
3.3. Atmospheric processing of organic chemicals

Of particular interest in the global environment are particulate organic compounds, which represent an important but poorly understood aerosol component. There have been many different organic chemicals identified in particles samples collected from ambient air through many techniques but the majority of the mass typically seen still remains unresolved and non-specific [*Jacobson et al.*, 2000; *Turpin et al.*, 2000]. Many studies have focused on quantifying the elemental carbon (EC) and organic carbon (OC) content of impactor or filter samples and the comparison of these quantities [e.g. *Turpin and Huntzicker*, 1991; *Turpin and Huntzicker*, 1995]. Both of these forms of carbon have been linked to anthropogenic emissions. Elemental carbon is a key component of primary carbonaceous particles, i.e. soot within primary particle emissions from combustion. Organic carbon has been found to be present in these particles, but is also observed in particles having originated from gas to particle conversion processes (secondary organic particles). The OC to EC ratio can be calculated for primary carbon activity (e.g. *Turpin and Huntzicker* [1995] found the ratio to be approximately 2.18) and organic carbon levels above this have been used to indicate the presence of secondary organic compounds.

A major source for these particle-phase chemicals is the low vapour pressure products of the oxidation of gas phase volatile organic chemicals by species such as O₃, OH and NO₃. The production rates are elevated in urban plumes, where both the precursors and radical concentrations are higher. In the case of the OH and O₃ oxidation processes, production rates are also enhanced during periods of strong sunlight, when photolysis rates are elevated. These low volatility products quickly condense onto existing particles or nucleate to form new particles [*Seinfeld and Pandis*, 1998, pp. 724-727]. The species produce, along with the primary organic species, may go on to react further in the particle phase, but these processes are currently very poorly understood; they may be heterogeneous reactions with gas phase oxidants or homogeneous reactions within the particles themselves or multiphase reactions during cloud processing.

The AMS is a very useful tool in understanding the composition and processes of organic particulates in the atmosphere, as it has been shown to be able to produce distinct mass spectra for different organic chemical species while still capturing the majority of the mass present. This capability, combined with its size and time

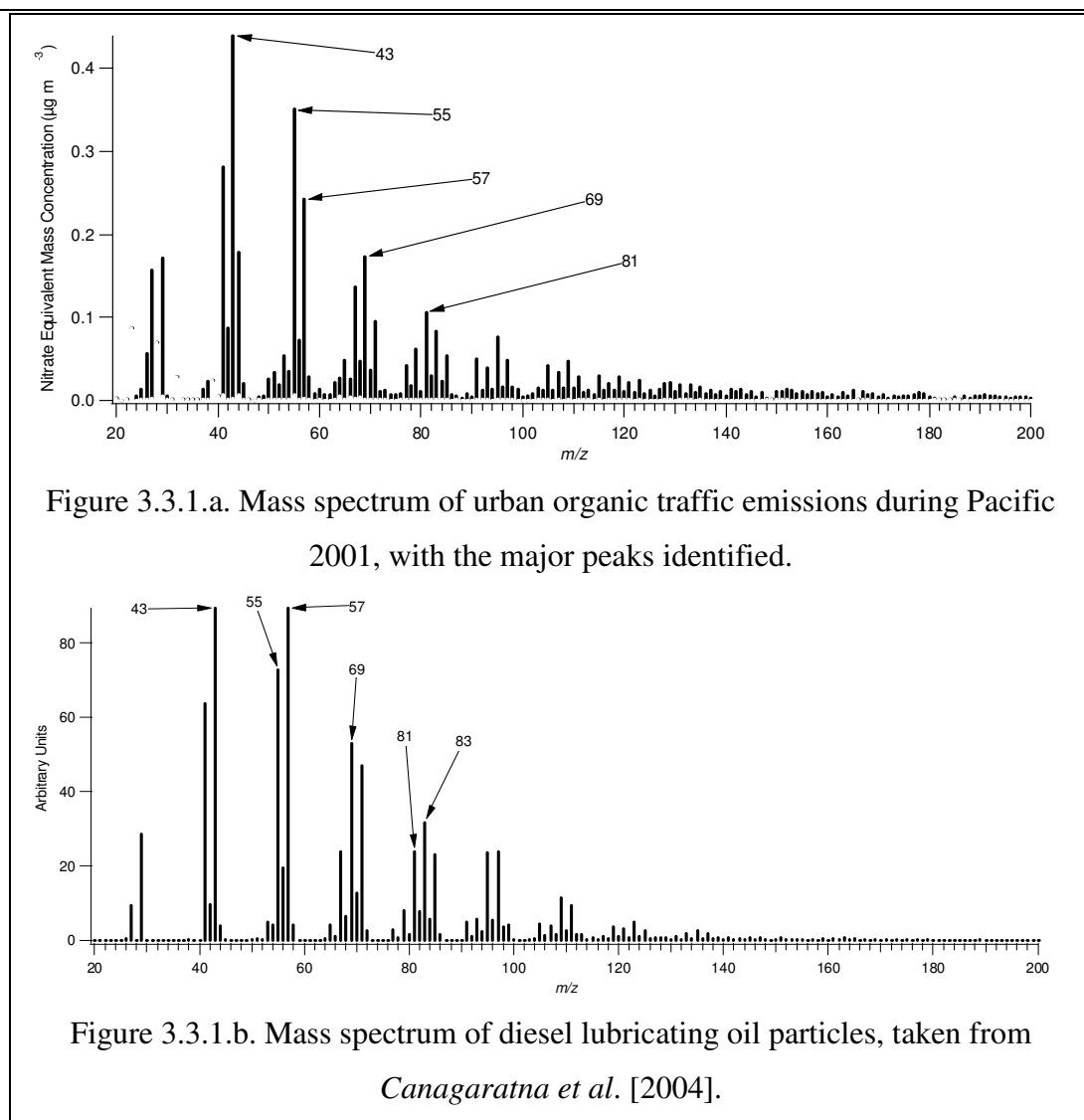
resolutions and the benefits of in situ analysis, means that the AMS has been able to provide a powerful and unique perspective on this complex aspect of aerosol chemistry.

