

## Supplement Material

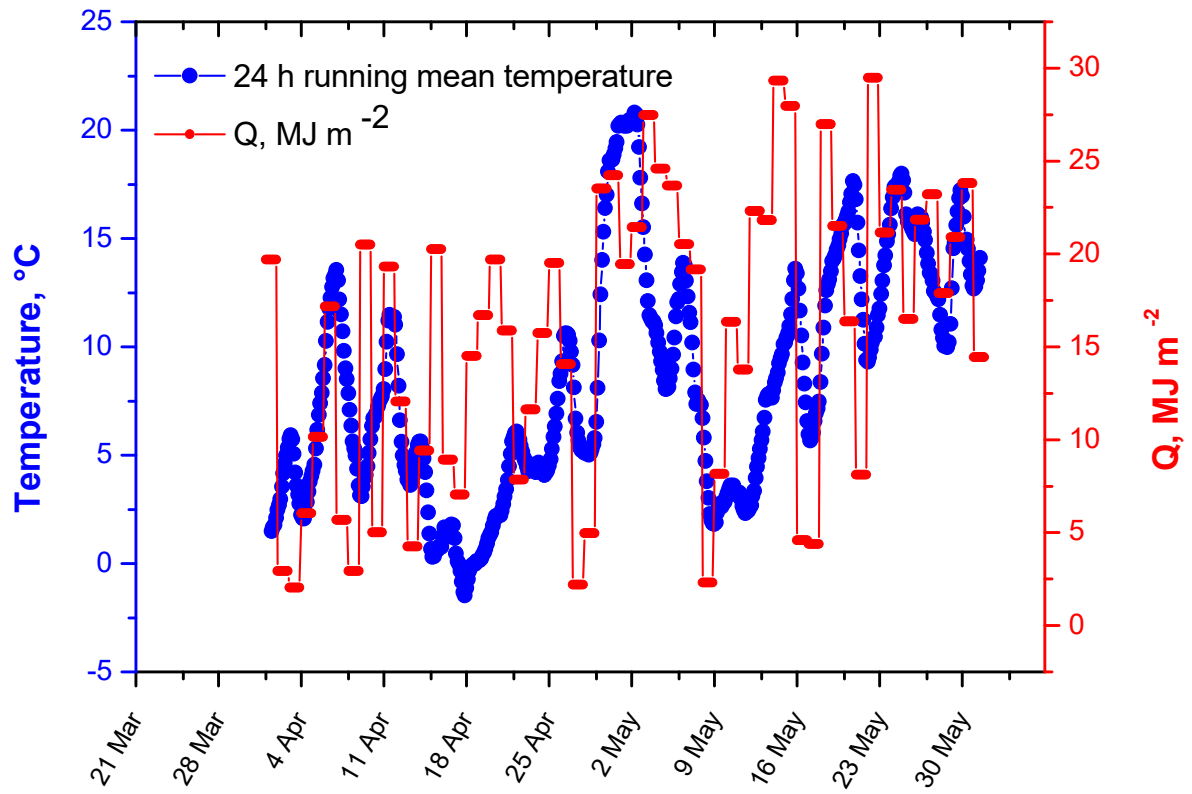


Fig.S1. 24 h running mean temperature,  $T$ , and daily doses of total shortwave irradiance,  $Q$ .

