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Supplement of

Evaluation of the performance of a particle concentrator for online instrumentation

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Supplements

Table S1. The shift of particles size for monodisperse AS and DOS particles in the m-VACES.

Particle size (nm)	AS % (nm)	DOS % (nm)
50	20 (10)	30 (5.9)
70	7.7 (5.4)	7.7 (5.4)
100	4.0 (4.0)	4.0 (4.0)
200	3.5 (7.0)	3.5 (7.0)
300	0.0 (0.0)	0.0 (0.0)

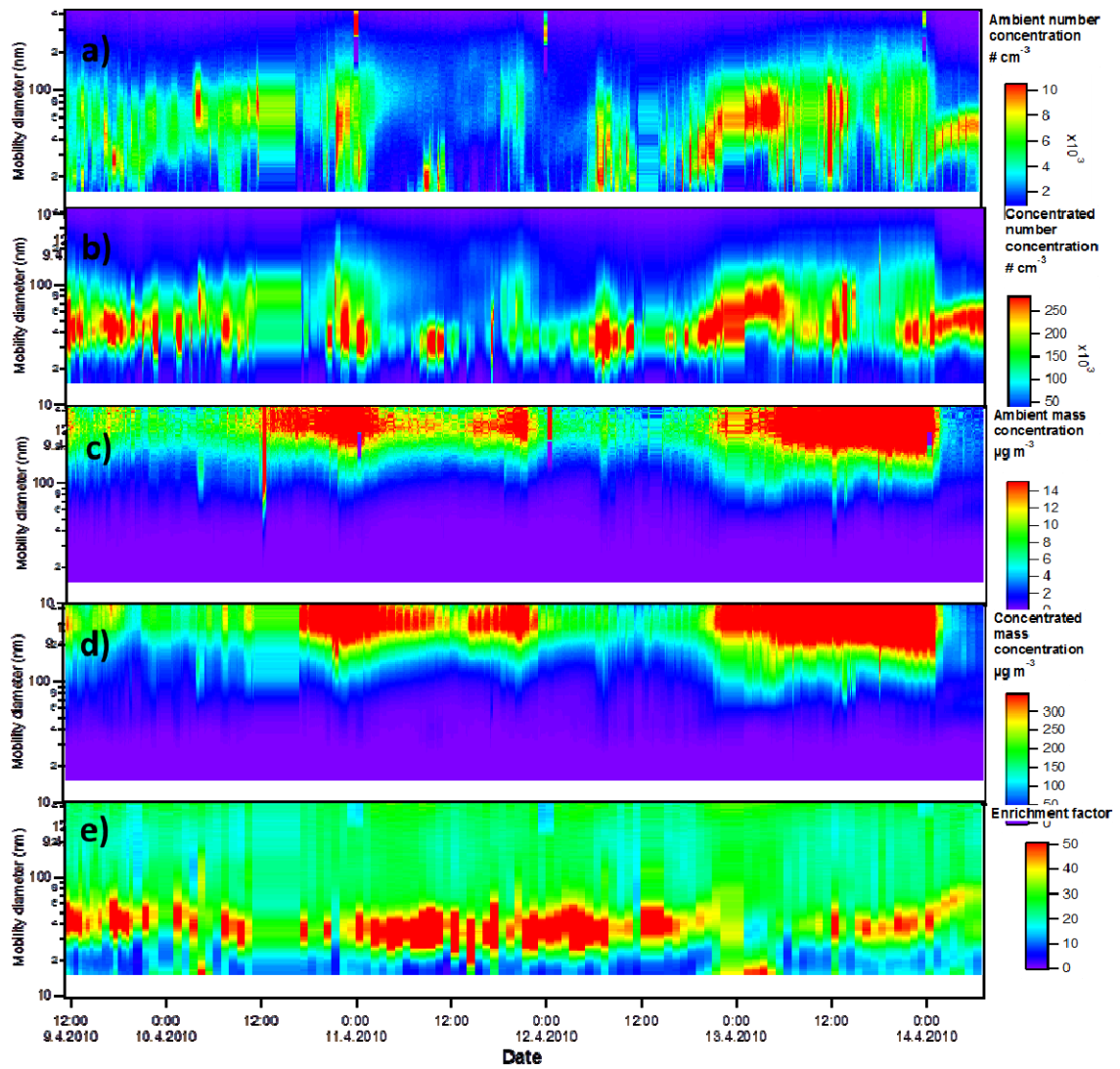


Fig. S1. Time series for the size distributions of particle number (a-b), mass (c-d) and enrichment factor. (a) and (c) are for ambient and (b) and (d) for concentrated aerosol. Particle mass was calculated by using the density of 1.48 g cm^{-3} .