3.3.1. Changes in particle composition with distance from source

As discussed above, the AMS is able to clearly observe and identify a mode of organic particles in urban environments associated with traffic emissions. Additional information regarding the chemical nature of these particles can be obtained by studying the signatures they give in the MS mode of operation. As mentioned before, one intrinsic limitation of the instrument is that it cannot distinguish the different particle types in this mode, so the overall signature is that of the particle ensemble. However, characteristics can be identified by comparing the ensemble mass spectra of different sites at different distances from the sources.

The best example of a sampling site dominated by local sources is Slocan Park (Pacific 2001), in particular during the night. The regional transport was largely dominated by relatively clean air from over the Pacific Ocean. At night, mixing would occur within a very shallow boundary layer, meaning that the traffic emissions would become very concentrated. This is especially pronounced during the second week of sampling, where there were reduced amounts of sunlight, meaning less photochemical processing and therefore less secondary particulate mass.

An example from one of these periods, shown in figure 3.3.1.a shows m/z 43 to be the major peak in the organic mass spectrum, with very little contribution from 44. The peaks at 55 and 57 are also very large and there are peaks continuing right into the extreme end of the mass spectrum. Between 55 and around 100, the larger peaks in the mass spectrum appear at mainly the odd-numbered m/z 's and display a periodicity of 14. This is indicative of the EI fragmentation of long-chained organic compounds which leaves an assortment of $R(CH_2)_n^+$ ions [McLafferty and Turecek, 1993, ch. 5] and also in agreement with the laboratory characterisation work discussed in section 2.5.1. For comparison, the diesel lubricating oil mass spectrum derived by Canagaratna *et al.* [2004], is shown in figure 3.3.1.b and is very similar, which further confirms that this is the likely composition of the mode.



In the other extreme, the MS signature consistently observed at the more remote sites shows a base peak at m/z 44 (figure 3.3.1.c). Apart from peaks at 43 and 55, there is very little mass observed in other channels. As discussed in section 2.5.1., 44 (CO_2^+) is indicative of di- and polycarboxylic acids and 43, while being a strong aliphatic peak (C_3H_7^+) can also be indicative of monocarboxylic acids, aldehydes and ketones (e.g. $\text{C}_2\text{H}_3\text{O}^+$). These patterns are therefore taken to indicate a high degree of chemical oxidation in the organics, which is expected, given the distance from major pollution sources. Following from this, it also implies that the organic fraction is mostly secondary in nature. During ITCT 2K2, this conclusion was supported by the organic to elemental carbon (OC/EC) ratio measurements, which consistently high at 20.1, averaged over the entire period (T. Bates, NOAA PMEL, personal communication, 2003).

