a retention time of 10 min.

The compound was also observed in positive mode as $[M+H]^+$ at m/z 214.08986 with the formula $C_{10}H_{16}NO_2S^+$ and follows similar pathway on the MS/MS analysis than in negative polarity in which the main features at 30 eV are: $m/z > 158.2$ ($C_6H_8NO_2S^+$, loss of 56 Da as C_4H_8), $m/z > 141.06$

($C_6H_5SO_2^+$, loss of 73 Da from $C_4H_{10}N$ plus $H\cdot$), m/z 72 ($C_4H_{10}N^+$ loss of 142 Da like hydrosulfonylbenzene, by cleavage of N–S bond); m/z 150 ($C_6H_8NO_2S^+$ corresponds to then neutral loss of 64 Da as SO_2 , also observed in positive polarity for sulfonamide fragmentation.^[3–5]

Lower intensity fragments at this energy are m/z 77.03859 corresponding to $C_6H_5^+$, generated by loss of 137 Da as $C_4H_{11}NSO_2$ by cleavage of S–Ar bond, and m/z 72.02077 ($C_4H_{10}N^+$ loss of 142 Da like $PhSO_2H$) by cleavage of S–N bond. At higher CID energies of 35 and 40 eV additional ions at m/z 95, 105, 106 originate from complicated rearrangements implying loss of SO and HNO.^[4]

We also identified the sodium adduct $[M+Na]^+ C_{10}H_{15}O_2NSNa^+$ at m/z 236.07140, the ammonium adduct $[M+NH_4]^+ C_{10}H_{18}N_2O_2S^+$ at m/z 231.11614 and the potassium adduct $[M+K]^+ C_{10}H_{14}NO_2S K^+$ at m/z 252.04545.

Carboxylic acids

Carboxylic acids are readily ionised in negative mode as deprotonated molecular ion ($[M-H]^-$); Losses of H_2O are likely due to dehydration from aliphatic hydroxyl groups.^[6] However, in specific cases a loss of water can be also observed from aliphatic monocarboxylic acids. Neutral loss of 44, indicative of decarboxylation^[7] was commonly observed.

m/z 89.02431 ($C_3H_5O_3^-$) at 25 eV the main fragment is 71 (loss of 18Da, H_2O), MS^3 of that fragment does not generate any fragments that indicate that the compound is an α -hydroxyl carboxylic acid. The formula was tentatively identified as **2-hydroxypropanoic acid or lactic acid**.

Peaks corresponding to other organics such as **oxalic acid** $C_2HO_4^-$ (m/z 88.98785), **malonic acid** $C_3H_3O_4^-$ (m/z 103.00347), **succinic acid** $C_4H_5O_4^-$ (m/z 117.01916), **benzoic acid** (m/z 121.02936), **phthalic acid** $C_7H_5O_2^-$ (m/z 165.01885), were also observed in our samples and confirmed with standard solutions.

The fragmentation pattern of alkyl mono carboxylic acids was dominated by loss of H_2O from the carboxyl moiety and very low-intensity peaks generated from C–C bond cleavage in the alkyl chain. For example m/z 115.07632 ($C_6H_{11}O_2^-$) has a main fragment at 25 eV at m/z 97 ($C_6H_9O^-$ loss of water) and m/z 71.01 (loss of 44 Da as C_3H_8 due to C–C cleavage. This compound was identified as **lactic acid**.

m/z 129.09191 ($C_7H_{13}O_2^-$) tentatively identified as **heptanoic acid**. The main observed fragment at 35 eV are m/z 111.05 ($C_7H_{11}O^-$ loss of water), m/z 83 ($C_5H_7O^-$ loss of 46 Da as water plus C_2H_4), m/z 85 ($C_4H_5O_2^-$ loss of 44 Da as C_3H_8), m/z 101 ($C_5H_9O_2^-$ loss of 28 Da as C_2H_4) with lower intensity ions at m/z 71 ($C_3H_3O_2^-$ loss of 58 Da, i.e. C_4H_{10}), m/z 67 ($C_4H_3O^-$ loss of 62 Da i.e. water plus 44 Da (C_3H_8)), m/z 59 ($C_2H_3O_2^-$ corresponding to the anion of acetic acid generated by a loss of 70Da as C_5H_{10}).