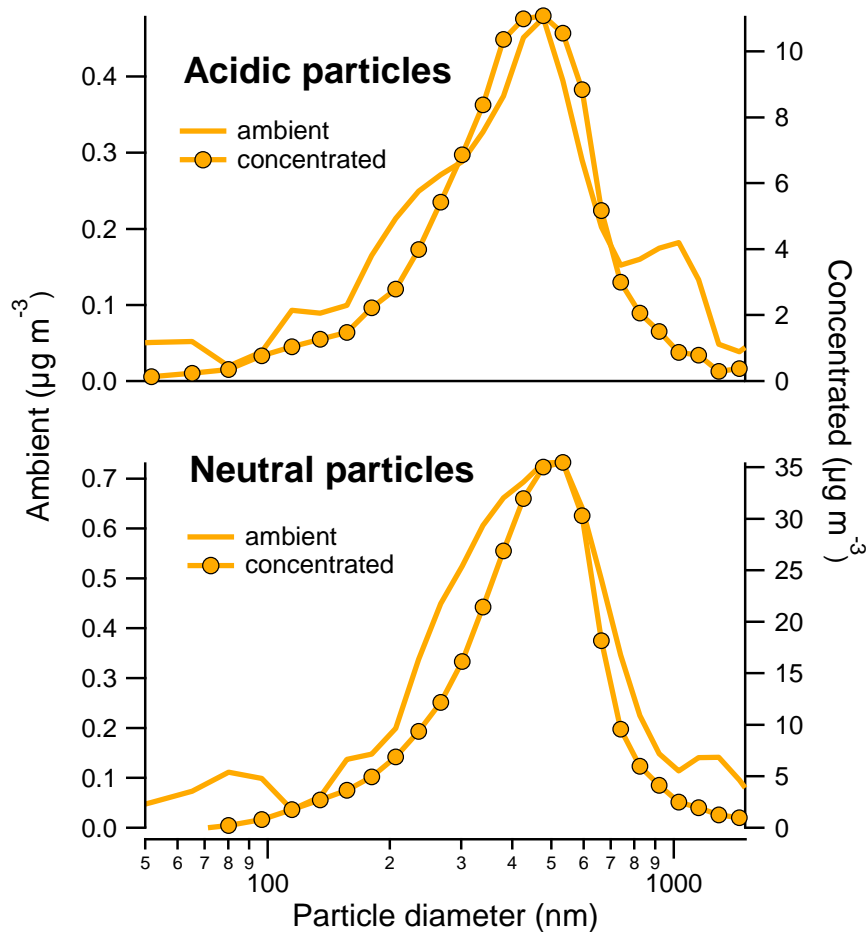


Fig. S2. Size distribution of ammonium during the period when the particles were acidic (April 12, 2010) and nearly neutral (April 13, 2010; 6 am to midnight). Ambient size distributions were smoothed by one point.

