Elucidating the determinants of aerosol composition through particle type based receptor modeling

Supplementary Material

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1 Semi-continuous measurements and meteorology

Figure S1 illustrates the meteorological conditions observed during the campaign, as well as $PM_{2.5}$ mass concentrations and trace gas mixing ratios. The mean temperature (T), relative humidity (RH) and wind speed (WS) of the campaign were 22°C, 64% and 3.1 m s^{-1}. The wind direction was highly variable throughout each day due to the measurement site's proximity to the Lake Erie, although the surface winds predominantly came from the south-west, with moderate influences from the north-west and north-east. A comparison with year-long meteorological data for the Windsor measurement site showed that wind direction observations for this campaign were close to the yearly average.

Overall, the $PM_{2.5}$ mass concentration during the study period was typical for the BAQS-Met region (Jeong et al., 2010), with an average value of 11.5 µg m^{-3}. Two high PM episodes were recorded during the study, the first spanning four days from 24-27 June ($PM_{2.5avg}$=20.3 µg m^{-3}), and the second from 9-10 July ($PM_{2.5avg}$=25.8 µg m^{-3}) (Figure 2). The first PM episode coincided with air masses following trajectories from the south , and was typified by slightly cooler but more humid and slower moving air from Ohio (T_{avg}=23.7°C, RH_{avg}=72.4%, WS_{avg}=2.9 m s^{-1}). The second PM episode was typified by hotter but less humid and faster moving air from the southwest (T_{avg}=27.6°C, RH_{avg}=65.5%, WS_{avg}=4.6 m s^{-1}). While some air masses originated from the less densely populated Canadian Prairie provinces, they typically passed over the Windsor/Detroit metropolitan area, bringing a more direct impact of fresher emissions to Harrow. The hourly average mixing ratios for O_3, NO, NO_2, NO_y, SO_2 and CO over the three weeks were 42.0, 0.7, 4.9, 7.4, 3.4 and 196.4 ppbv respectively with hourly maxima of 83.1, 34.3, 25.6, 27.5, 56.0 and 668.4 ppbv respectively.

2 ATOFMS Particle Types

Forty-six particle types were generated using the ART-2a clustering algorithm, of which the top 33 most populous (with > 500 particles) were classified into seven broad categories based on their mass spectra, time series and size distributions for describing PMF results. The particle size distribution, particle type mass spectra by family, and their respective contributions are shown in Figures S2 - 9 and Table 1 respectively. The seven families were EC_OC, EC, OC_S_N, OC, AMINE, FIREWORKS and DUST and are described below.

Particle type families were named based on their characteristic chemical species although the FIREWORKS and DUST families were named as their source classes as their chemistry and temporal trends were definitive.

2.1 EC_OC Particle Type Family

Four particle types contributed to the EC_OC family and comprised 22% of the total measured particles. These particle types were named EC_OC as they all contained elemental carbon (EC), as denoted by carbon ion fragments at $C_{\pm 12n}$ with $n \leq 5$, along with positive ion organic carbon (OC) fragments. The organic ion fragments were noted at m/z +27 [$C_2H_3^+$] and m/z +43 [$C_2H_3O^+$]; while peaks observed at m/z +43 could have isobaric interferences from other ions such as [$C_3H_7^+$], [$C_2H_5N^+$], and [$CHNO^+$], the lack of expected corresponding fragments at other m/z's indicates that m/z +43 is likely dominated by the oxidized organic fragment [$C_2H_3O^+$]. Varying degrees of chemical processing were observed in these particle types as demonstrated by their sulphate content. Both C1 and C4 contained significant amounts of sulphate, as represented by the m/z -97 [HSO_4^-] ion, with C1 appearing the most aged of all EC_OC particle types due to its significantly higher sulphate content. These particle types were likely neutralized due to their significant [NH_4^+] levels. Sulphate peaks were only weakly evident in C3 and C8, and appeared to be below detection levels. However the weak overall signal of these particle types precluded the conclusion of unaged particles. Thus varying levels of sulphate combined with oxidized organic fragments indicate that these particle types were moderately to highly aged elemental carbon particles.