***m/z* 143.10762** ($C_8H_{15}O_2^-$) tentatively identified as **octanoic acid** has main fragment ions at *m/z* 125.06 ($C_8H_{13}O^-$ loss of water), *m/z* 99.08 ($C_5H_7O_2^-$ loss of 44 Da, i.e. C_3H_8) and *m/z* 97.07 ($C_5H_5O_2^-$ loss of 46 Da, i.e. C_3H_8 and H_2). Lower intensity ions were detected at *m/z* 80.94 (loss of 62 Da, i.e. water and 44 Da (C_3H_8)), *m/z* 69.61 ($C_4H_5O^-$ loss of 74 Da, i.e. water plus 56 Da (C_4H_8)), *m/z* 74.95 (loss of 68 Da, i.e. C_5H_8), *m/z* 70.09 ($C_4H_5O^-$ loss of water and 52 Da (C_4H_4)).

***m/z* 157.12329** ($C_9H_{17}O_2^-$) tentatively identified as **nonanoic acid**. At 35 eV the main ions are *m/z* 93 ($C_6H_5O^-$ loss of 64 Da, i.e. H_2O plus 44 Da (C_3H_8) plus H_2), *m/z* 139 ($C_9H_{15}O^-$ loss of H_2O), *m/z* 113 ($C_6H_9O_2^-$ loss of 44 Da (C_3H_8)), *m/z* 129 ($C_7H_{13}O_2^-$ loss of 28 Da (C_2H_4)), *m/z* 111 ($C_6H_7O_2^-$ loss of 46 Da, i.e. $C_3H_8 + H_2$), *m/z* 97 ($C_6H_9O^-$ loss of 60 Da, i.e. $H_2O + 42$ Da (C_3H_6)), *m/z* 115 ($C_6H_{11}O_2$ loss of 42 Da (C_3H_6)). Lower intensity ions were observed at *m/z* 83.14 ($C_5H_7O^-$ loss of 74 Da from H_2O plus 56 Da (C_4H_8)), *m/z* 65.1 (C_4HO^- loss of 92 Da, from the fragment observed at *m/z* 93 followed by a loss of 28 Da (C_2H_4)) and *m/z* 59 corresponding to the anion of acetic acid.

In addition, MS^3 of the fragment *m/z* 139 ($C_9H_{15}O^-$) at 25 eV produces three main fragments at *m/z* 111 ($C_7H_{11}O^-$ loss of H_2O), *m/z* 97 ($C_6H_9O^-$, loss of 42 Da (C_3H_6)) and *m/z* 121 ($C_8H_9O^-$, loss of water); MS^3 of *m/z* 111 ($C_6H_7O_2^-$) produces ions at *m/z* 83 ($C_5H_7O^-$ loss of 28 Da (C_2H_4)), and *m/z* 93 ($C_6H_5O^-$ loss of H_2O), which confirm the proposed structure.

***m/z* 145.05099** ($C_6H_9O_4^-$) was tentatively identified as an **alkylated C_6 -dicarboxylic acid**, e.g. dimethylsuccinic acid. Main fragment were observed at 15 eV at *m/z* 83 (C_5H_7O loss of 62 Da i.e. CO_2 plus H_2O), *m/z* 101 ($C_5H_9O_2^-$ loss of 44 Da, i.e. CO_2), *m/z* 127 ($C_6H_7O_3^-$ loss of water). Lower intensity ions were observed at *m/z* 118 ($C_4H_6O_4^-$ loss of 27 Da i.e. C_2H_2 plus H), *m/z* 99 ($C_5H_7O_2^-$ loss of 46 i.e. CO_2 plus H_2 or formic acid), *m/z* 81 ($C_5H_5O^-$ loss of 64 Da i.e. $CO_2 + H_2O + H_2$).

***m/z* 147.02968** ($C_5H_7O_5^-$) was tentatively identified as **hydroxypentanedioic acid**. Main fragments were observed at 25 eV at *m/z* 128 ($C_5H_5O_4^-$ neutral loss of H_2O indicative of a presence of one hydroxyl), *m/z* 103 ($C_4H_7O_3^-$ neutral loss of 44 Da, i.e. CO_2 , indicative of a presence of one carboxylic group), *m/z* 85 ($C_4H_5O_4^-$ neutral loss of 62 Da, i.e. $CO_2 + H_2O$) indicative of one carboxylic group followed by the hydroxy group,^[8] *m/z* 61 (HCO_3^- , neutral loss of 86 Da, i.e. $C_4H_6O_2$).