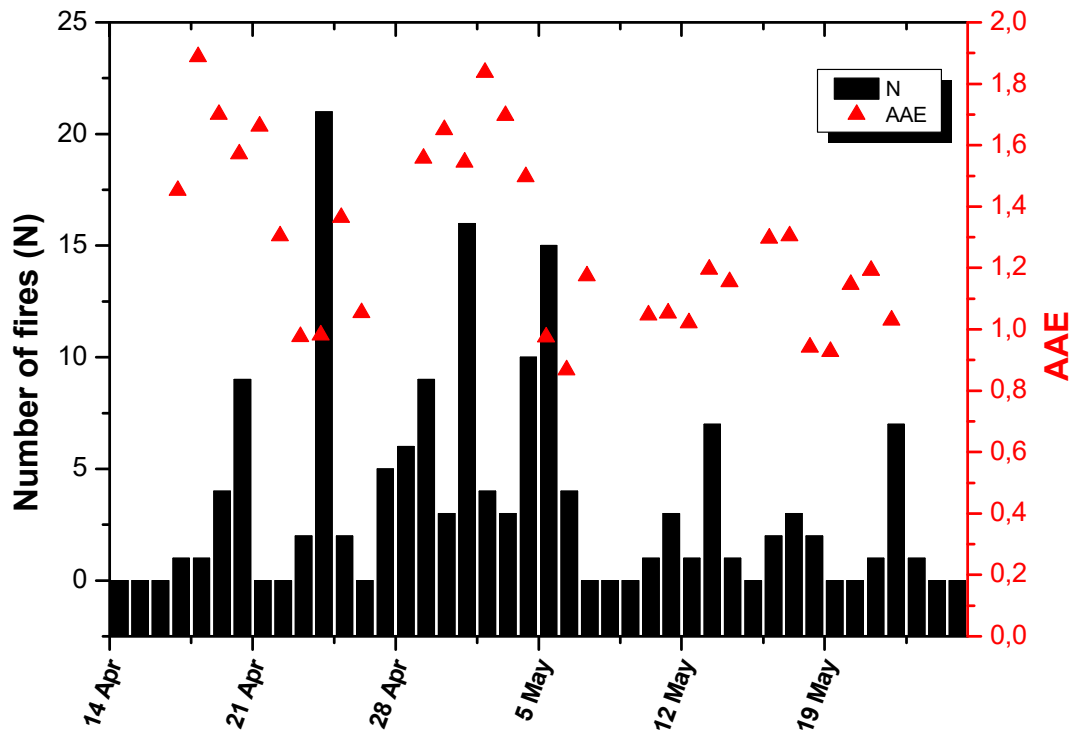


Fig. S2. Number of fires (N) along backward trajectories and Absorption Angstrom Exponent (AAE) (red triangles) during sampling period.

