Supporting Information

NMR Aerosolomics: A tool for analysis of polar compounds in atmospheric aerosols

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Table S1. List of the compounds supplemented into the ChemomX database.

| Chenomx ID | Compound                             | M   | CAS RN   |
|------------|--------------------------------------|-----|----------|
| 100001     | methanesulfonic acid                 | 96.11 | 75-75-2 |
| 100002     | trimesic acid                        | 210.14 | 554-95-0 |
| 100004     | dimethylsulfate                      | 126.13 | 77-78-1 |
| 100005     | isophthalic acid                     | 166.13 | 121-91-5 |
| 100006     | 3,4-dihydrobenzoic acid              | 154.12 | 99-50-3 |
| 100007     | 3-hydroxybenzoic acid                | 138.12 | 99-06-9 |
| 100008     | terephthalic acid                    | 166.13 | 100-21-0 |
| 100009     | 4-hydroxybenzaldehyde                | 122.12 | 123-08-0 |
| 100010     | syringaldehyde                       | 182.17 | 134-96-3 |
| 100011     | hydroxymethanesulfonic acid          | 96.10  | 6035-47-8 |
| 100012     | 4-oxopimelic acid                    | 174.15 | 502-50-1 |
| 100013     | 1,2,4-benzenetetracarboxylic acid    | 210.14 | 528-44-9 |
| 100014     | hydroxymalonic acid                  | 120.06 | 80-69-3 |
| 100015     | 4-methylcatechol                     | 124.14 | 452-86-8 |
| 100016     | 4-acetylbutyric acid                 | 130.14 | 3128-06-1 |
| 100017     | glyoxylic acid                       | 74.04  | 298-12-4 |
| 100018     | pyromellitic acid                    | 254.15 | 89-05-4 |
| 100019     | 4-nitrophenol                        | 139.11 | 100-02-7 |
| 100020     | 2-hexanone                           | 180.16 | 591-78-6 |
| 100021     | 5-oxoazelaic acid                    | 202.20 | 57822-06-7 |
| 100022     | 2-methylbutyric acid                 | 102.13 | 116-53-0 |
| 100023     | ethanesulfonic acid                  | 110.13 | 594-45-6 |
| 100024     | methanedisulfonic acid               | 176.17 | 503-40-2 |
| 100025     | ethyl sulfate                        | 126.13 | 540-82-9 |
| 100026     | methanesulfonic acid                 | 80.11  | 17696-73-0 |
| 100027     | hydroxymethanesulfonic acid          | 112.11 | 870-72-4 |
| 100028     | isethionic acid                      | 126.13 | 107-36-8 |
| 100029     | 3-mercapto-1-propanesulfonic acid    | 156.22 | 49594-30-1 |
| 100030     | cis-2-butene-1,4-diol                | 88.11  | 6117-80-2 |
| 100031     | tricarballylic acid                  | 176.12 | 99-14-9 |
| 100032     | ribitol                              | 152.15 | 488-81-3 |
| 100033     | hexanoic acid                        | 116.16 | 142-62-1 |
| 100034     | ethylenediamine                      | 60.10  | 107-15-3 |
| 100035     | nitromethane                         | 61.04  | 75-52-5 |
| 100036     | diethylamine                         | 73.14  | 109-89-7 |
| 100037     | triethylamine                        | 101.19 | 121-44-8 |
| 100038     | nitropropane                         | 89.09  | 108-03-2 |
| 100039     | triethanolamine                      | 149.19 | 102-71-6 |
| 100040     | dipropylamine                        | 101.19 | 142-84-7 |
| 100041     | tripropylamine                       | 143.27 | 102-69-2 |
| 100042     | phthalimide                          | 147.13 | 85-41-6 |
| 100043     | 3-hydroxy-1-propanesulfonic acid     | 140.16 | 15909-83-8 |
| 100044     | mesaconic acid                      | 130.10 | 498-24-8 |
| 100045     | 1,2-dihydroxy-1,2-ethanedisulfonic acid | 222.19 | 18381-20-9 |
| 100046     | 2,5-furan dicarboxylic acid         | 156.09 | 3238-40-2 |
| 100047     | xylitol                              | 152.15 | 87-99-0 |
| 100048     | heptanoic acid                       | 130.18 | 111-14-8 |
| 100049     | cis-pinonic acid                     | 184.23 | 17879-35-5 |
Figure S1. $^1$H NMR spectrum of winter aerosol sample QB390 (PM$_{10}$, upper trace) and blank sample (lower trace).
Table S2. Combining of summer samples together according to similar weather conditions during sample collection.