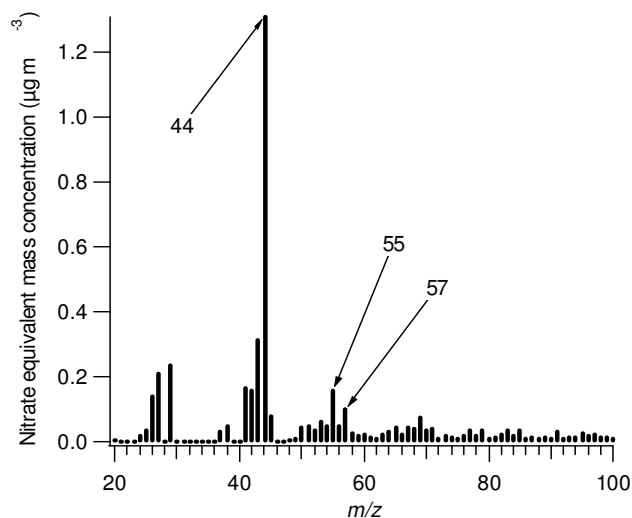


Figure 3.3.1.c. Mass spectrum of chemically aged accumulation mode organics from ACE-Asia, with the major peaks identified.

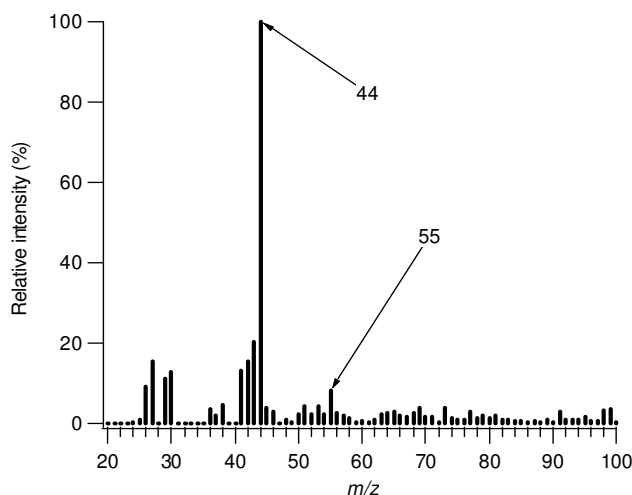


Figure 3.3.1.d. Mass spectrum of particles composed of fulvic acid, a chemical standard that has been used as a model for the water-soluble organic fraction of aerosol.

The fact that carboxylic acid groups, which are the most oxidised type, have a strong presence indicates that the organic fraction has undergone a lot of chemical ageing. The abundance of these polar organic compounds is consistent with various other analytical work, for example *Decesari et al.* [2001], that has shown that these types of compounds are responsible for the majority of the water-soluble organic carbon present in atmospheric aerosol, which in turn makes up the majority of the total organic carbon fraction at remote locations. In particular, polycarboxylic acids have been found to make up a significant portion. Furthermore, there is evidence to suggest that this organic fraction tends to combine in the particle phase over time to form ‘humic-like’

substances [*Jang and Kamens, 2001; Kalberer et al., 2004; Limbeck et al., 2003*], which are complex macromolecular organic chemicals that feature large numbers of oxidised functional groups.

It has been found previously that fulvic acid standards (which can also be described as being humic-like in nature) reproduce the analytical behaviour of the ambient polycarboxylic acids very well [*Fuzzi et al., 2001; Kiss et al., 2001*]. When an atomised sample of fulvic acid was introduced into the AMS, the resultant mass spectrum (figure 3.3.1.d), was found to be almost identical the common organic signature found at remote sites (M.R. Alfarra, UMIST, unpublished laboratory data, 2002). As well as further qualifying its suitability as a model for this fraction, the implications of this result are that after a sufficiently long oxidation time, particulate organics ultimately exhibit very similar characteristics, namely those of the ‘humic like’ substances, regardless of initial origin. This chemical ageing could partly be taking place in the particle phase after condensation, through either hetero- or homogeneous reactions.