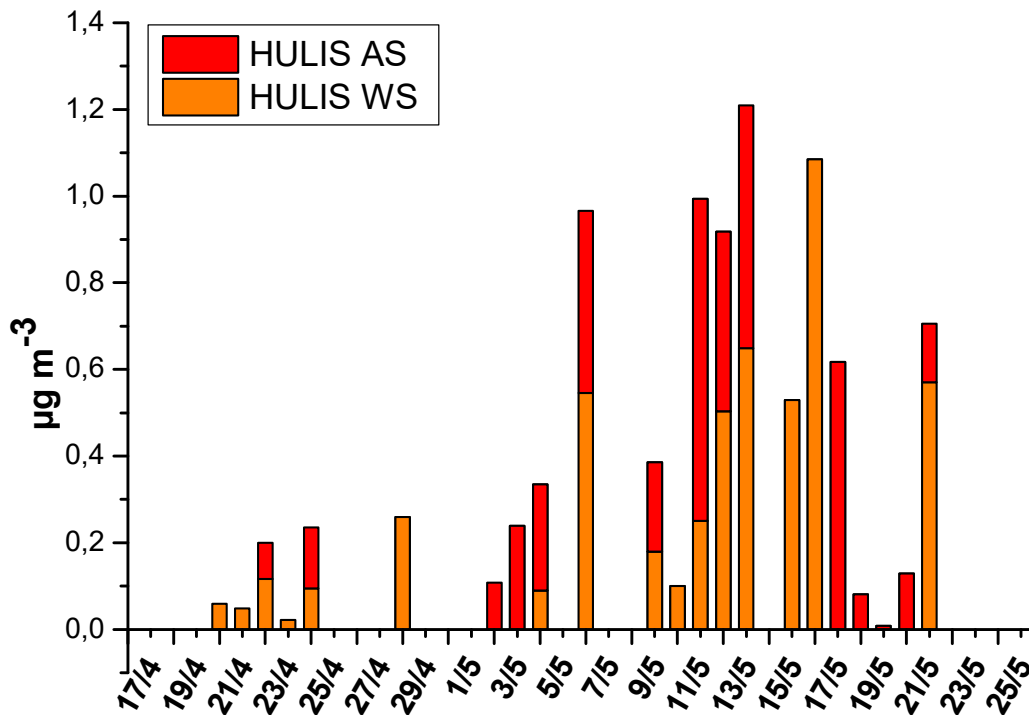


Fig.S3. Concentrations of water soluble (HULIS -C-WC) and alkali soluble (HULIS-C-AS) compounds.

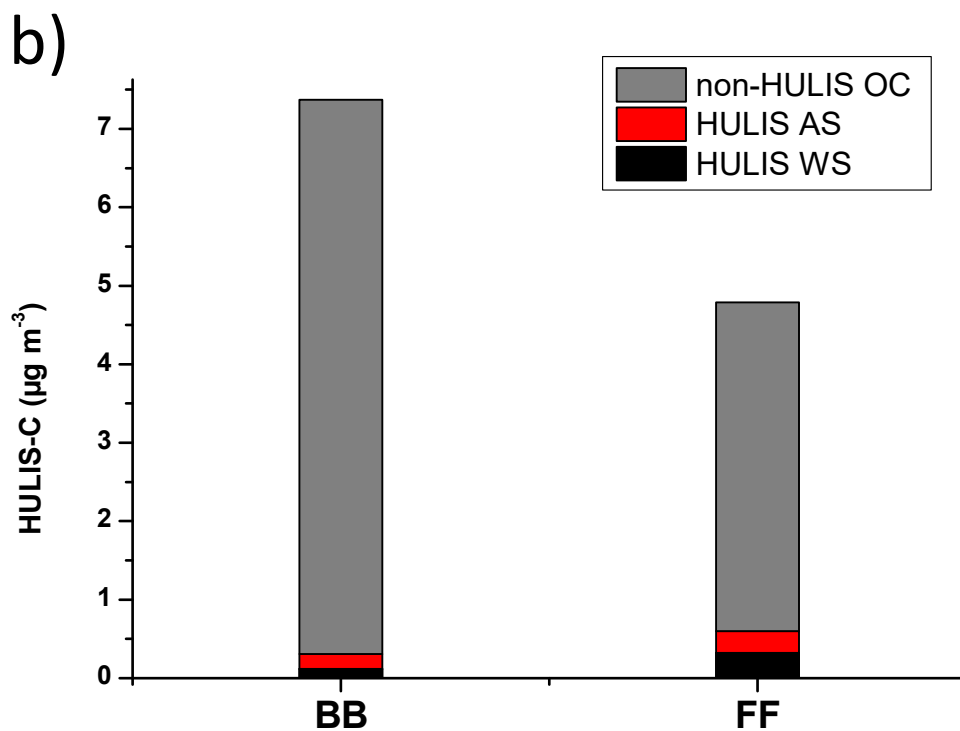
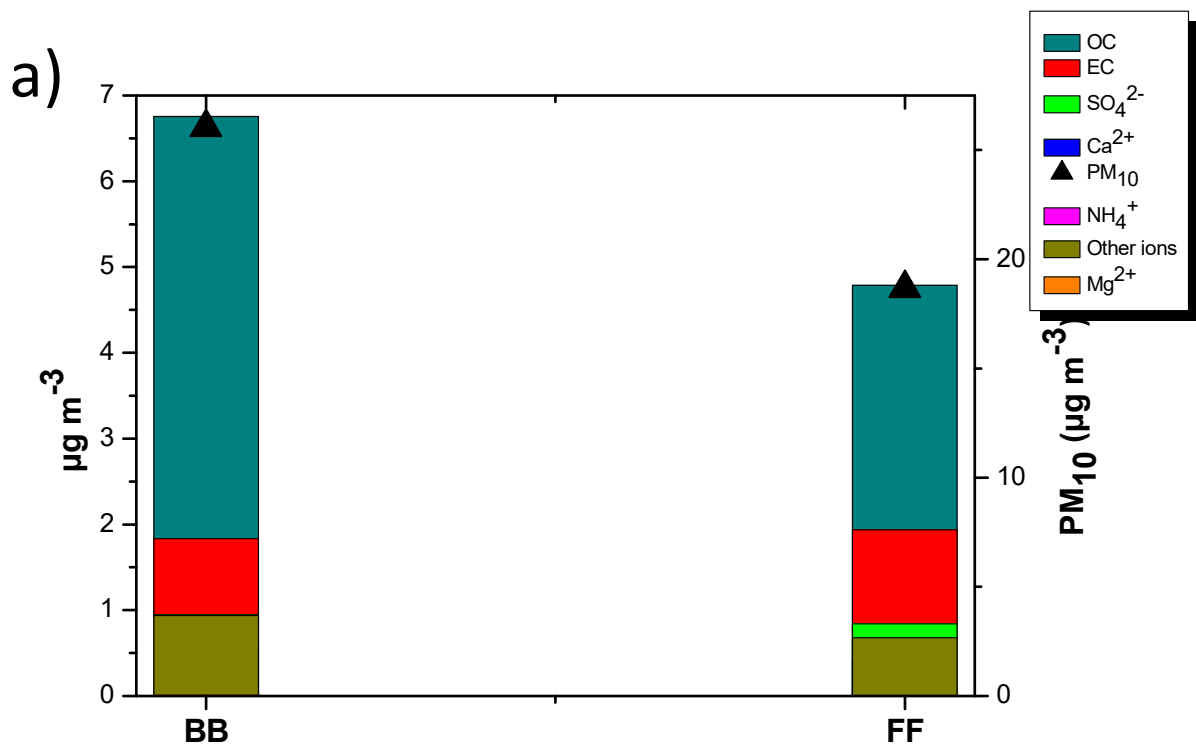