2.2 EC Particle Type Family

The EC family consisted of only two particle types, C11 and C16, and represented 6% of the measured particles by ATOFMS. These types were named EC due to elemental carbon ion fragments $C_{\pm 12n}$, with $n \leq 12$ and 8 in the positive and negative ion spectra respectively. While these two particle types were generally similar in their mass spectra, their size distributions suggested very different histories. The C11 particle type was the smallest amongst all 33, with a geometric mean diameter of 0.32μm. Such a small diameter EC particle type typically suggests fossil fuel combustion emissions. However, a strong peak at m/z 23 [Na^+] in this particle type was unusual; this type of particle has only been observed in two other ambient studies (Dall'Osto and Harrison, 2006; Moffet et al., 2008), whereby in both it could not be conclusively identified. It remains possible it is associated with diesel fuel combustion emissions, as source emissions tests conducted by Spencer et al. have found trace amounts of sodium and phosphate in the mass spectra of resulting particles (Spencer et al., 2006). By contrast, the C16 particle type did not contain any detectable sodium, was much larger in geometric mean diameter (0.76μm), and displayed significantly higher sulphate and nitrate peaks than C11. As such, the C16 particle type was likely associated with aged elemental carbon emissions. Hence both particle types were linked with primary elemental carbon emissions of different atmospheric ages.

2.3 OC_S_N Particle Type Family

Making up 27% of the measured particles, the OC_S_N family (C2, C5, C6, C7, C10, and C14) was named as such due to significant contributions from organic compounds, sulphate and nitrate. All particle types in this family were identified by their high [K^+] and organics ion counts in the positive spectrum. The organics were suspected to be oxidized as all of the particle type mass spectra displayed peaks at m/z -89 [$(COO)_2H^-$], indicative of highly oxidized organic carbon. The sulphate and nitrate content in the particle types was useful for understanding differences in chemical processing in these particle types. For instance, C2, C6, and C7 all contained significant sulphate as well as sulphuric acid [$H(HSO_4)_2^-$], the latter a marker of particle acidity, with C7 as the most acidic among these particle types. The formation of sulphuric acid in these particles could be the result of heterogeneous production on particle surfaces, uptake of $SO_{2(g)}$ and subsequent oxidation in the aqueous phase, or homogeneous oxidation of $SO_{2(g)}$ in the gas phase and subsequent condensation on particle surfaces (Whiteaker and Prather, 2003; Ault et al., 2010). All of these particle types appeared related to biomass burning emissions; this was suspected not only from their very high [K^+] peaks, but also from the presence of organic acid fragments in their mass spectra such as m/z -45 [$CHOO^-$], -59 [$C_2H_3O_2^-$] and -71 [$C_3H_3O_2^-$], all of which have been associated with the fragmentation of the biomass burning tracer levoglucosan (Silva et al., 1999; Qin and Prather, 2006). Interestingly, the C7 particle type showed the lowest organic acid and highest sulphuric acid peaks, an effect which may be the result of a sulphuric acid coating preventing measurement of organic acids present in the core of these particles. Organic nitrate ions present in these particles, such as m/z -26 [CN^-] and 42 [CNO^-], further supported the notion of a biomass burning emissions source (Dall'Osto and Harrison, 2006). While the C5 particle type appeared similar to others in the OC_S_N family in terms of its [K+], organic, sulphate and nitrate content, it did display significant differences to suggest another source-type. First, its OC and EC peaks were much higher, with prominent $C_{\pm 12n}$, $n \leq 5$. Second, its temporal trend was significantly different than the others, and was nearly identical to C8, a member of the EC_OC family. Consequently the emissions source-type for C5 was inconclusive. In summary, the OC_S_N family comprised mostly biomass burning particles having undergone a range of chemical processing with the possibility of another source-type having produced C5.

2.4 OC Particle Type Family

While many of the particle types identified in this study contained significant amounts of OC, the OC particle type family particles (C13, C15, C18, C27, and C30), which accounted for 12% of the measured was named as such as it appeared to have the highest organic content relative to other species such as EC and secondary inorganics. In fact, the negative ion mass spectra for all particle types within this family contained relatively low signal compared to some other particle types (i.e. EC_OC family), which suggested they experienced little chemical processing. Most particle types from this family (C13, C15, C18 and C30) were all very similar to one another, and also appeared similar to several particle types in the OC_S_N family due to high [K^+] and oxidized organic carbon peaks. This combination would typically suggest biomass burning emissions, as suspected for most of the OC_S_N particle types, yet the lack of expected associated levoglucosan related peaks indicated this could not be the case. Moreover, aromatic fragments, such as m/z +51 [$C_4H_3^+$], 63 [$C_5H_3^+$], 77 [$C_6H_5^+$], 91 [$C_7H_7^+$], 115 and 128 (Liu et al., 2003), alluded that these particles did not arise from secondary organic aerosol from biogenic emissions; fragments such as m/z +63 and 128 suggested the presence of polycyclic aromatic hydrocarbons (PAH's) in these particles (Qin and Prather, 2006). The C27 particle type within this family appeared significantly different than the others; significant contributions from high molecular weight fragments were noted in the positive and negative ion mass spectra, likely from either oligomeric species or PAH's, or a combination thereof (Gross et al., 2006; Denkenberger et al., 2007; Qin and Prather, 2006). Thus all of the OC particle types contained significant organic carbon levels and appeared to have undergone little chemical processing.