While the two key signatures discussed are the two most common that have been observed in the atmosphere, it must be stressed that they are by no means the only ones seen. For example, distinctly different organic mass spectra have been observed close to non-traffic sources of organic chemicals, such as in forest environments [*Allan et al., 2003c; Allan et al., 2004a*]. MS signatures of partly aged organics have also been found to exhibit subtle differences to these spectra, so with further analysis tool development, intermediate states could conceivably be identified and extracted from sites downwind of urban sources. Also, the presence of polycyclic aromatic hydrocarbons (PAHs) has been reported by other groups when sampling heavily polluted urban environments (N. Takegawa, University of Tokyo, Unpublished field data 2002).

3.3.2. Comparison with volatile organic carbon distribution

ITCT 2K2 presented a good opportunity to compare quantitatively the organic chemicals observed in the particle phase with the AMSs and those in the gas phase observed with the GC-MS-FID. When qualitatively comparing simple time series, similarities can be noted with the total AMS-measured organic loading and the concentrations of tracers measured with the GC-MS-FID. Figure 3.3.2.a shows, as an example, a comparison between MTBE and benzene. Both are directly emitted by motor vehicles and their fuel and subsequently degrade in the atmosphere, largely as a result of

OH oxidation, at different rates. Using measured reaction rates and assuming an OH concentration of 10^6 molecules cm^{-3} , MTBE has an estimated chemical lifetime (k^{-1}) in the atmosphere of around 3.6 days [Wallington *et al.*, 1989], whereas that of benzene is approximately 9.7 days [Semadeni *et al.*, 1995]. The downward trend in the benzene data during the experiment is the seasonal benzene cycle that is ubiquitous of long-lived hydrocarbons in the northern mid latitudes [Goldstein *et al.*, 1995; Jobson *et al.*, 1994].

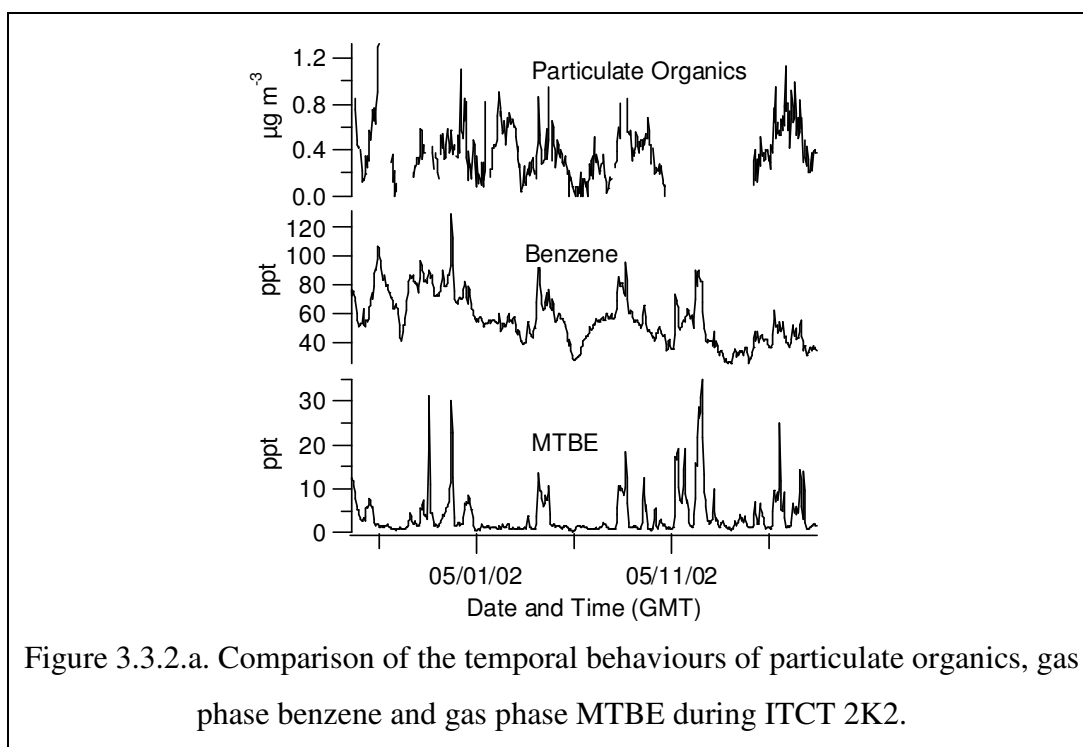
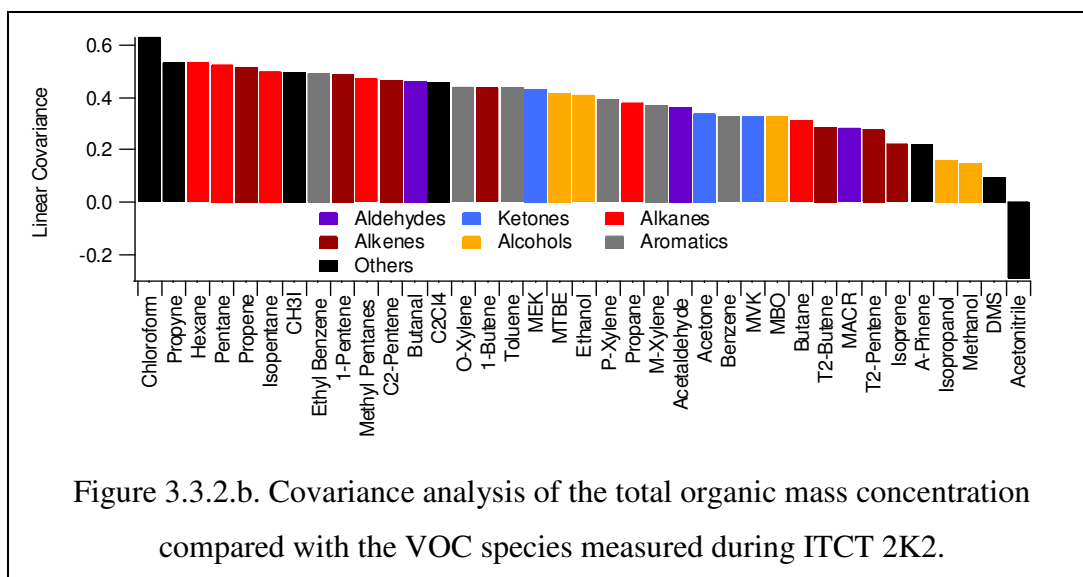