***m/z* 171.10241** ($C_9H_{15}O_3^-$) and ***m/z* 171.13877** ($C_{10}H_{19}O_2^-$). For the C_9 species higher intensity fragments were observed than for the C_{10} compound. At 25 eV the main observed fragments were *m/z* 127 ($C_8H_{15}O$ loss of CO_2), *m/z* 153 ($C_9H_{13}O_2$ loss of water), *m/z* 125 ($C_8H_{13}O^-$ loss of 46 Da, i.e. $CHOOH$), *m/z* 83 ($C_5H_7O^-$ loss of 88 Da, i.e., CO_2 plus C_3H_8) and *m/z* 96 ($C_4HO_3^-$ due to a neutral loss of 74 Da, i.e. $C_5H_{12} + H_2$), *m/z* 169 ($C_9H_{13}O_3^-$ loss of H_2), *m/z* 111 ($C_7H_{11}O^-$ loss of 60 Da). MS^3 of 127.11308 ($C_8H_{15}O^-$), at 30 eV shows fragments at *m/z* 125 ($C_8H_{13}O^-$ due to a loss of H_2), *m/z* 71 ($C_4H_7O^-$) and *m/z* 53 ($C_3H_2O^-$ due to the C–C cleavage of the alkyl chain, with a loss of 56 Da, i.e. C_4H_8).

This fragmentation pathway is consistent with the observed in previous studies of oxo-carboxylic acids^[9] and laboratory experiments of oleic acid degradation products and the $C_9H_{15}O_3^-$ compound was tentatively identified as **oxononanoic acid**.

$C_{10}H_{19}O_2^-$ was tentatively identified as **decanoic acid**. As expected the fragments are similar to the monocarboxylic acids described before. Main fragments include at 35 eV m/z 127 ($C_7H_{11}O_2$ loss of 44 Da ((C_3H_8)) followed by m/z 125 ($C_8H_{13}O$ loss of 46 Da explained by loss of water plus C_2H_4), m/z 83 (C_5H_7O due to a loss of $H_2O + C_5H_{10}O$), m/z 111 ($C_7H_{11}O^-$ loss H_2O plus 42 Da, i.e. C_3H_6).

m/z **187.09807** ($C_9H_{15}O_4^-$) was tentatively identified as **azaleic acid**. At 25 eV the main fragment is m/z 125 ($C_8H_{13}O^-$ due to a loss of 62 Da, from a combined loss of H_2O and CO_2 , typical for diacids with $C > 6$).^[6] Other lower intensity fragments include m/z 143 ($C_8H_{15}O_2^-$ loss of CO_2), m/z 97 ($C_6H_9O^-$ due to a loss of 90 Da, i.e. H_2O plus CO_2 plus C_2H_4), m/z 169 ($C_9H_{13}O_3^-$ loss of H_2O), m/z 141 ($C_8H_{13}O_2^-$ loss of 46 Da), m/z 160 ($C_7H_{12}O_4^-$ loss of 27 Da, explained by the loss of 26 (C_2H_2) and H^-); m/z 111 ($C_7H_{11}O^-$ loss of 76Da, i.e. $H_2O + C_2H_2O_2$) m/z 123 ($C_8H_{11}O^-$ loss of 64 Da), m/z 83 ($C_5H_7O^-$ loss of 104 Da).