Fig S4. a) PM<sub>10</sub> and concentrations of main aerosol constituents ( OC, EC, ions) , and b) HULIS-AS and HULIS WS (alkali and water- soluble fraction) and non-HULIS OC during BB-affected and FF periods.

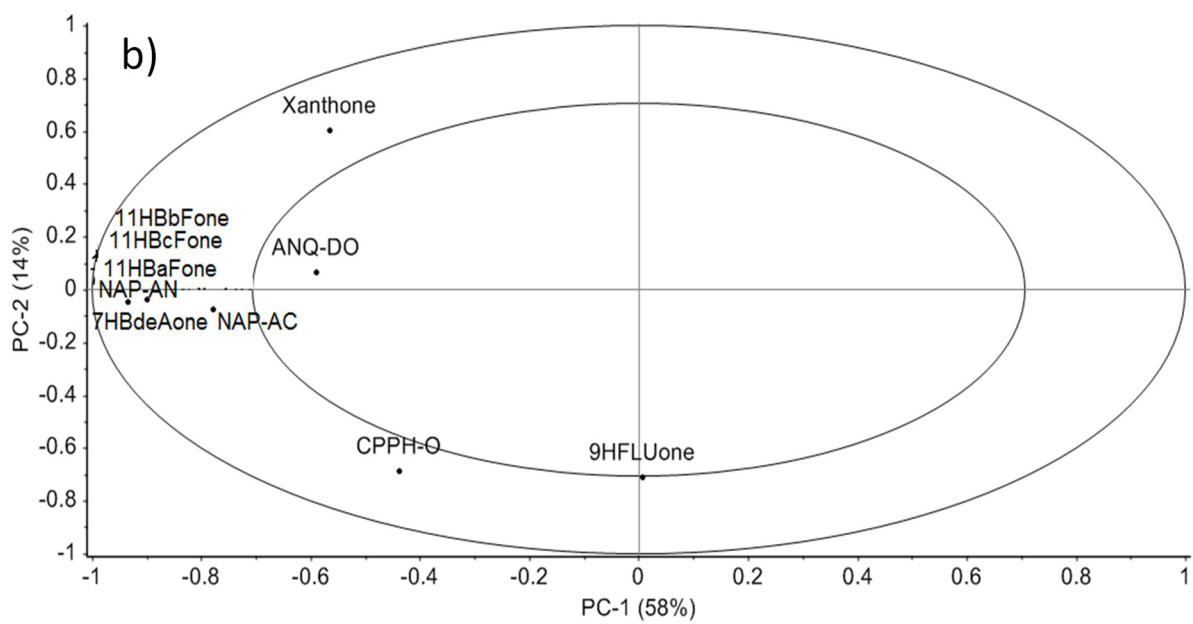
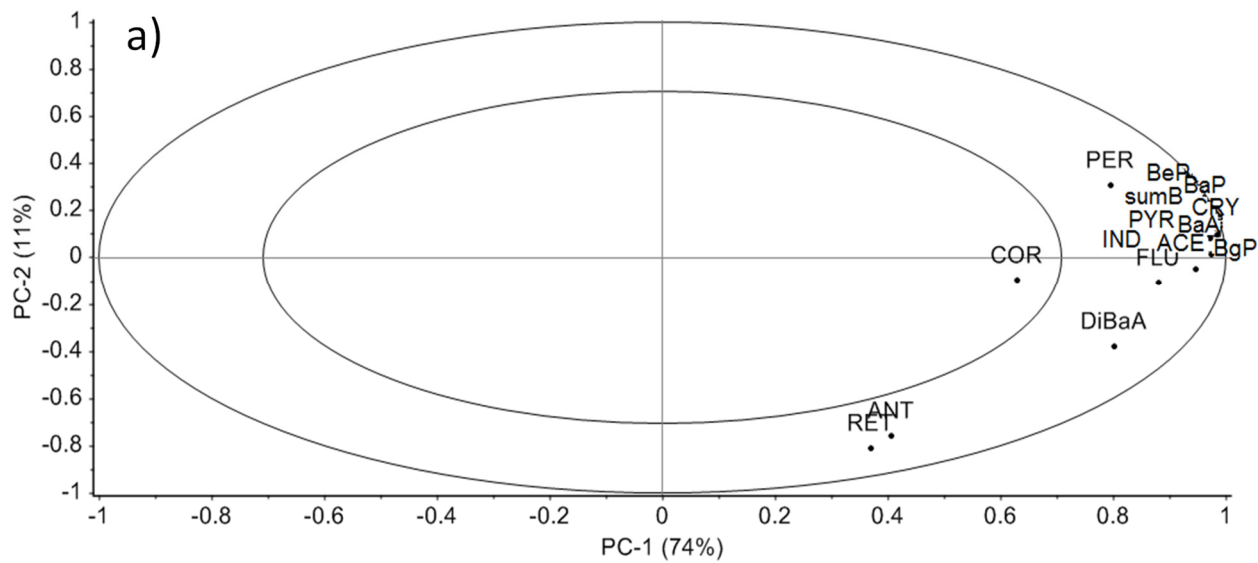
### **PCA correlation loadings.**