2.5 AMINE Particle Type Family

Two particle types, C9 and C20, contained significant contributions from amine compounds and together represented a small fraction of the measured particles (6%). Typified by high mass spectral contributions at m/z +59 [$N(CH_3)_3^+$], as well as significant contributions of other organic species, these particle types appeared episodically, mostly in one large episode beginning at approximately 22:00 on 4 July, diminishing at approximately 04:00 the next morning. The episodic appearance of these particle types can likely be attributed to gaseous phase trimethylamine (TMA) partitioning to acidic particles through cloud/fog processing, as reported by (Rehbein et al., submitted); this was supported by a strong temporal association with periods of high relative humidity (>90%), and particle acidity as denoted by a sulphuric acid peak at m/z -195 [$H(HSO_4)_2^-$]. Laboratory experiments performed by Rehbein et al. successfully related the uptake of gaseous amines into the particle phase with particle acidity, with higher acidity leading to increased amine uptake (Rehbein et al., submitted). These experiments showed that TMA, when measured by ATOFMS, fragments primarily to the m/z +59 peak, which is the same distinguishing peak in these amine particle types. Given the low wind speeds associated with the episodic appearance of these particles, it is likely that TMA and possibly other amine species partitioned to pre-existing particles rather than amine-containing particles having been transported to the measurement region.

2.6 FIREWORKS Particle Type Family

Four particle types were related to fireworks emissions, and represented 9% of the measured particles. These large-diameter particle types (D_{va} > 0.8µm), which represented 9% of the total measured particles, dominated a particle event observed in the early morning of 5 July. The AMINE and FIREWORKS particle types showed very similar temporal trends, however the FIREWORKS types peaked three hours later at approximately 07:00. Such a temporal difference indicates that a different source or atmospheric process is responsible for their presence. Generally, the mass spectra and size distributions were very similar for these particle types, supporting a common source-type. A fireworks source-type was suggested for these particle types due to the significant contributions from potassium chloride and potassium nitrate fragments to their mass spectra (e.g. peaks at m/z +39 [K^+], m/z +113/115 [K_2Cl^+], m/z +125 [$K_2NO_2^+$], m/z +140 [$K_2NO_3^+$] and m/z -163 [$K(NO_3)_2^-$]). Also observed were significant contributions from alkali metal cations as denoted by peaks at m/z +23 [Na^+], +24 [Mg^+], +40[Ca^+] and +96 [Ca_2O^+], and discernable peaks at m/z +138 [Ba^+] and +154 [BaO^+]. All of these species have been noted in previous fireworks studies: KNO_3, a major component of “black powder”, the oxidant used to ignite the fireworks (Drewnick et al., 2006; Vecchi et al., 2008), in conjunction with the ATOFMS’ very high sensitivity to K (Gross et al., 2000), may both explain the very high K ion signals within these particle types. Alkali and alkaline earth metals such as Na, Mg, Ca and Ba have been associated with the combustion of fireworks (Vecchi et al., 2008; Joly et al., 2010), species which have been detected in pyrotechnic particles measured by the ATOFMS in a study in Riverside, California (Liu et al., 1997). The significant contributions from [NO^-] species could either be attributed to condensation of nitrate, or nitrate from the combustion of black powder. Thus these particle types appeared to be related to a particular source or fireworks, and were likely transported to the site, given their off peak hour appearance in the very early morning.

2.7 DUST Particle Type Family

Ten particle types contributed to the DUST family(C17, C21, C22, C24, C25, C26, C29, C31, C32, and C33), all of which exhibited large geometric mean vacuum aerodynamic diameters ranging from 0.64 to 1.42 µm; together they totalled 18% of the total measured particles. These particle types were defined by very high peaks associated with several dust related species, such as m/z +23 [Na^+], 27 [Al^+], +40 [Ca^+] and +56/57 [$CaO/CaOH^+$]. While these particle types appeared spectrally similar to the fireworks particles, they showed distinctly different temporal trends, appearing much more frequently. Some particle types within this family were very distinct and could be attributed to various types of dust. For instance, C22 contained silicates (e.g. m/z -60 [SiO_2^-] and -76 [SiO_3^-]) and phosphates (e.g. m/z -63 [PO_2^-] and -79 [PO_3^-]), both of which have been related to aged soil dust (Liu et al., 2003). Also, C29 appeared to be related to sea salt due to significant contributions from m/z +23 [Na^+] and large geometric mean diameter (D_{va} = 1.42µm); the lack of m/z -35 [Cl^-] indicated that these particles are not pure NaCl. Rather the significant nitrate content suggested these particles experienced significant chemical processing: gaseous nitric acid likely reacted with NaCl particles to form HCl, thus displacing the Cl and introducing nitrate into the particles (Zhuang et al., 1999). The significant nitrate content in all of these particle types indicated they have all experienced some degree of chemical processing.