| Date      | $T_{max}$ [°C] | $T_{min}$ [°C] | Rainfall [mm] | Solar radiation [h] | Particle size [$\mu$m] | Code | Blending (label) |
|-----------|----------------|----------------|---------------|----------------------|------------------------|------|-----------------|
| 25.06.2008 | 30.0           | 13.0           | 10.1          | 7.8                  | 10                     | Q6143| 1 (Q6143)       |
| 01.07.2008 | 27.0           | 10.2           | 0             | 15.3                 | 2.5                    | Q6149| 2 (B6149)       |
| 07.07.2008 | 20.0           | 13.0           | 2             | 2.8                  | 2.5*                   | QB153| 3 (QB153)       |
| 07.07.2008 | 20.0           | 13.0           | 2             | 2.8                  | 10*                    | Q6155| 4 (QB6155)      |
| 13.07.2008 | 15.4           | 11.0           | 12.7          | 0                    | 2.5                    | Q6157| 5 (QB6157)      |
| 19.07.2008 | 23.7           | 12.8           | 0             | 4.3                  | 2.5                    | Q6161| 3 (QB6153)      |
| 19.07.2008 | 23.7           | 12.8           | 0             | 4.3                  | 10                     | Q6163| 6 (QB6163)      |
| 25.07.2008 | 27.6           | 14.6           | 20.3          | 5.2                  | 2.5                    | Q6165| 7 (QB6165)      |
| 25.07.2008 | 27.6           | 14.6           | 20.3          | 5.2                  | 10                     | Q6167| 8 (QB6167)      |
| 31.07.2008 | 30.0           | 14.4           | 0             | 11.0                 | 2.5                    | Q6169| 9 (QB6169)      |
| 31.07.2008 | 30.0           | 14.4           | 0             | 11.0                 | 10                     | Q6171| 8 (QB6171)      |
| 06.08.2008 | 25.6           | 10.8           | 0             | 12.3                 | 2.5                    | Q6173| 2 (QB6149)      |
| 06.08.2008 | 25.6           | 10.8           | 0             | 12.3                 | 10                     | Q6174| 10 (QB6175)     |
| 12.08.2008 | 28.8           | 16.0           | 1.2           | 3.5                  | 2.5                    | Q6177| 9 (QB6169)      |
| 18.08.2008 | 28.7           | 14.0           | 7.8           | 11.8                 | 2.5                    | Q6181| 7 (QB6156)      |
| 24.08.2008 | 20.4           | 7.8            | 0.2           | 2.8                  | 10                     | Q6187| 4 (QB6155)      |
| 30.08.2008 | 23.1           | 8.6            | 0             | 8.4                  | 2.5                    | Q6189| 3 (QB6153)      |
| 30.08.2008 | 23.1           | 8.6            | 0             | 8.4                  | 10                     | Q6191| 6 (QB6163)      |
| 05.09.2008 | 25.7           | 14.0           | 0.2           | 5.3                  | 10                     | Q6193| 10 (QB6175)     |
| 05.09.2008 | 25.7           | 14.0           | 0.2           | 5.3                  | 2.5                    | Q6195| 2 (QB6149)      |

*misclassified samples according to particle size

Table S3. Combining of winter samples together according to similar weather conditions during sample collection.