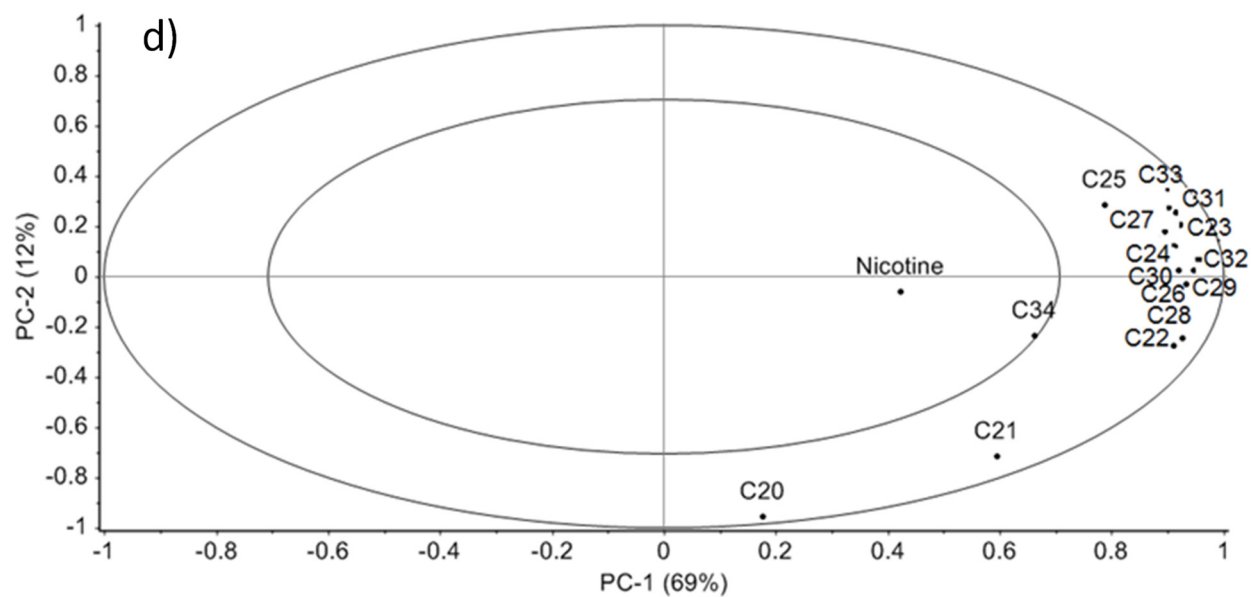
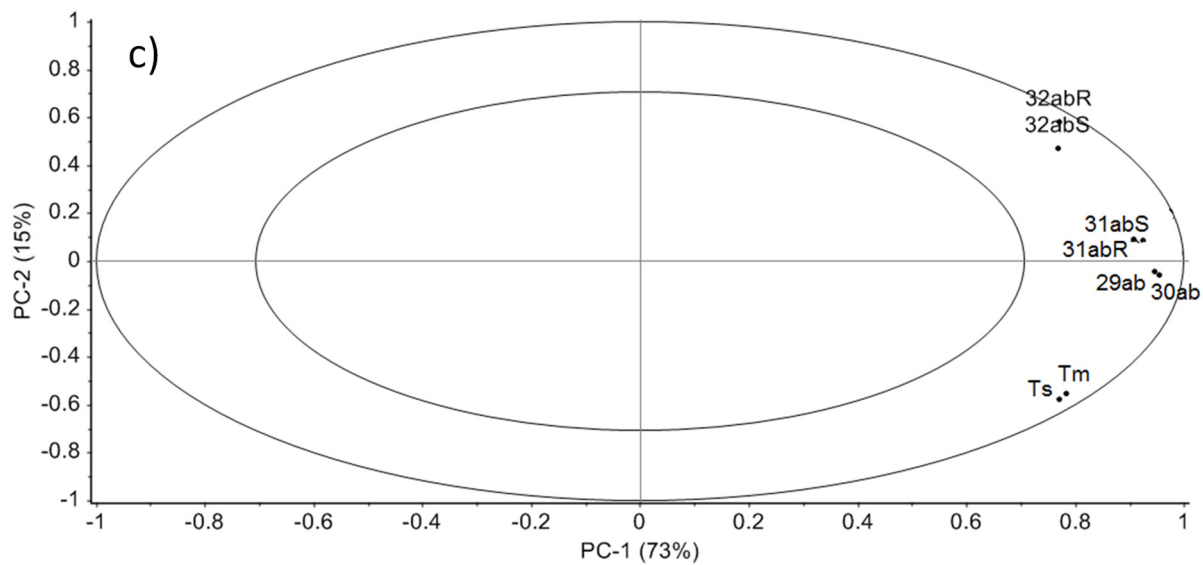
PCA correlation loadings for quantified compounds are shown in Fig. S5. PAHs confirm a strong relation within one cluster formed by PYR, FLU, BaA, CRY, sumB, ACE, BeP, BaP, IND, and BgP. which takes place closer to the outer ellipse (Fig. S5). PER and DiBaA are quite distant from this cluster having lower PC1~0.8 and PC2 loadings of -0.4 and 0.4, respectively. While ANT and RET are strongly correlated, COR shows a lower correlation with all other PAHs. PER, DibaA, ANT and RET can be found in middle part of the plot between the inner and outer ellipses while COR is located in the inner ellipse.