m/z **281.24900** ($C_{18}H_{33}O_2^-$) was tentatively identified as **oleic acid**.^[10] The main fragments at 40 eV are m/z 263 ($C_{18}H_{31}O$ loss of water), m/z 237 ($C_{15}H_{25}O_2$ loss of 44 Da (C_3H_8)), m/z 219 ($C_{15}H_{23}O^-$ loss of 62 Da, i.e. water + C_3H_8), m/z 97 ($C_5H_5O_2^-$ loss of 184 Da i.e. $C_{13}H_{26}$: $CH_3(CH_2)_7CH=CH(CH_2)_2CH_3$ plus H_2), m/z 155.17 ($C_9H_{15}O_2$, loss of 126 Da), which is one of the most important fragments because it shows the position of a $C=C$ bond; m/z 183.19 ($C_{11}H_{19}O_2^-$, loss of 98Da), m/z 125.14 ($C_7H_9O_2^-$ loss of 156 Da), m/z 111 ($C_6H_7O_2^-$ loss of 170 Da). In addition, the loss of CH_2 units were observed: m/z 251 ($C_{16}H_{27}O_2$), m/z 237 ($C_{15}H_{25}O_2$), m/z 223 ($C_{14}H_{23}O_2^-$), m/z 209 ($C_{13}H_{21}O_2^-$), m/z 195 ($C_{12}H_{19}O_2^-$), m/z 181 ($C_{11}H_{17}O_2^-$), m/z 167 ($C_{10}H_{15}O_2^-$); m/z 141 ($C_8H_{13}O_2^-$); m/z 127 ($C_7H_{11}O_2^-$), m/z 113 ($C_6H_9O_2^-$), m/z 99 ($C_5H_7O_2^-$) and m/z 85 ($C_4H_5O_2^-$).

N-containing compounds

m/z **154.01436** ($C_6H_4O_4N^-$) was tentatively identified as **nitro catechol**. At 30 eV the main fragments are m/z 124 ($C_6H_4O_3^-$, loss of 30Da, i.e. NO); m/z 123 ($C_6H_3O_3^-$ loss of 31Da, i.e. HNO), m/z 95 ($C_5H_3O_2^-$ due to the loss of 59 Da, i.e. $HNO-CO$) and m/z 108 ($C_6H_4O_2^-$, i.e. loss of 46 Da (NO_2)). The fragment pattern is consistent with reports in literature.^[11]

m/z **100.07565** ($C_5H_{10}ON^+$) detected in positive mode was tentatively identified as **pentamide**: Most abundant fragments at 35 eV are m/z 72 (C_3H_6NO loss of 28 Da from the alkyl chain), m/z 83 ($C_5H_7O^+$ loss of 17 Da, NH_3 indication of an amino group), and m/z 82 ($C_5H_8N^+$ loss of H_2O), m/z 58 ($C_3H_8N^+$ loss of 42 Da) and m/z 59 ($C_3H_7O^+$ loss of 41 Da, i.e. C_2H_3N), indicatives of an amide functionality.^[10,12] Other fragments: m/z 72 ($C_3H_6NO^+$ loss of 28 Da), and m/z 57 ($C_3H_5O^+$ loss of 43 Da, i.e. C_2H_5N). This compound belongs to the same homologous series as oleamide.

***m/z* 198.18530** ($C_{12}H_{24}ON^+$) detected in positive mode was tentatively identified as **dodecamide**. Main fragments at 35 eV are *m/z* 163 ($C_{12}H_{19}$ loss of 35 Da, i.e. NH_3 and water indicative of an amide functionality), *m/z* 180 ($C_{12}H_{22}N$ loss of water). Less intense ions are *m/z* 97 (C_7H_{13} loss of 101Da), *m/z* 83.14 ($C_6H_{11}^+$ loss of 115Da), *m/z* 69 (C_3H_9 loss of 129Da), *m/z* 128 ($C_7H_{16}ON$ loss of 70Da, i.e. C_5H_{10}). Those pathways are similar to the ones observed for oleamide and other fatty acid amides.^[10] In MS^3 of *m/z* 180 the following fragments were observed: *m/z* 163 ($C_{12}H_{19}^+$ loss of 17 Da, i.e. NH_3 , which confirms the amide functionality), *m/z* 152 ($C_{10}H_{18}N^+$ loss of 28 Da, i.e. C_2H_4), *m/z* 138 ($C_9H_{16}N^+$ loss of 42 Da (C_3H_8)), *m/z* 124 ($C_8H_{14}N^+$ loss of 56 Da (C_4H_8)), *m/z* 110 ($C_7H_{12}N^+$ loss of 70 Da (C_5H_{10})).