| Date      | $T_{max}$ [°C] | $T_{min}$ [°C] | Rainfall [mm] | Snowfall [cm] | Solar radiation [h] | Particle size [$\mu$m] | Code | Blending (label) |
|-----------|----------------|----------------|---------------|---------------|----------------------|------------------------|------|-----------------|
| 06.11.2008 | 8.2            | 5.6            | 0             | 0             | 0                    | 2.5                    | Q8140| 1 (Q8140)       |
| 28.11.2008 | 1.2            | -1.5           | 0             | 0             | 0.1                  | 1.7                    | Q8176| 2 (Q8176)       |
| 28.11.2008 | 1.2            | -1.5           | 0             | 0             | 1.7                  | 10                     | Q8178| 3 (Q8178)       |
| 03.01.2009 | -3.6           | -12.6          | 0             | 1             | 7.2                  | 2.5                    | Q8180| 4 (Q8180)       |
| 03.01.2009 | -3.6           | -12.6          | 0             | 1             | 7.2                  | 10                     | Q8182| 5 (Q8182)       |
| 09.01.2009 | -9.0           | -11.4          | 0             | 6             | 0                    | 2.5                    | Q8184| 4 (Q8180)       |
| 15.01.2009 | 0.4            | -7.5           | 0             | 5             | 0                    | 2.5                    | Q8188| 4 (Q8180)       |
| 15.01.2009 | 0.4            | -7.5           | 0             | 5             | 0                    | 10                     | Q8190| 6 (Q8190)       |
| 15.01.2009 | 0.4            | -7.5           | 0             | 5             | 0                    | 10                     | Q8449| 6 (Q8190)       |
| 21.01.2009 | 1.0            | -1.2           | 0.7           | 0             | 0                    | 2.5                    | Q8192| 7 (Q8192)       |
| 21.01.2009 | 1.0            | -1.2           | 0.7           | 0             | 0                    | 10                     | Q8194| 8 (Q8194)       |
| 21.01.2009 | 1.0            | -1.2           | 0.7           | 0             | 0                    | 10                     | Q8451| 8 (Q8194)       |
| 27.01.2009 | 2.0            | -1.1           | 0             | 0             | 0                    | 2.5                    | Q8407| 7 (Q8192)       |
| 08.02.2009 | 2.0            | -2.0           | 0             | 0             | 0.4                  | 2.5                    | Q8515| 7 (Q8192)       |
| 04.03.2009 | 7.0            | 2.0            | 0             | 0             | 0                    | 2.5                    | Q8531| 9 (Q8531)       |
| 10.03.2009 | 6.0            | 0.9            | 5.5           | 0             | 1.7                  | 2.5                    | Q8535| 9 (Q8531)       |
| 16.03.2009 | 8.6            | 3.7            | 0.5           | 0             | 1.0                  | 2.5                    | Q8539| 10 (Q8539)      |
| 16.03.2009 | 8.6            | 3.7            | 0.5           | 0             | 1.0                  | 10                     | Q8541| 11 (Q8541)      |
| 22.03.2009 | 6.6            | -0.4           | 0             | 0             | 1.0                  | 2.5                    | Q8543| 10 (Q8539)      |
| 28.03.2009 | 14.3           | 3.4            | 0.2           | 0             | 1.6                  | 10                     | Q8561| 11 (Q8541)      |
| Compound               | S4.1 | S4.2 | S4.3 | S4.4 | S4.5 | S4.6 | S4.7 | S4.8 | S4.9 | S5.1 | S5.2 | S5.3 | S5.4 | S5.5 | S5.6 |
|-----------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Sulfocyanate acid     | 0.0757 | 0.0333 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| 2-Hydroxybenzenesulfonic acid | 0.0647 | 0.0333 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| Hydroxylized benzenesulfonic acid | 0.0717 | 0.0361 | 0.0165 | 0.0905 | 0.0785 | 0.0384 | 0.0762 | 0.0797 | 0.0732 | 0.0303 | 0.0391 | 0.0131 | 0.0135 | 0.0121 | 0.0309 |
| Sulfocyanate acid | 0.0305 | 0.0222 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| 2-Hydroxybenzenesulfonic acid | 0.0647 | 0.0333 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| Hydroxylized benzenesulfonic acid | 0.0717 | 0.0361 | 0.0165 | 0.0905 | 0.0785 | 0.0384 | 0.0762 | 0.0797 | 0.0732 | 0.0303 | 0.0391 | 0.0131 | 0.0135 | 0.0121 | 0.0309 |
| Sulfocyanate acid | 0.0305 | 0.0222 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| 2-Hydroxybenzenesulfonic acid | 0.0647 | 0.0333 | 0.0097 | 0.0738 | 0.0612 | 0.0305 | 0.0694 | 0.0610 | 0.0564 | 0.0263 | 0.0351 | 0.0103 | 0.0105 | 0.0089 | 0.0252 |
| Hydroxylized benzenesulfonic acid | 0.0717 | 0.0361 | 0.0165 | 0.0905 | 0.0785 | 0.0384 | 0.0762 | 0.0797 | 0.0732 | 0.0303 | 0.0391 | 0.0131 | 0.0135 | 0.0121 | 0.0309 |

Note: underlined compounds have adjusted P-value <0.01 after Benjamini-Hochberg correction.
Spiking experiments