Figure 3.3.2.a. Comparison of the temporal behaviours of particulate organics, gas phase benzene and gas phase MTBE during ITCT 2K2.

Linear covariance analysis was performed using the AMS data and all the species measured by the GC-MS-FID. This analysis was applied to the entire data series at once, made possible by the similarities in the air histories, as shown by the back trajectory analysis; there were no sudden air mass history changes that would have created large positive or negative artefacts in the comparisons. The AMS data used are those from the ARI instrument during low inlet temperature sampling, as this is thought to have the highest signal to noise ratio and not be subject to as much chemical thermal fragmentation as the UMIST instrument. However, when the analyses were repeated for the UMIST instrument and the ARI high inlet temperature time series, they produced qualitatively similar results.

When the total loading of particulate organics is compared to the different gas phase components (figure 3.3.2.b), a positive correlation is noted with most gas phase species, with the hydrocarbons having the strongest relationship. The majority of chloroform in the atmosphere is biogenic in origin although there are anthropogenic

sources as well [Laternus *et al.*, 2002]. It has a long atmospheric lifetime (112 days using the conditions assumed above [Atkinson *et al.*, 1997]), so most of the fluctuations seen will mainly be due to emission events, hence the strong relationship to the particle phase organics. Anthropogenic activity may be a contribution, but biogenic activity over the ocean is also a potential source. However, there is little correlation with DMS, another biogenic product, indicating that this particular fraction does not share a common source with the particulate organics or go on to contribute to this fraction. There is an anticorrelation with acetonitrile, likely because lower acetonitrile concentrations are indicative of oceanic uptake and suppressed mixing within the atmospheric boundary layer (as postulated by Millet *et al.* [2004]), under which conditions the particulate organic concentration at the ground will be elevated.



Further information can be gathered by looking at the contribution to the organics from particular m/z 's. When the covariance analysis against the gas phase VOC is repeated using the logarithm of the fraction of the organics at m/z 44 (figure 3.3.2.c), the strongest relationship is observed with oxidized species such as aldehydes and ketones, which are the products of photochemistry in the gas phase. Weak anticorrelation is noted with the hydrocarbons and a stronger anticorrelation with the short-lived combustion species, such as the methylbenzenes, is observed. Note that none of the covariance values are particularly large, but this is mainly due to the low organic mass loadings in the particle phase and the inherent amount of random noise in the time series. Conversely, if the analysis is repeated for the fraction of m/z 57 (figure 3.3.2.d), the order of the gases is reversed, with the short lived combustion tracers correlated and the oxidation products anticorrelated.