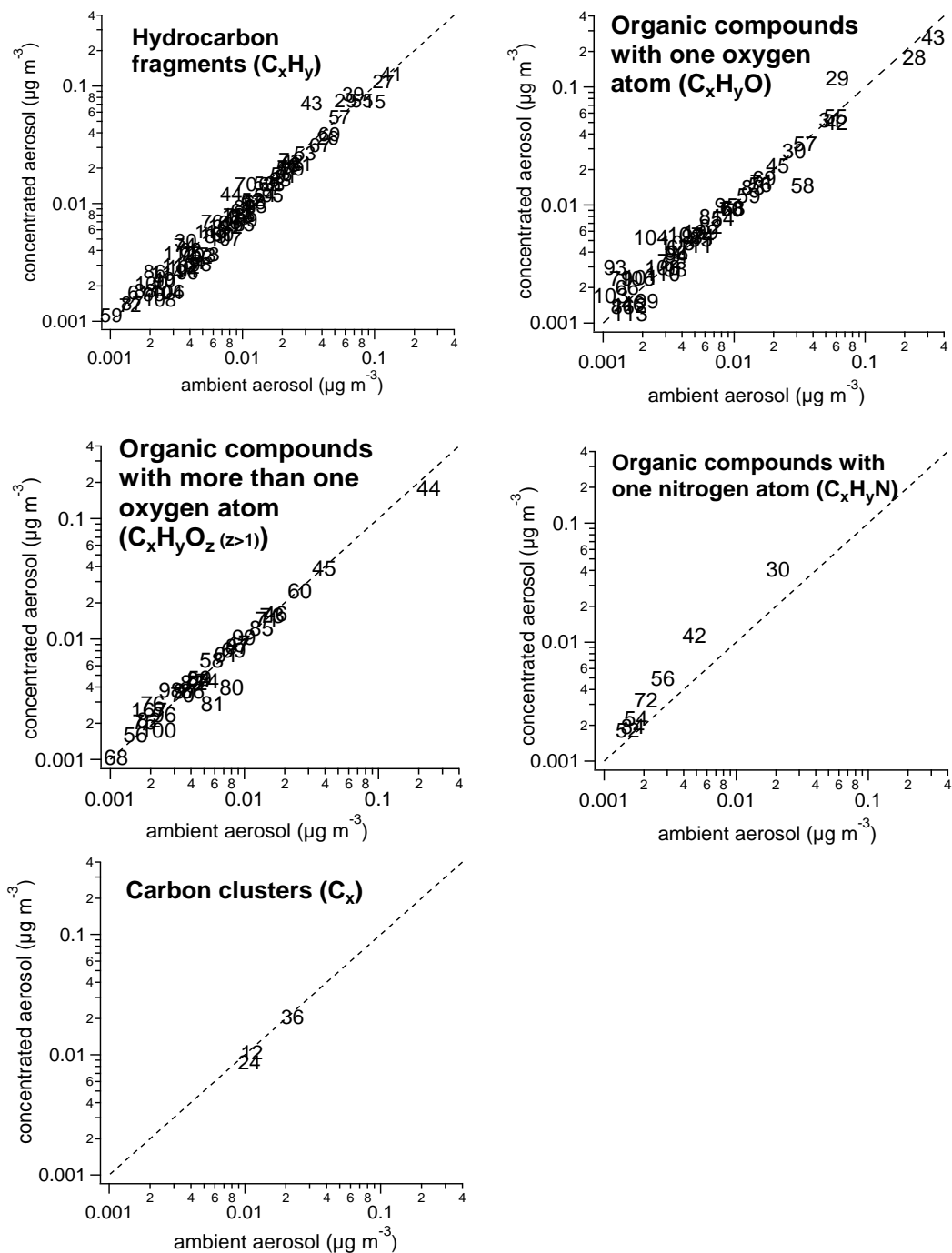


Fig. S3. Scatter plots of the mass fragments in ambient and concentrated OA separated into different compound classes. Carbon clusters (C_x) were measured only with the laser on and the concentration of C_1 (m/z 12) according to the fragmentation Table in Onasch et al. (2012). Concentrated aerosol is divided by the average EF for organics (27.08; a, c-e) and r-BC (37.61; b) (Table 2). One to one ratio is shown by dash lines.

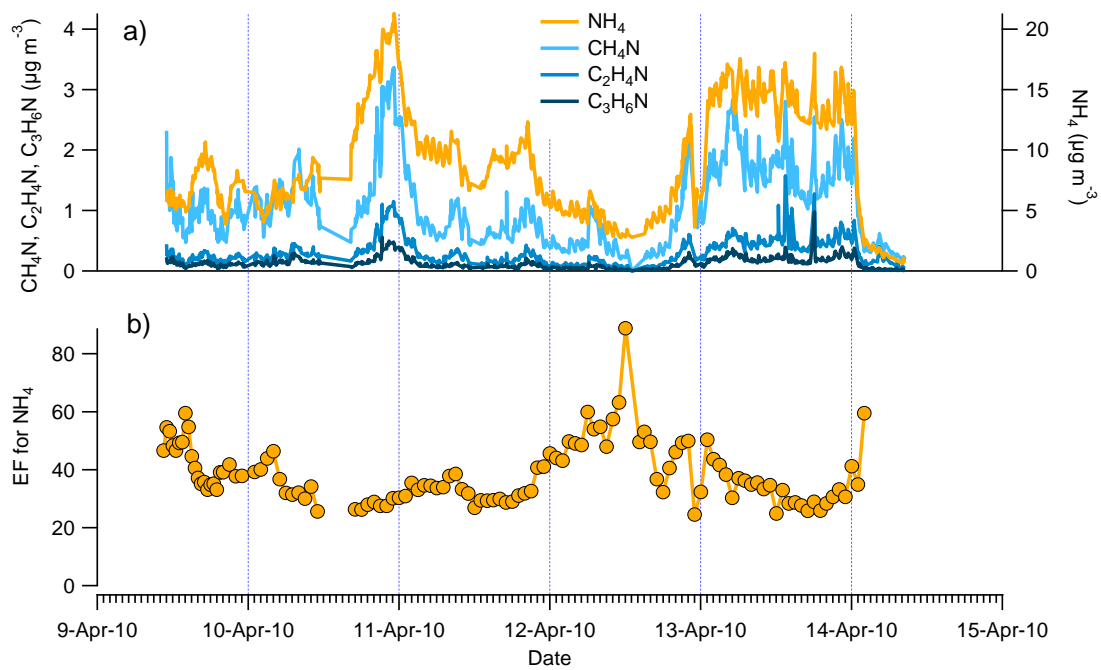


Fig. S4. Time series of ammonium and amines for the concentrated aerosol (a) and the enrichment factor for ammonium (b).