The spiking experiments were performed during revision process of the manuscript on editor’s request in order to confirm the presence of new compounds in aerosol samples. For this purpose, all samples of winter aerosol were merged into one sample. The original summer samples were not available any more, therefore, different samples which were collected at the same location in 2016 were merged and used in these experiments. Approximately one third of the sample was used for spiking \(^1\)H NMR experiments and the rest of the sample was used for analysis by complementary techniques (see below). The spiking experiments were performed at 500 MHz NMR spectrometer. The \(^1\)H NMR spectra were recorded before and after addition of a solution containing approx. 0.01 mM of compound standards. Figures S2-S3 show a comparison of relevant parts of the original and spiked spectra for 10 compounds. The spiking experiments were performed only for assigned compounds that have not been identified in atmospheric aerosol samples before, namely 2-hydroxyisobutyric, 2-oxoisocaproic, 3-hydroxyisovaleric, 4,6-dioxoheptanoic, glucaric and hydroxymethanesulfonic acids. The spiking experiments confirmed three of these compounds - 2-hydroxyisobutyric, 3-hydroxyisovaleric and 4,6-dioxoheptanoic acids, other three compounds were not confirmed due to low concentration. Moreover, four compounds were proposed to be present in atmospheric aerosols by several studies, but have not yet been identified, specifically trimethylglycine, methanesulfinic acid, propylene glycol and imidazole. First three compounds were confirmed by the spiking experiments, whereas the signals of imidazole disappeared from the original aerosol sample analyzed due to hydrogen-deuterium exchange.

![Spiking experiments](image)

Figure S2. \(^1\)H NMR spectrum before (a) and after (b) spiking experiment in the sample of summer aerosol.
Figure S3. $^1$H NMR spectrum before (a) and after (b) spiking experiment in the sample of winter aerosol.

A compound assignment and its quantification in Chenomx

The spectrum of QB167 summer sample was chosen for presentation of compound assignment using Chenomx software. The first trace in Figure S8 shows the assignment of arabitol (blue) and mannitol (red). The isolated signals of both compounds are well recognized guiding the compound identification and the concentration of compound is then derived according to the best fit of all signals. Next two traces show glucose (red) versus the already assigned pattern (blue). Levoglucosan (red) on the fourth trace shows three isolated signals used for compound identification and the rest of the fitted signals in the crowded region. The fifth trace shows hydroxyacetone (left, red) with one isolated signal and one in the shoulder of another signal, while phthalate (right, red) represents a diluted compound. In this case, the spectrum fit provides more accurate concentration than a plain signal integration. Trehalose on the sixth trace is another example of compounds suffering from severe signal overlap. Cis-pinonic acid on seventh and eighth trace is another example of compound with two isolated signals and a severe signal overlap of the rest of the molecule.
Figure S4. The assignment and compound fitting in the Chenomx software; 1) mannitol (red) and arabitol (blue), 2) and 3) glucose (red), 4) levoglucosan (red), 5) hydroxyacetone (left-red), phthalic acid (right-red), 6) trehalose (red), 7) and 8) cis-pinonic acid (red).
Complementary analyses

Ion chromatography

The content of anions, cations and carbohydrates in merged summer and winter aerosol samples were analyzed by ion chromatography (Dionex 5000 system). An IonPac AS11-HC 2 x 250 mm column was used for anions using concentration gradient of hydroxide eluent, IonPac CS18 2 x 250 mm for cations using methanesulfonic acid solution as an eluent. Both anion and cation set-up lines were equipped with electrochemical suppressors. External calibration was done provided using NIST traceable calibration solutions. Carbohydrate analysis was performed on Thermo Scientific ICS5000+ system (former Dionex) equipped with High pressure anion exclusion chromatography with pulsed amperometric detection (HPAE PAD). The filtered solution was analyzed using Dionex CarboPac MA1 4x250mm + guard 4x50mm column, NaOH gradient, ICS-5000+ ED detector in PAD mode with disposable gold electrode.

Gas chromatography – mass spectrometry

Samples for GC-MS analysis were derivatized by silylation. A lyophilized sample was silylated by N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) in a pyridine/heptane mixture at 75°C for 2 hours. The reaction mixture was then subjected to GC-MS (HP 5973, Hewlett Packard). The compound separation was achieved by interaction with the standard DB-5MS stationary phase. The compound identification was based on its elution time and ion fragmentation.