S-containing compounds

***m/z* 277.18379** ($C_{14}H_{29}SO_3^-$) was tentatively identified as **tetradecanesulfonic acid**. The main fragments observed are: *m/z* 233 ($C_{11}H_{21}SO_3^-$ loss of 44 Da (C_3H_8)), *m/z* 205 ($C_9H_{17}SO_3^-$ loss of 72 Da, (C_5H_{12})), *m/z* 134 ($C_4H_6SO_3^-$), *m/z* 81 (corresponds to HSO_3^-) those last ions are the indicatives of the presence of SO_3H in the parent compound. Lower intensity ions are; *m/z* 259 ($C_{14}H_{27}SO_2^-$ loss of water), *m/z* 249 ($C_{12}H_{25}SO_3$ loss of 28 Da (C_2H_4)), *m/z* 97 (CH_5O_3S , loss of 180 Da), *m/z* 121 ($C_3H_5SO_3$ loss of 156 Da ($C_{11}H_{24}$)). Other lower intensity peaks are, *m/z* 221 ($C_{10}H_{21}SO_3^-$ loss of 56 Da (C_4H_8)), *m/z* 189 ($C_9H_{17}SO_2^-$ loss of 88 Da probably water plus 70 Da from C_5H_{10}), *m/z* 176 ($C_7H_{12}SO_3$ loss of 101), *m/z* 156 ($C_7H_8SO_2$ loss of 120 Da), *m/z* 147 ($C_5H_7SO_3$), *m/z* 121 ($C_{14}H_{29}SO_3$ loss of 156Da ($C_{11}H_{24}$)).

***m/z* 305.211606** ($C_{16}H_{33}SO_3^-$) was tentatively identified as **hexadecanesulfonic acid**. Main fragment is *m/z* 80.93 corresponding to HSO_3 . Fragments of alkyl chain are very similar to the fragmentation pattern of $C_{14}H_{29}SO_3^-$, indicating that two species belong to the same compound class. At 25 eV main fragments are *m/z* 249 ($C_{12}H_{23}SO_3^-$ loss of 56 Da), *m/z* 261 ($C_{13}H_{25}SO_3^-$ loss of 44 Da (C_3H_8)), *m/z* 229 ($C_{13}H_{25}SO_3^-$ loss of 76Da (C_5H_{12})).

***m/z* 311.16910** ($C_{17}H_{27}SO_3^-$), possibly a **derivative of benzene sulfonic acid**. Main fragments at 25 eV are *m/z* 183 ($C_8H_7SO_3^-$, which may contain an aromatic ring due to the high DBE = 4), *m/z* 197 ($C_9H_9SO_3^-$ loss of 114Da from the alkyl chain), *m/z* 89 ($C_2H_2O_2S$).

***m/z* 239.02278** ($C_7H_{11}O_7S^-$) possibly an **organo sulfate**. At 35 eV, the main fragments are *m/z* 195 ($C_6H_{11}O_5S$ loss of CO_2 imply a carboxylic acid functionality), *m/z* 221 ($C_7H_9O_6S^-$ loss of water), *m/z* 96 (HSO_4^-), *m/z* 178 (loss of 60.18 Da), Fragments at *m/z* 81 corresponds to HSO_3^- (loss of 158 Da) and *m/z* 97 (HSO_4^-) are indicative of sulfate groups.

Figs S1 and S2 show the same dataset as in Fig. 2 and 3 in the main paper, displaying the full range of the O/C and H/C ratios.