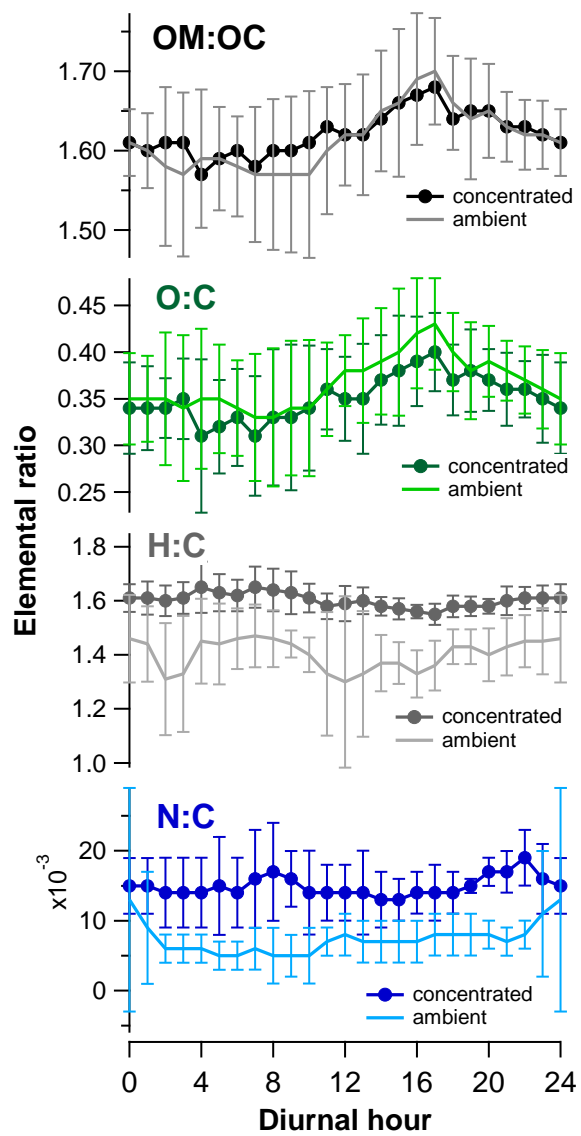


Fig. S5. Diurnal trends for OM:OC, O:C, H:C and N:C for concentrated and ambient OA.