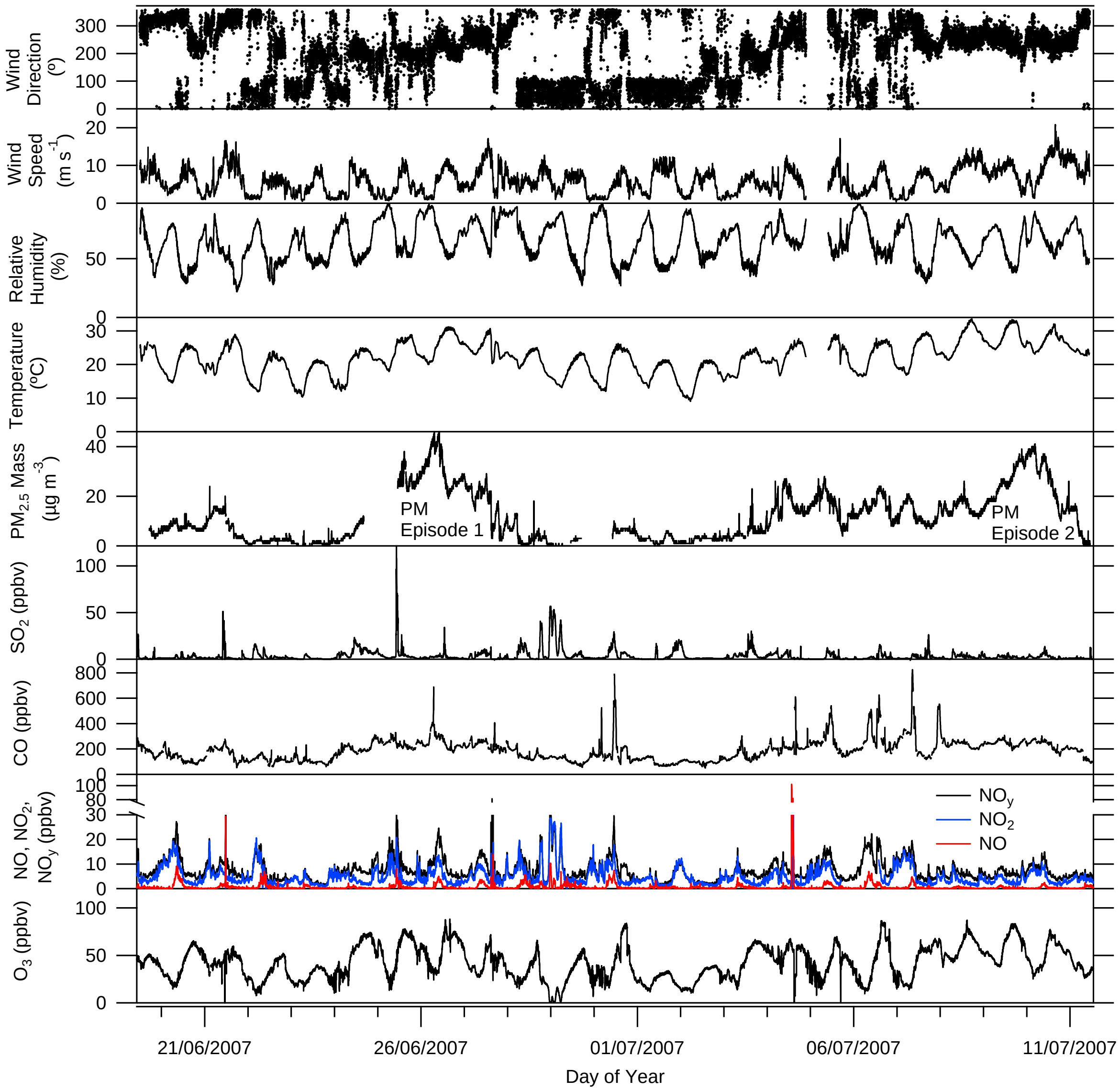

Figure S1: Time series of meteorological measurements (wind direction, wind speed, relative humidity, and temperature) as well as PM$_{2.5}$ mass concentration (including the two PM episodes) and trace gases (SO$_2$, CO, NO/NO$_2$/NO$_y$ and O$_3$) collected at the Harrow measurement site from 19 June – 11 July 2007.