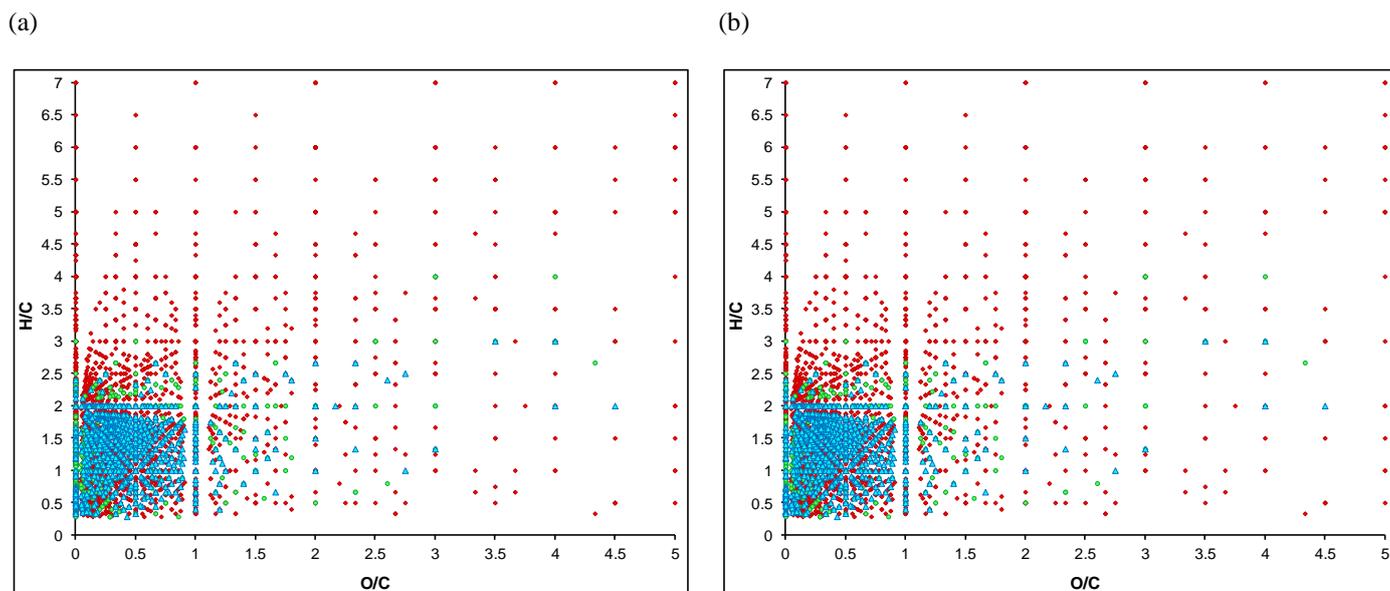


Fig. S1. Elemental ratio H/C v. O/C of each formula detected in the (a) summer and (b) winter sample for the whole data set. N-containing compounds (◆), CHOS and CHS subgroups (●), CHO compounds (▲). Data were recorded in negative polarity.

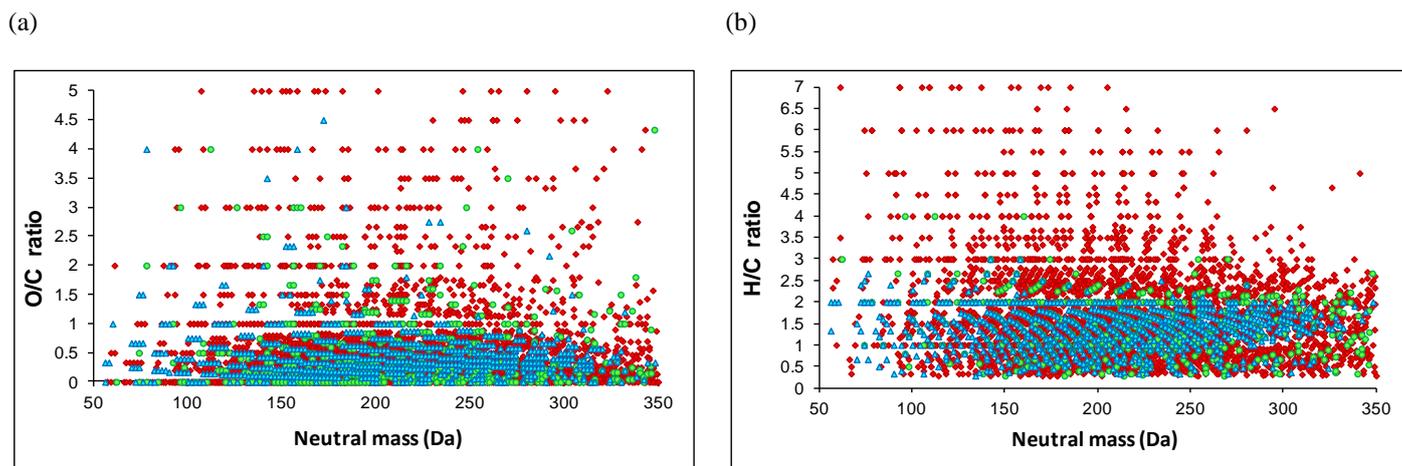


Fig. S2. (a) O/C and (b) H/C of compounds detected in the summer sample as a function of their neutral molecular mass for the whole dataset.