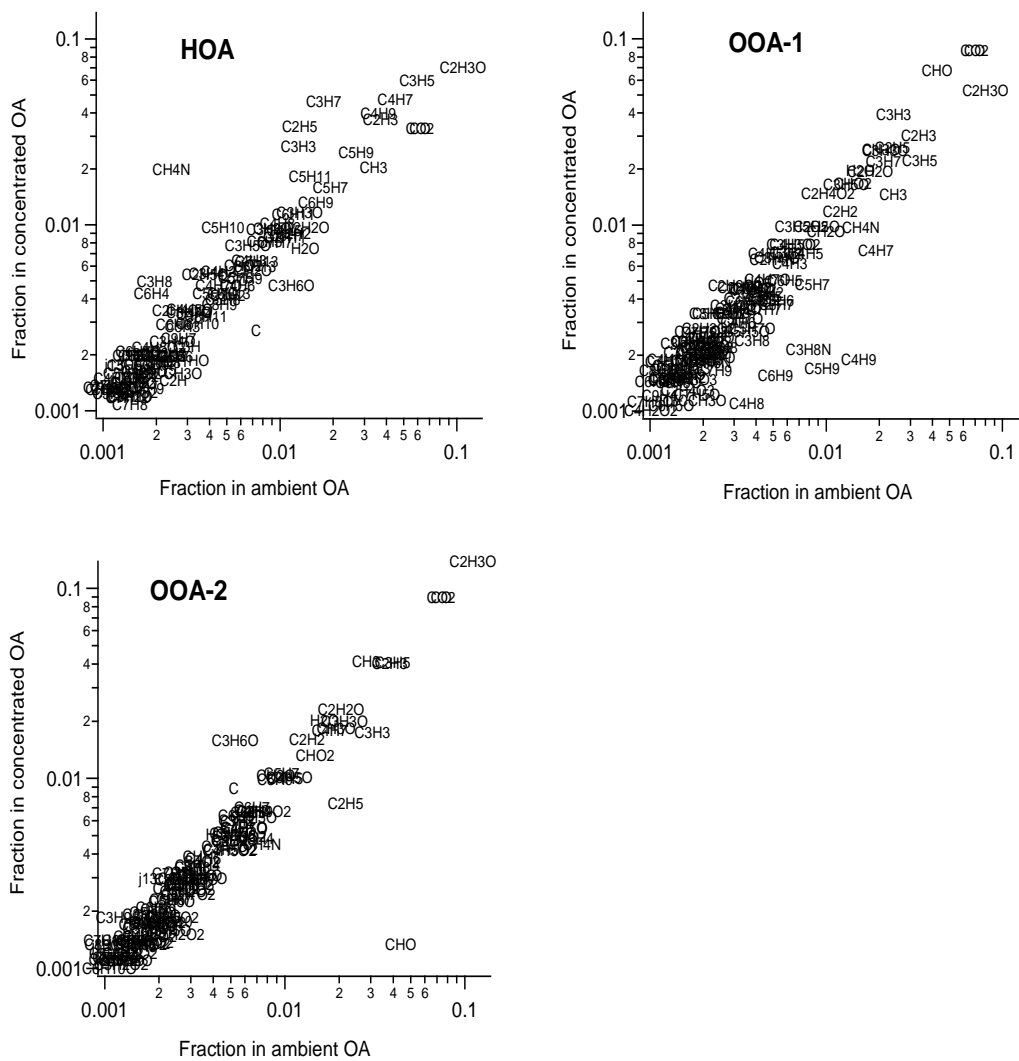


Fig. S6. Correlation of mass spectra for PMF factors for ambient and concentrated OA.

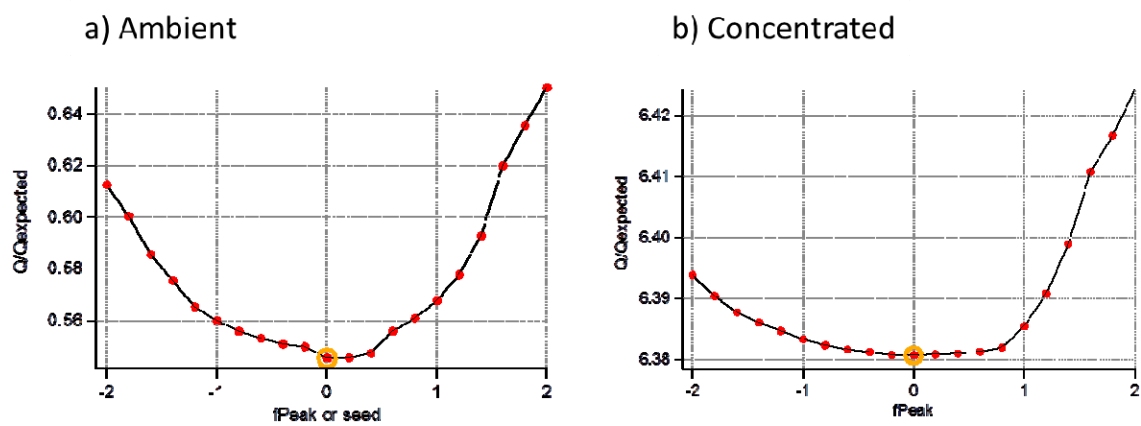
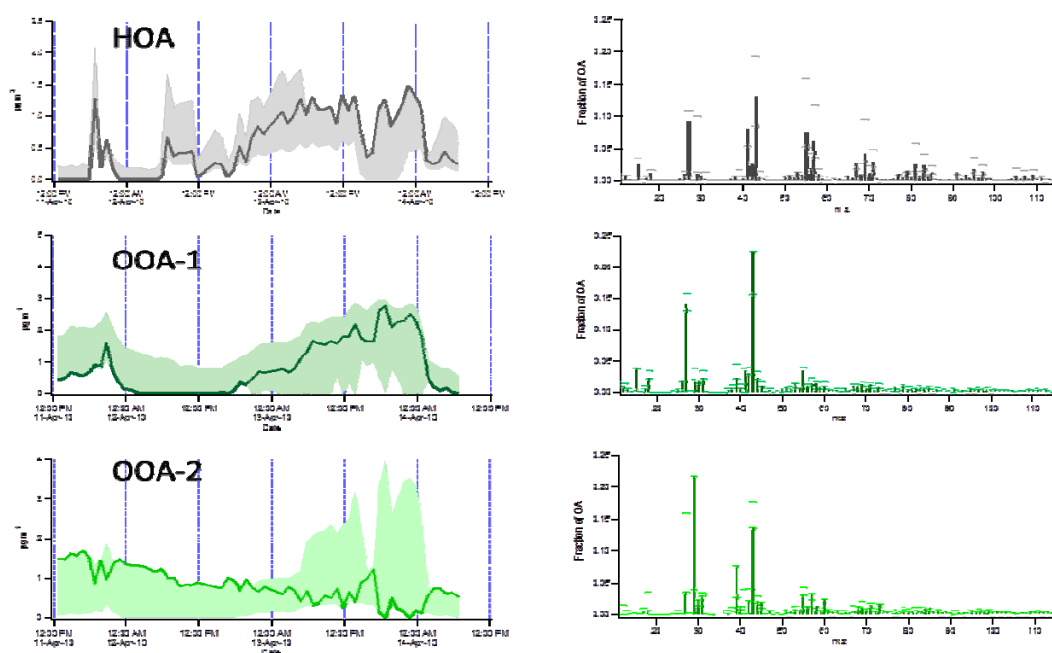