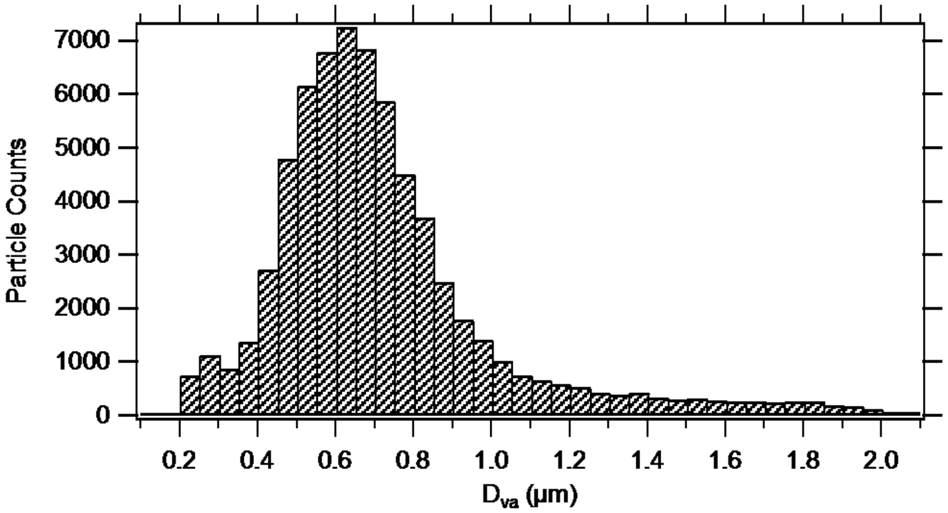

Figure S2: Size distribution of particles desorbed and ionized by ATOFMS during the BAQS-Met campaign.

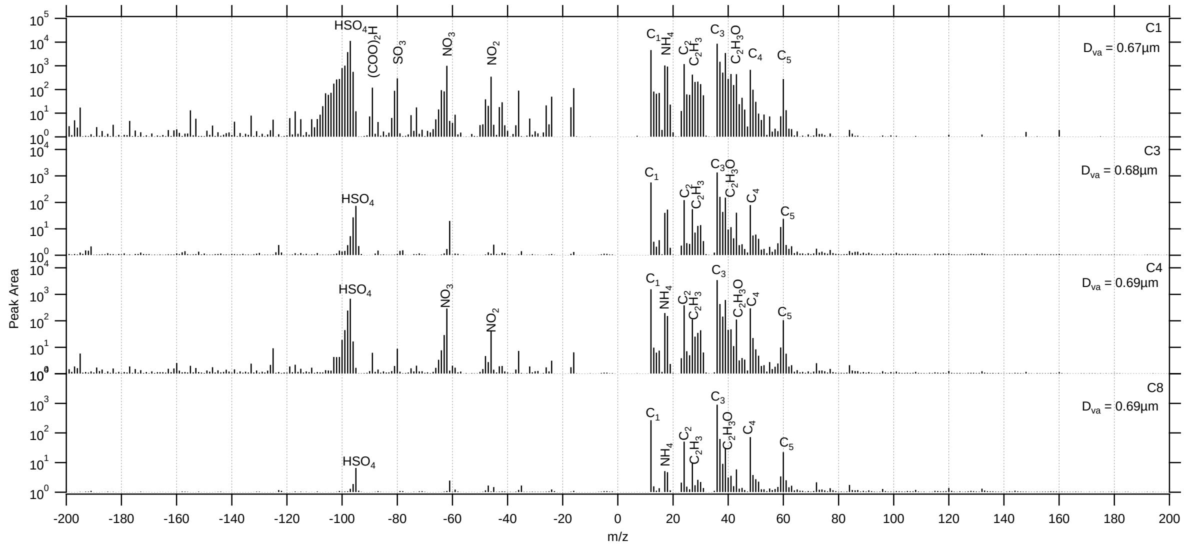

Figure S3: Average mass spectra for particle-types within the EC_OC family.

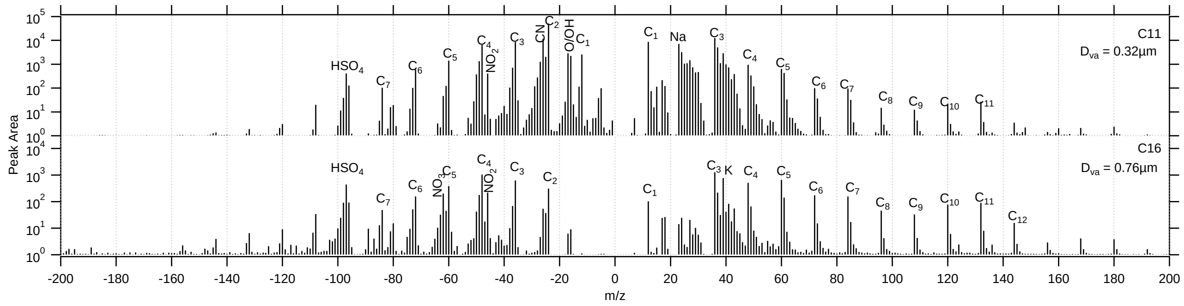

Figure S4. Average mass spectra of particle types within the EC family.

