Supporting information for

Comparison of Heated Electrospray Ionization and Nanoelectrospray Ionization Sources Coupled to Ultra-High-Resolution Mass Spectrometry for Analysis of Highly Complex Atmospheric Aerosol Samples

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Figure S-1. KMD overlaid plot (for CHO, CHON, CHOS the combined subgroups) from a sample analysed using the HESI source at 350 °C and 200 °C.

Figure S-2. Top panel: VK plots for CHO containing molecular formulae obtained from the HESI and nano-ESI analyses of the aerosol sample subjected to SPE and methanol extraction. Bottom panel: VK plots for CHO containing molecular formulae obtained from the sample extracted with methanol and SPE.

| Sample ID | Sample (stort) | collection | Sample (and) | collection | OC µg/cm ² | OC unc* |
|--------------------------|----------------|------------|--------------|------------|-----------------------|--------------------|
| | (start) | 1 | (end) | | | µg/cm ² |
| | Date | Time | Date | Time | | |
| | DD- | nn:mm | DD- | nn:mm | | |
| | MMM-YY | | MMM- | | | |
| | | | YY | | | |
| UCCIK_07 ¹ | 20-Jul-14 | 19:00 | 21-Jul-14 | 06:59 | 2.54 | 0.33 |
| UCCIK_08 ¹ | 21-Jul-14 | 07:00 | 21-Jul-14 | 18:59 | 2.57 | 0.33 |
| UCCIK_09 ¹ | 21-Jul-14 | 19:00 | 22-Jul-14 | 06:59 | 3.48 | 0.37 |
| UCCIK_10 ¹ | 22-Jul-14 | 07:00 | 22-Jul-14 | 18:59 | 3.33 | 0.37 |
| UCCIK_11 ¹ | 23-Jul-14 | 07:00 | 23-Jul-14 | 18:59 | 5.19 | 0.46 |
| UCCIK_13 ² | 23-Jul-14 | 23:00 | 24-Jul-14 | 02:59 | 4.48 | 0.42 |
| UCCIK_14 ² | 24-Jul-14 | 03:00 | 24-Jul-14 | 06:59 | 2.20 | 0.31 |
| UCCIK_16 ² | 24-Jul-14 | 11:00 | 24-Jul-14 | 14:59 | 4.49 | 0.42 |
| UCCIK_17 ² | 24-Jul-14 | 15:00 | 24-Jul-14 | 18:59 | 6.42 | 0.52 |
| UCCIK_18 ² | 24-Jul-14 | 19:00 | 24-Jul-14 | 22:59 | 4.01 | 0.40 |
| UCCIK_19 ² | 24-Jul-14 | 23:00 | 25-Jul-14 | 02:59 | 4.84 | 0.44 |
| UCCIK_20 ² | 25-Jul-14 | 03:00 | 25-Jul-14 | 06:59 | 3.63 | 0.38 |
| UCCIK_21 ¹ | 25-Jul-14 | 07:00 | 25-Jul-14 | 10:59 | 3.57 | 0.38 |
| UCCIK_22 ¹ | 25-Jul-14 | 11:00 | 25-Jul-14 | 14:59 | 5.53 | 0.48 |
| UCCIK_23 ¹ | 25-Jul-14 | 15:00 | 25-Jul-14 | 18:59 | 5.18 | 0.46 |
| UCCIK_24 ¹ | 25-Jul-14 | 19:00 | 25-Jul-14 | 22:59 | 5.02 | 0.45 |
| UCCIK_25 ¹ | 25-Jul-14 | 23:00 | 26-Jul-14 | 02:59 | 4.96 | 0.45 |
| UCCIK_26 ² | 26-Jul-14 | 03:00 | 26-Jul-14 | 06:59 | 3.47 | 0.37 |
| UCCIK_27 ² | 26-Jul-14 | 07:00 | 26-Jul-14 | 10:59 | 2.14 | 0.31 |
| UCCIK_28 ² | 26-Jul-14 | 11:00 | 26-Jul-14 | 14:59 | 2.4 | 0.32 |
| UCCIK_29 ² | 26-Jul-14 | 15:00 | 26-Jul-14 | 18:59 | 2.88 | 0.34 |
| UCCIK_FB1 ^{1,2} | 28-Jul-14 | 11:00 | 28-Jul-14 | 11:02 | 0.17 | 0.21 |
| UCCIK_FB2 ^{1,2} | 28-Jul-14 | 11:03 | 28-Jul-14 | 11:05 | 0.12 | 0.21 |
| UCCIK_FB3 ^{1,2} | 28-Jul-14 | 11:06 | 28-Jul-14 | 11:08 | 0.24 | 0.21 |

Table S-1. Atmospheric aerosol filter sample collection periods and corresponding Organic Carbon (OC) concentration on the collected filters.

* UNC is an associated uncertainty (1 standard deviation). UCCIK_FB01- UCCIK_FB03 are procedural blank samples.

¹Samples used for SPE and methanol extraction experiments

²Samples used for salt spiking experiments



Figure S-1. KMD overlaid plot (for CHO, CHON, CHOS the combined subgroups) from a sample analysed using the HESI source at 350 °C (red crosses) and 200 °C (black circles).



Figure S-2. Top panel: VK plots for CHO containing molecular formulae obtained from the HESI (plot a) and nano-ESI (plot b) analyses of the aerosol sample subjected to SPE (blue circles) and methanol (red crosses) extraction. Bottom panel: VK plots for CHO containing molecular formulae obtained from the sample extracted with methanol (plot c) and SPE (plot d). The red crosses in plots c and d correspond to data obtained from HESI and black squares correspond to data obtained from nano-ESI source.