Fig. S7. The variation of Q/Q_{expected} with the value of f_{PEAK} for ambient (a) and concentrated (b) PMF solution.

a) Ambient



b) Concentrated

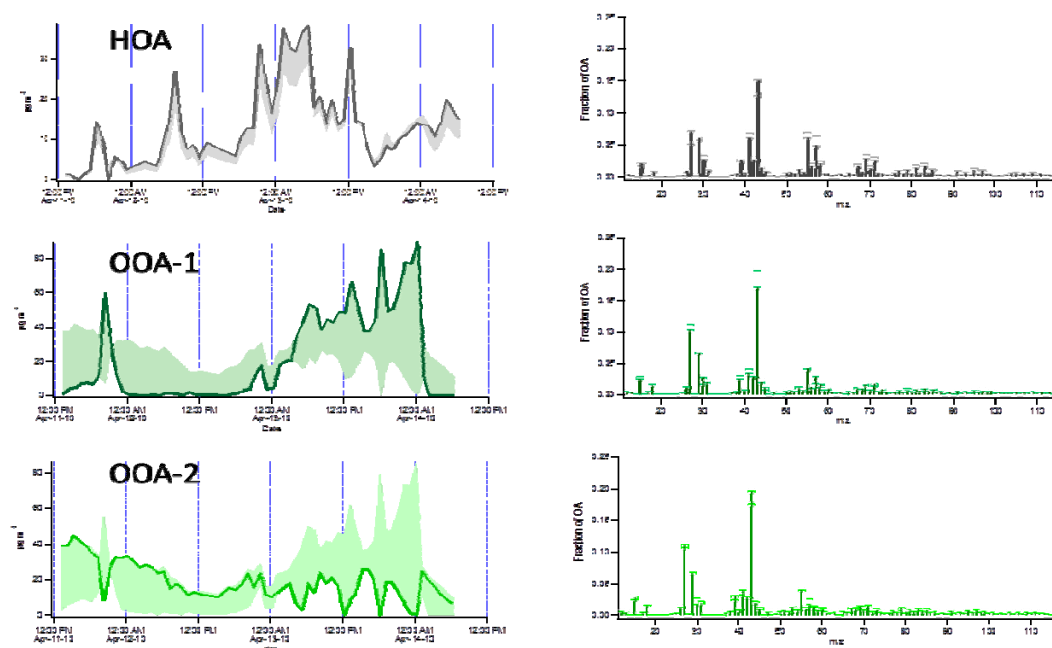


Fig. S8. The variation of time series and mass spectra for the PMF factors with the fPEAK values from -0.4 to 1.6. Ambient (a) and concentrated (b) OA.

Detection of trace elements

HR-AMS can detect several trace elements with lower melting and boiling points in near real-time (Salcedo et al., 2012), and furthermore, the SP-AMS can detect some additional metals and trace elements due to the laser vaporizer (Onasch et al., 2012). However, the concentrations of trace metals are typically very low in ambient air, especially in Finland, and therefore their real-time detection is challenging. Thus the use of a concentrator may allow the real-time detection of elements that otherwise could not be observed.

Five trace elements were detected in ambient air without the m-VACES; aluminum, vanadium, iron, zinc and rubidium. Except zinc, all of the elements were most likely associated with the laser vaporization as there was a steep drop in the recorded concentrations when the laser vaporizer was switched off. Rubidium can undergo surface ionization with a tungsten vaporizer making its quantification difficult (Drewnick et al., 2006), similar to sodium and potassium. In this study surface ionization in tungsten vaporizer was not likely to be a confounding issue, as rubidium seemed to be totally vaporized by the laser and not hit the tungsten vaporizer, however, surface ionization can also take place on the hot surface of the r-BC particles discussed more in Carbone et al. (2014). Slow evaporation is another issue related to the detection of semi-refractory elements with the AMS, requiring special data analysis procedures (Salcedo et al., 2012). Zinc signals were consistent with slow evaporation at tungsten vaporizer the ratio of closed to open being around 0.70 and 0.25 for ambient and concentrated aerosol, respectively (Fig. S9). However, a part of the difference could be due to the uncertainty in the detection of low signal for Zn.