Fig. S3 shows Kendrick mass defect (KMD) (CH_2) series in the CHO subgroup only found in summer. One of the longest CH_2 series in Fig. S3 contains six members of which the smallest compound has an elemental composition of $\text{C}_{11}\text{H}_7\text{O}_2^-$ ($m/z = 171.04515$, DBE = 8), which was tentatively identified as naphthoic acid or methylnaphthalenedione (see inset in Fig. S4). This series is also highlighted with a red line in Fig. 5.

Fig. S4 shows all series (marked with different colour) in which the formula $\text{C}_{11}\text{H}_8\text{O}_2$ is included using several different KMD reference masses as indicated in the caption of Fig. S4. Thus, besides being part of a CH_2 series $\text{C}_{11}\text{H}_7\text{O}_2$ is also part of a series with a mass difference of H_2O (up to $\text{C}_{11}\text{H}_{18}\text{O}_7$), a series with a mass difference of H_2 (up to $\text{C}_{11}\text{H}_{22}\text{O}_2$), a series with a mass difference of O

(up to $C_{11}H_8O_5$), a series with a mass difference of CO (up to $C_{13}H_8O_4$), and series with a mass differences of CH_2O , H_2O_2 , CH_4 , CH_2O_3 and CH_3O .

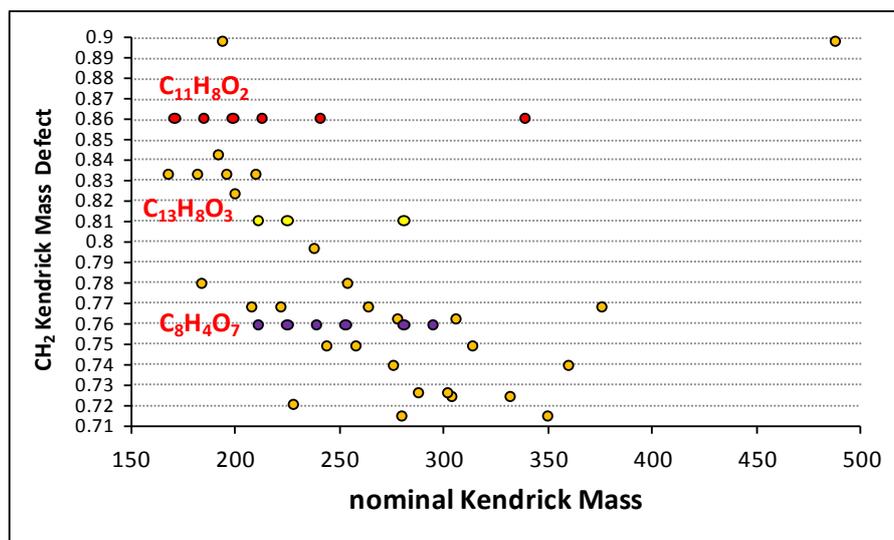


Fig. S3. KMD (CH_2) series only present in summer samples of the CHO subgroup (negative polarity, DBE > 5). The formulas indicate the initial compound of the CH_2 -series.