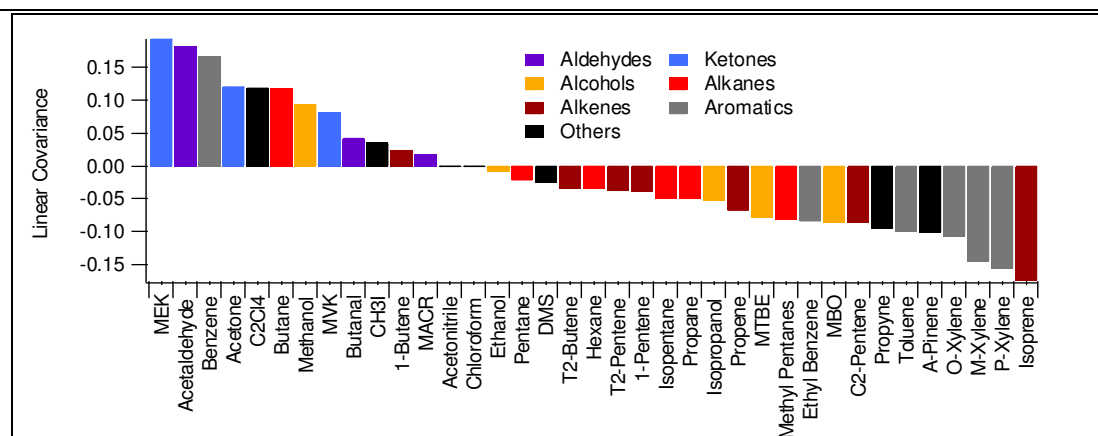


Figure 3.3.2.c. Covariance analysis of the m/z 44 fraction of the AMS-reported organics and the VOC species. Note that the oxidation products have positive covariances while the short-lived combustion products are anticorrelated.

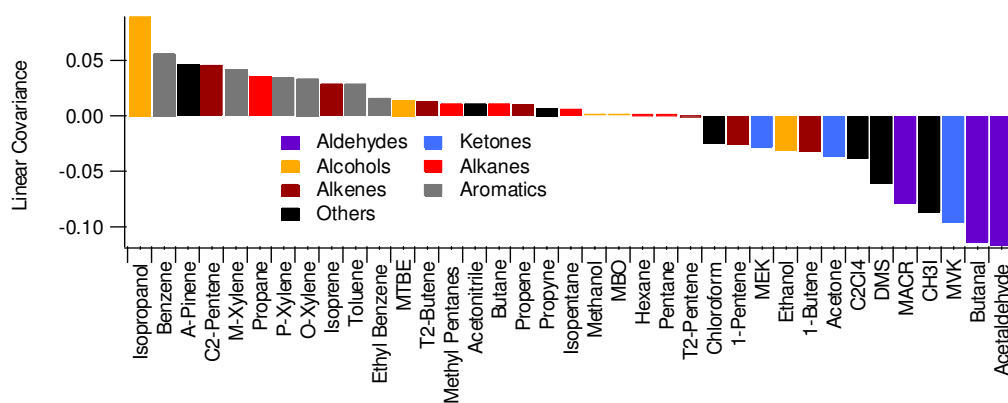


Figure 3.3.2.d. Covariance analysis of the m/z 57 fraction of the AMS-reported organics. The order of the covariances is roughly reversed compared to the analysis for m/z 44, with the oxidation products anticorrelated and the combustion products correlated.

This comparison offers an entirely self-consistent view of the behaviour of the organic chemicals in the particle phase. The analysis gives direct evidence that the oxidized organic species tend to dominate in the particle phase when the air has undergone sufficient photochemical ageing since the emission of the organic precursors. Conversely, during times of high gas phase concentrations of less oxidized chemicals and short-lived combustion tracers, the less oxidized species have more of a presence in the particle phase.

Correlation is seen between α -pinene and isoprene and the m/z 57 fraction because these are produced biogenically in forests and will therefore be more prevalent in air that has spent significant time over land, which will also contain more primary

organics due to traffic emissions. There are no apparent relationships with acetonitrile, meaning that while its behaviour is reflected in the overall loading of particulate organics, it does not affect their composition, strengthening the above hypothesis that an atmospheric mixing effect is largely responsible for the temporal behaviour of acetonitrile.