Trace elements gave rather similar EFs to the other species measured, however, the standard deviations for EFs were large probably due to the high uncertainty associated with the determination of their low ambient concentrations (Table 2). Of all the elements, rubidium had the smallest enrichment factor and aluminum the highest. EFs were calculated for the most abundant isotopes (m/z 26.982 for Al, m/z 50.944 for V, m/z 55.935 for Fe, m/z 84.912 for Rb), except for zinc that was detected at the isotope ^{68}Zn (m/z 67.925). All the other isotopes of V, Fe and Zn could not be resolved from the

neighboring peaks or were below their detection limits. The isotopic ratio of ^{85}Rb and ^{87}Rb is shown in Fig. S10 for open and closed modes. The isotopic ratio of ^{87}Rb to ^{85}Rb was near the natural isotopic ratio of 0.386 for both the modes. Unfortunately, it was not possible to investigate size-dependent EFs for trace elements as they composed only a minor fraction of the total signal at each unit mass. Additionally, due to the limited data coverage from the laser vaporizer, diurnal patterns for the EF could not be calculated.

Aluminum, iron and rubidium correlated with r-BC. This suggests that they have similar combustion-related origins in Helsinki, mostly in the form of traffic sources, either from exhaust or non-exhaust (e.g. road dust) emissions. Zinc has been shown to be associated with regional or long-range transported air masses in Helsinki whereas vanadium has more local sources like heavy oil combustion (Pakkanen et al., 2001).

Besides those five trace elements that were detected in ambient air without the concentrator, three additional elements were detected only with the m-VACES. These elements were strontium, zirconium and cadmium (Fig. S11) and they were identified based on their exact m/z . Strontium was detected at m/z 87.906 and zirconium at m/z 89.905 that were their most abundant isotopes. Cadmium was observed at m/z 111.903. Unfortunately, any other isotopes of these elements could not be detected, and therefore their existence could not be verified by the isotopic ratios. Of those three, only strontium seemed to be associated with r-BC and vaporized with the laser. However, because zirconium in its elemental form requires about 4400 °C to be vaporized, one possibility is that this trace element was associated with other elements forming for example salts or oxides that could be vaporized with lower temperatures. Neither zirconium nor cadmium showed evidence of slow evaporation in tungsten vaporizer indicated by a signal in the closed mode.

Strontium and zirconium did not have any clear correlation with the other species measured whereas cadmium correlated with organics and r-BC. That was unexpected as cadmium did not seem to be in the same particles with r-BC (detected also without laser). Previously cadmium has been related to several sources in Helsinki and it was found to

be mostly regional or long-range transported (Pakkanen et al., 2001). Strontium, on the other hand, has been associated with traffic-related components from vehicle motor oil but it can also originate from crustal material. Zirconium has not been reported in Helsinki urban air before but in US it has been reported e.g. from the emission of the coal-fired boilers and in samples of geological material (Watson et al., 1995).

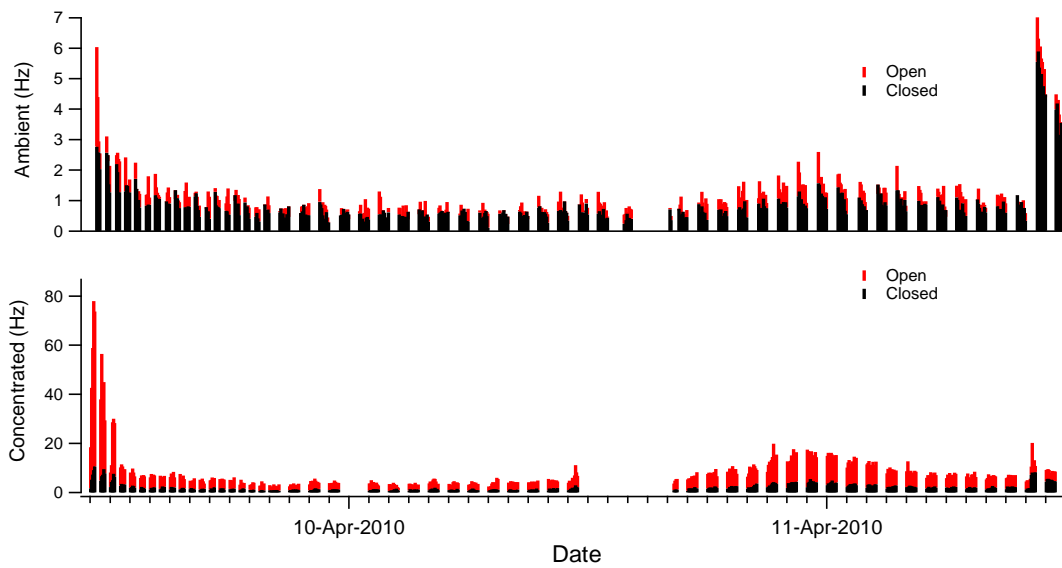


Fig. S9. Slow evaporation of zinc. Open and closed signal for ambient and concentrated aerosol.