2D NMR spectroscopy

COSY spectra of merged summer and winter aerosol samples were measured using a Varian Inova 500 MHz spectrometer equipped with the Ultra Shim System II. A 5 mm probe with inner 1H coil for maximum sensitivity was used for the experiment. The residual solvent signal is suppressed by presaturation. COSY spectra were acquired at 25°C with 1 s presaturation, 0.2 s acquisition, 1 s relaxation delay, 6 kHz spectral width and 400 accumulation scans per 256 increments. Total experimental time was 36 hours (Figures S5 and S6).

A HSQC spectrum of merged winter sample was collected on Bruker Advance III HD 600 MHz instrument equipped with a cryo-probe using hsqcetgp experiment at the Institute of Organic Chemistry and Biochemistry in Prague. The spectrum was acquired at 25°C with, 0.08 s acquisition, 1.5 s relaxation delay, 6.6 kHz (1H) and 30 kHz (13C) spectral width and 128 accumulation scans per 256 increments. Total experimental time was 15 hours (Figure S7).

A comparison of chemical composition in summer and winter aerosol sample obtained by different methods is summarized in Table S5.

Table S5. An overview of chemical composition of aerosol samples obtained by different methods.

|                  | 1D NMR | 2D NMR | GC-MS | IC | Spiking |
|------------------|--------|--------|-------|----|---------|
| 2,3-Dihydroxy-2-methylpropanoic acid | ✔      | ✔      |       |    |         |
| 2-Hydroxybutyric acid | ✔      | ✔      |       |    |         |
| 2-Hydroxyglutaric acid | ✔      |       | ✔     |    |         |
| 2-Hydroxysobutyric acid | ✔      | ✔      |       | ✔  |         |
| 2-Methylglutaric acid | ✔      | ✔      |       |    |         |
| 2-Oxoglutaric acid | ✔      | ✔      |       |    |         |
| 3,4-Dihydroxybenzoic acid | ✔      | ✔      |       |    |         |
| 3-Hydroxybenzoic acid | ✔      | ✔      |       |    |         |
| 3-Hydroxybutyric acid | ✔      | ✔      |       |    |         |
| 3-Hydroxyisovaleric acid | ✔      | ✔      |       |    |         |
| 3-Hydroxypropanoic acid | ✔      | ✔      |       |    |         |
| 4,6-Dioxoheptanoic acid | ✔      | ✔      |       |    |         |
| 4-Hydroxybutyric acid | ✔      | ✔      |       |    |         |
| Chemical Name                      | Presence | Notes |
|-----------------------------------|----------|-------|
| 4-Oxopimelic acid                | ✓        |       |
| Acetamide**                       | ✓        |       |
| Acetic acid                       | ✓        | ✓     |
| Acetoacetic acid**                | ✓        |       |
| Adipic acid                       | ✓        | ✓     |
| Alanine                           | ✓        | ✓     |
| Arabitol                          | ✓        | ✓     |
| Azelaic acid                      | ✓        |       |
| Benzoic acid                      | ✓        |       |
| Butyric acid**                    | ✓        |       |
| Capric acid                       | ✓        |       |
| Caprylic acid                     | ✓        |       |
| cis-Pinonic acid*                 | ✓        |       |
| Citraconic acid                   | ✓        |       |
| Diethylyamine                     | ✓        | ✓     |
| Dimethyl sulfate**                | ✓        |       |
| Dimethyl sulfone**                | ✓        |       |
| Dimethylamine*                    | ✓        |       |
| D-Threitol                        | ✓        | ✓     |
| Erythritol                        | ✓        | ✓     |
| Ethanol                           | ✓        | ✓     |
| Ethanolamine                      | ✓        | ✓     |
| Ethyl sulfate**                   | ✓        |       |
| Ethylene glycol**                 | ✓        |       |
| Ethylenediamine**                 | ✓        |       |
| Formic acid                       | ✓        | ✓     |
| Fructose                          | ✓        | ✓     |
| Fructose                          | ✓        | ✓     |
| Fumaric acid                      | ✓        | ✓     |
| Galactosan                        | ✓        |       |
| Galactose                         | ✓        |       |
| Glucitol                          | ✓        | ✓     |
| Glucose                           | ✓        | ✓     |
| Glutaric acid                     | ✓        | ✓     |
| Glyceric acid                     | ✓        |       |
| Glycerol                          | ✓        | ✓     |
| Glycine                           | ✓        | ✓     |
| Glycolic acid                     | ✓        | ✓     |
| Glyoxylic acid**                  | ✓        |       |
| Heptanoic acid                    | ✓        |       |
| Hexanoic acid**                   | ✓        |       |
| Hydroxyacetone**                  | ✓        |       |
| Hydroxymalonic acid**             | ✓        |       |
| Hydroxymethanesulfonic acid*      | ✓        |       |
| Imidazole*                        | ✓        |       |
| Inositol                          | ✓        | ✓     |
| Isopropanol                       | ✓        | ✓     |
| Lactic acid                       | ✓        | ✓     |
| Lactose**                         | ✓        |       |
| Chemical Name               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
|-----------------------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Levoglucosan                | ✓ | ✓ | ✓ | ✓ | ✓ | | | | | | | | | | | | | | | | | | | | | | |
| Levulinic acid              | ✓ | ✓ | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Maleic acid                 | ✓ | ✓ | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Malic acid                  | ✓ | ✓ | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Malonic acid                | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Mannitol                    | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Mannosan                    | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Mannose                     | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methanesulfinic acid        | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methanesulfonic acid        | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methanol**                  | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methylamine*                | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methylmalonic acid**        | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Methylsuccinic acid         | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| N,N-Dimethylformamide**     | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Nonanoic acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Oxalic acid                 | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Phthalic acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Pimelic acid                | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Propionic acid              | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Propylene glycol            | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Pyromellitic acid**         | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Pyruvic acid                | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Sebacic acid                | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Suberic acid**              | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Succinic acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Sucrose                     | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Syringic acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Tartaric acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Terephthalic acid           | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Tetramethylammonium         | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Trehalose                   | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Tricarballylic acid         | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Triethylamine               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Trimethylamine              | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Trimethylglycine            | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Valeric acid**              | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Vanillic acid               | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Xylose                      | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |

*Identification based on available literature

**Tentative assignment based just on precise chemical shift in 1H NMR spectrum.
Figure S5. COSY spectrum of summer aerosol sample.
Figure S6. COSY spectrum of winter aerosol sample.
Figure S7. HSQC spectrum of winter aerosol sample.
Figure S8. The comparison of multivariate statistical analysis in summer aerosol samples; non-targeted analysis (left) and targeted analysis (right).

Figure S9. The comparison of multivariate statistical analysis in winter aerosol samples; non-targeted analysis (left) and targeted analysis (right).

Figure S10. The comparison of multivariate statistical analysis in all aerosol samples; non-targeted analysis (left) and targeted analysis (right).
Table S6. List of statistically significant compounds identified by the Wilcoxon rank-sum test.

| Compound                             | Adjusted P-values from Wilcoxon test |
|--------------------------------------|--------------------------------------|
| 2-Hydroxyisobutyric acid             | 0.00630                              |
| 3-Hydroxyisovaleric acid             | 0.00293                              |
| 4,6-Dioxyoheptanoic acid             | 0.01098                              |
| Adipic acid                          | 0.00151                              |
| Arabinol                             | 0.01098                              |
| Azelaic acid                         | 0.00078                              |
| Butyric acid                         | 0.00741                              |
| cis-Pinonic acid                     | 0.00293                              |
| Dimethylamine                        | 0.00030                              |
| Formic acid                          | 0.00293                              |
| Glucitol                             | 0.00054                              |
| Glucose                              | 0.01006                              |
| Glutaric acid                        | 0.00394                              |
| Glycerol                             | 0.01082                              |
| Hydroxyacetone                       | 0.00630                              |
| Imidazole                            | 0.00293                              |
| Levoglucosan                         | 0.00030                              |
| Malonic acid                         | 0.00748                              |
| Mannitol                             | 0.00630                              |
| Methanesulfonic acid                 | 0.00630                              |
| Methanesulfonic acid                 | 0.00078                              |
| Methylsuccinic acid                  | 0.00293                              |
| Phthalic acid                        | 0.00989                              |
| Pimelic acid                         | 0.00030                              |
| Propionic acid                       | 0.00920                              |
| Sebacic acid                         | 0.00045                              |
| Suberic acid                         | 0.00151                              |
| Terephthalic acid                    | 0.00920                              |
| Trehalose                            | 0.01098                              |
| Trimethylglycine                     | 0.03894                              |
| Valeric acid                         | 0.00293                              |

Note: underlined compounds have adjusted $P$-value <0.01 after Benjamini-Hochberg correction.