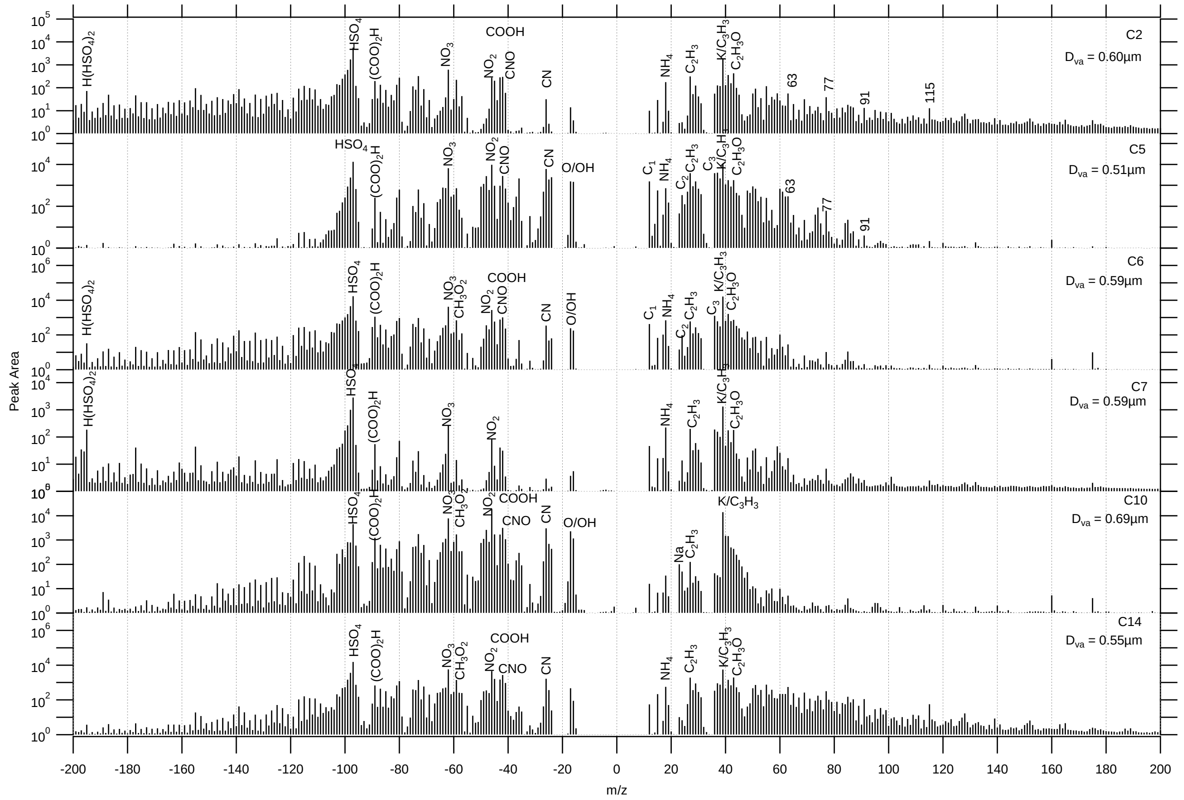

Figure S5: Average mass spectra of particle types within the OC_S_N family.