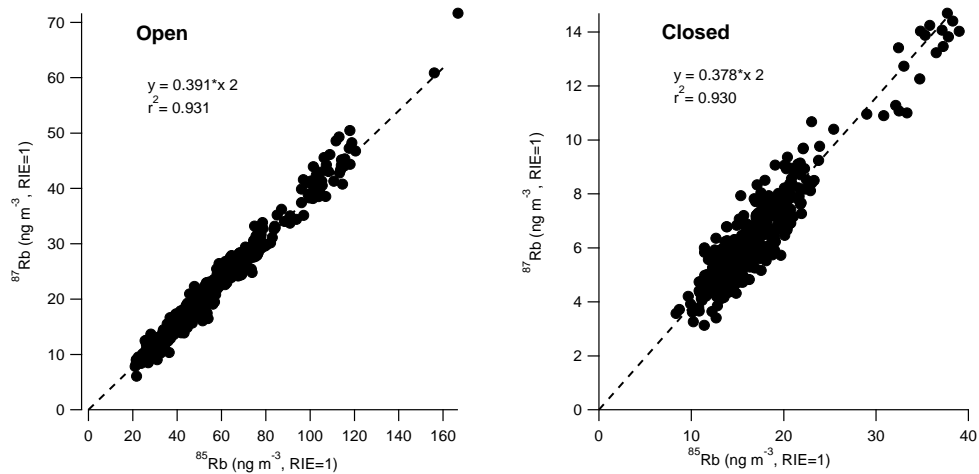


Fig. S10. Scatterplot of signal from ^{87}Rb and ^{85}Rb for open and closed modes. Expected and natural isotopic ratio is shown by a dash line.

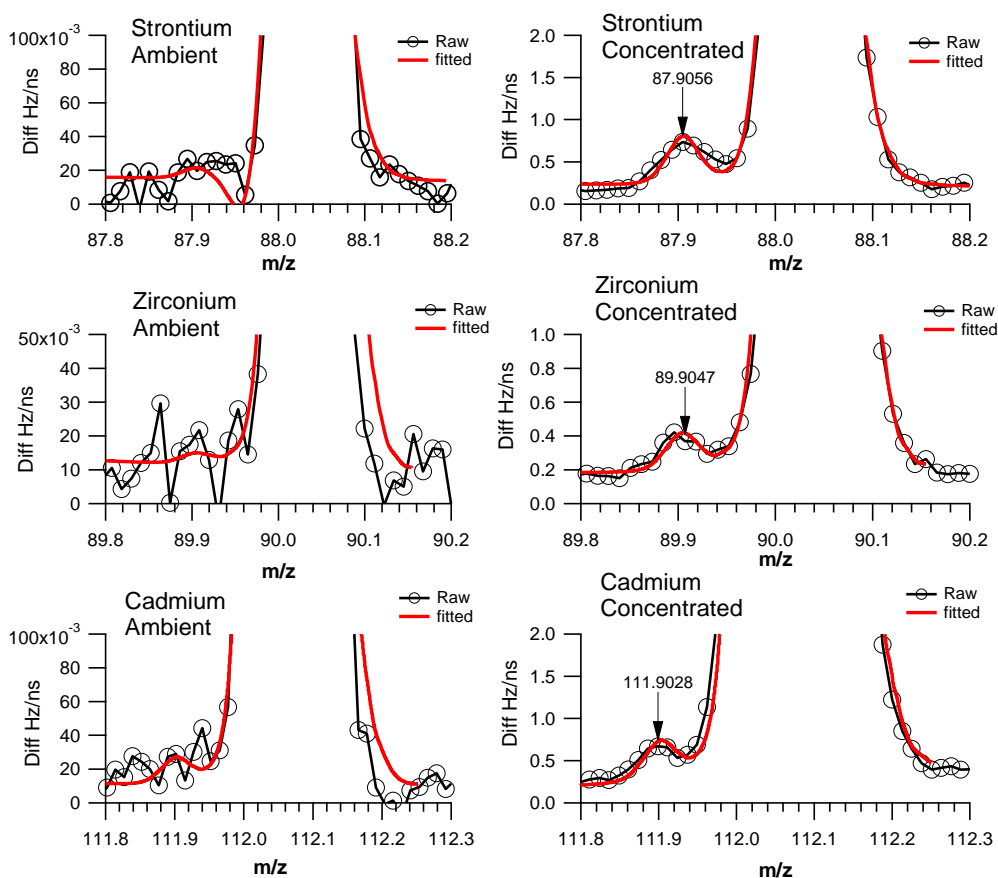


Fig. S11. Strontium, zirconium and cadmium peaks for ambient and concentrated aerosol. Additional isotopes of these ions could not be detected.

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