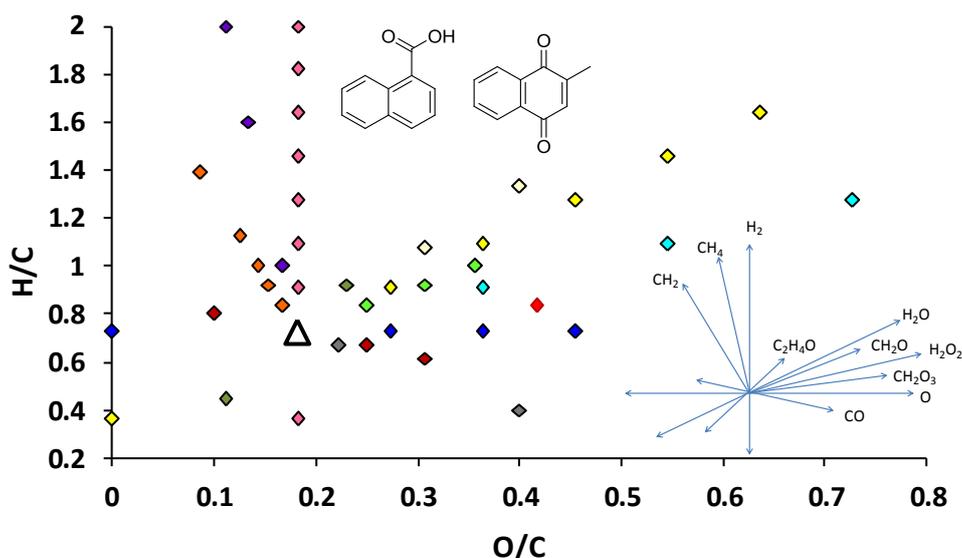


Fig. S4. O/C v. H/C of homologous series containing $C_{11}H_8O_2$ (Δ). Colours indicate different KMD reference masses of the homologous series: CH_2 (\blacklozenge), H_2O (\blacklozenge), O (\blacklozenge), CO (\blacklozenge), H_2 (\blacklozenge), C_2H_4O (\blacklozenge), CH_4 (\blacklozenge), CH_2O (\blacklozenge), C_2H_2 (\blacklozenge), H_2O_2 (\blacklozenge), CH_2O_3 (\blacklozenge). The CH_2 series is only present in summer. The inset contains two of the possible structures for $C_{11}H_8O_2$ and the indication of their related KMD series.

Fig. S5 shows the difference in distribution of components from different subgroups as observed in positive and negative polarity.

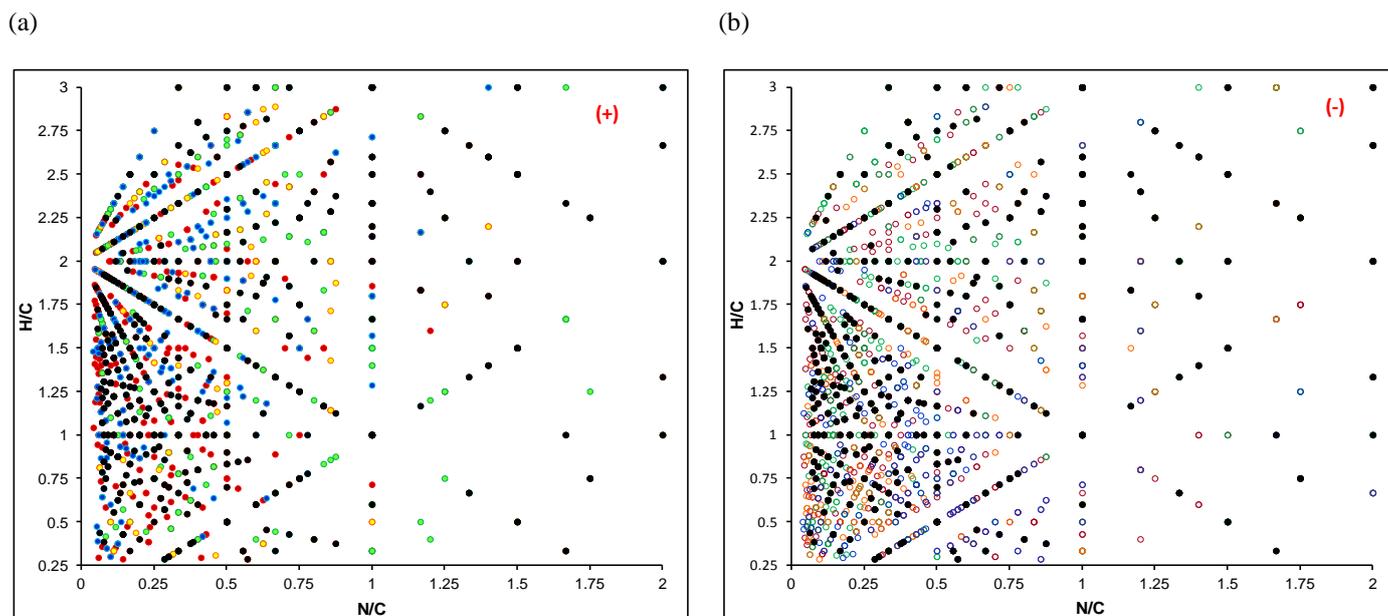


Fig. S5. N-containing compounds (a) positive polarity (b) negative polarity. Black full signs represent the components measured in both polarities. CHNO (red), CHNOS (green), CHNS (yellow), CHN (blue).

References

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