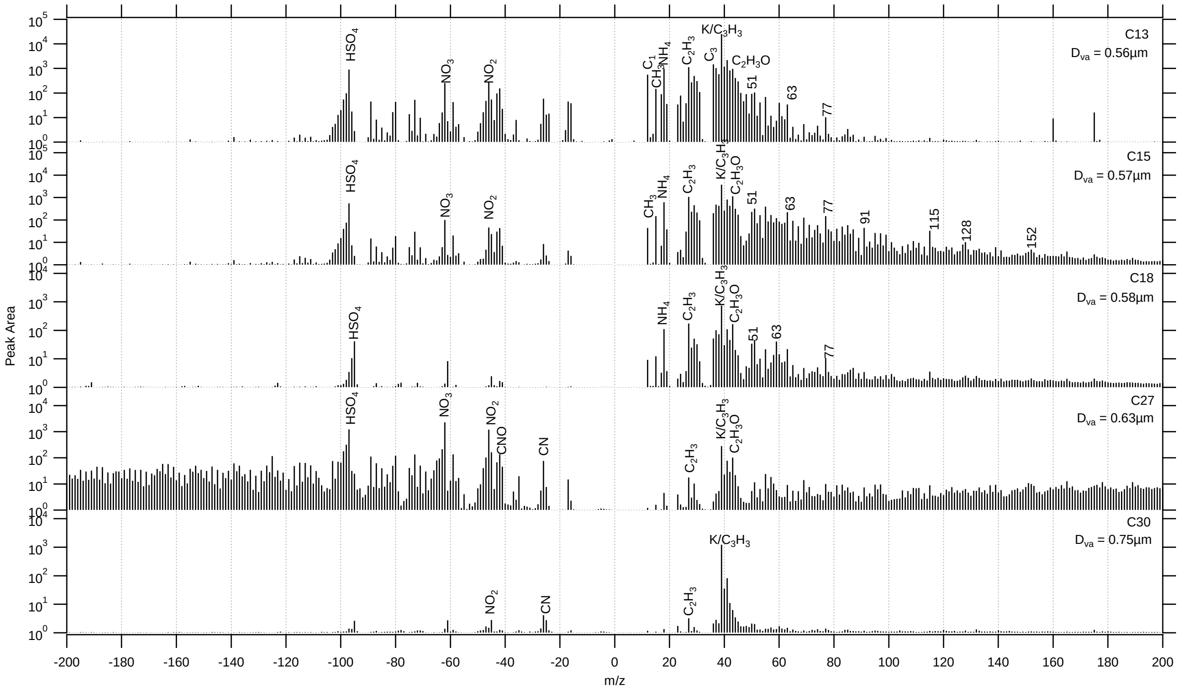

Figure S6: Average mass spectra of particle-types within the OC family.

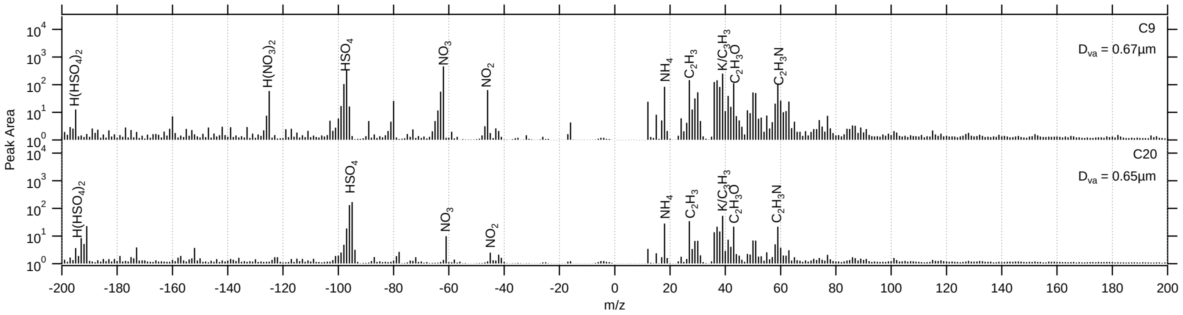

Figure S7: Average mass spectra of particle-types within the AMINE family.

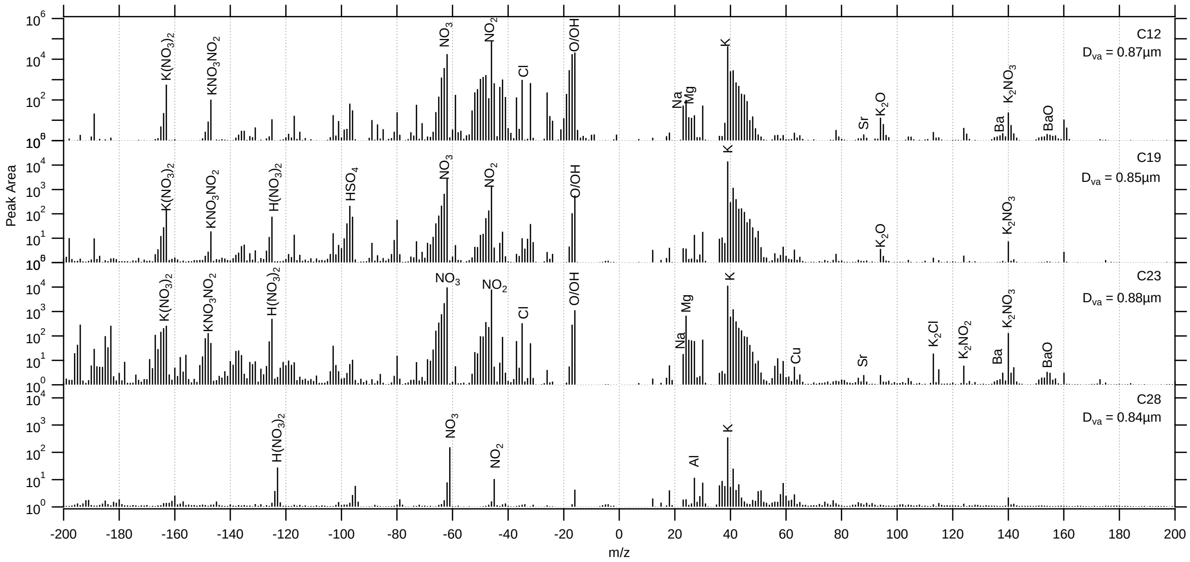

Figure S8: Average mass spectra of particle-types within the FIREWORKS family.

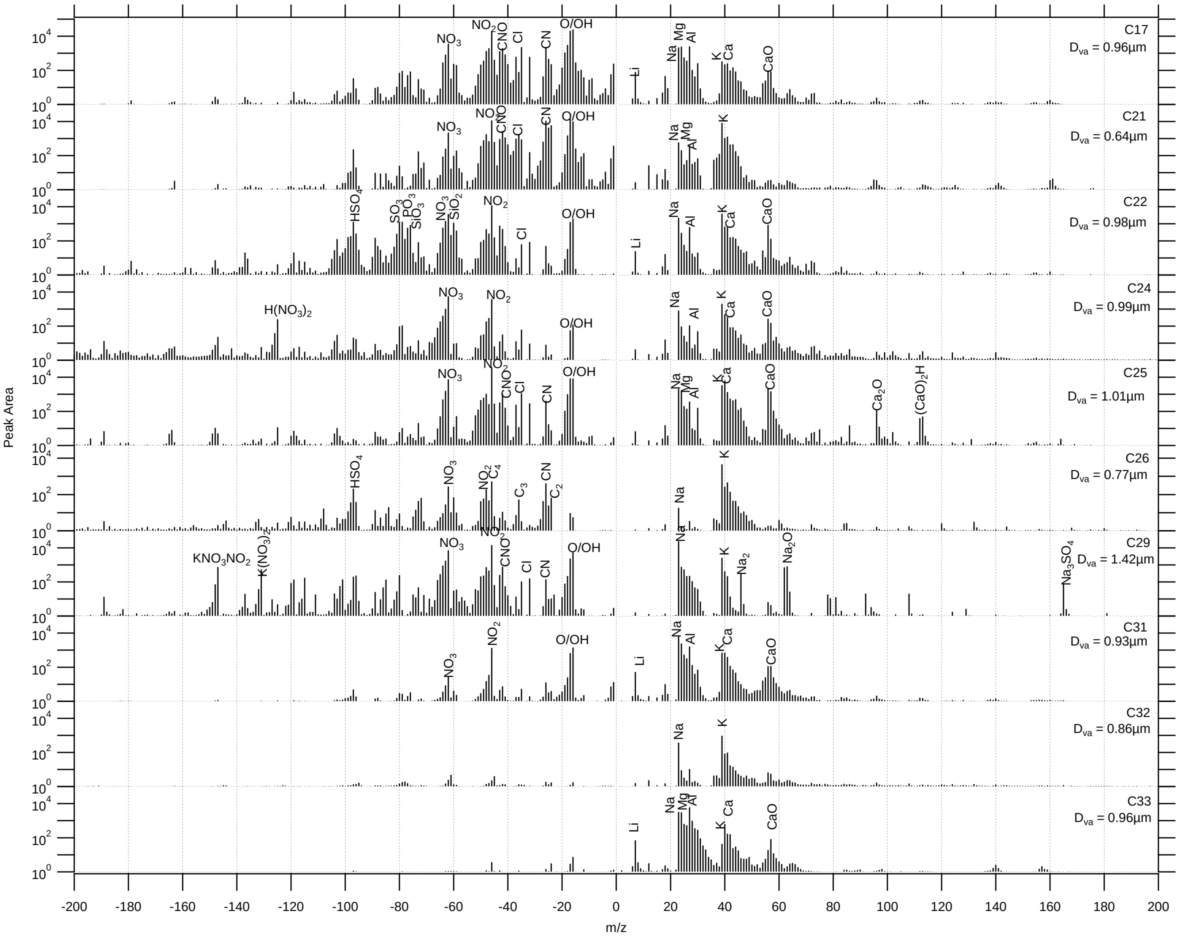

Figure S9: Average mass spectra of particle-types within the DUST family.

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