NAP-AC, CPPH-O, ANQ-DO, Xanthone and 9HFLUone show different positions in the correlation loadings. The distance to the first cluster of chemical compounds indicates a different emission source. More specifically, NAP-AC, Xanthone, CPPH-O and 9HFLU are between the two ellipses quite close to the inner ellipse while ANQ-DO is outside of the inner ellipse that represents 50% of the total explained variance.

The correlation loadings of alkanes show a big cluster composed of C23, C24, C26, C27, C29, C30, C31, C32 and C33 nearby the outer ellipse that represents 100% of the total explained variance. C25 is quite distant from this cluster but still near to the outer ellipse. C20, C21 and C34 are quite distant from the rest of alkanes showing a weak correlation with them and indicating the different emission sources. C20, C21, C22, C25, C28 and C34 have different positions in correlation loadings, they are located distant from the first cluster of chemical compounds. Furthermore, C22 and C28 are close to each other, confirming a high correlation.

The correlation loadings of sugars show a first cluster composed by Mol, Fru, Tre and Aol and a second cluster composed by Glu and Suc. These two groups are close to the outer ellipse that represents 100% of the total explained variance. Ino, Xol and Eryth can be found in between the two ellipses while Gse, Cel is outside of the inner ellipse that represents 50% of the total explained variance.





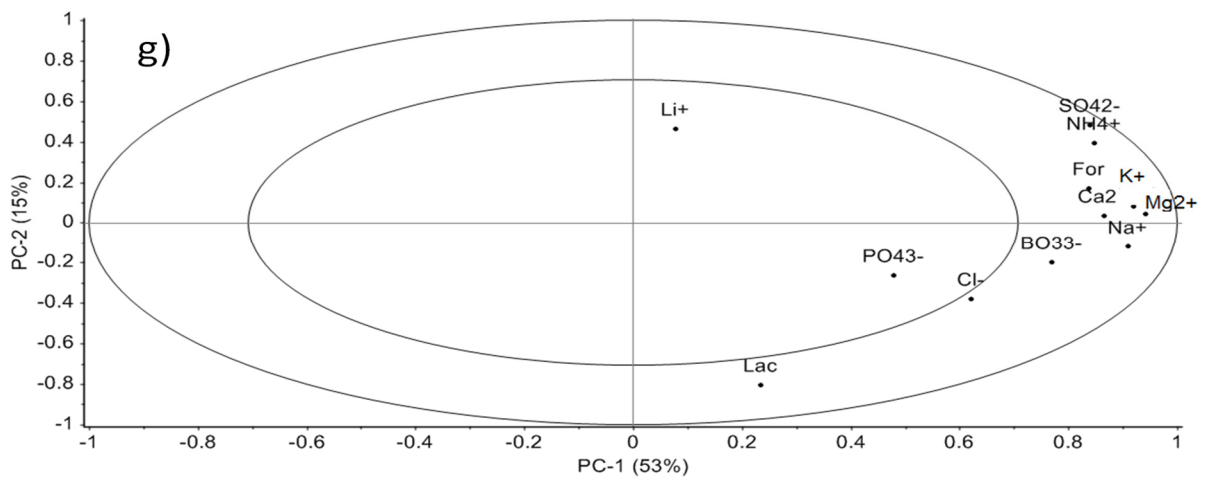
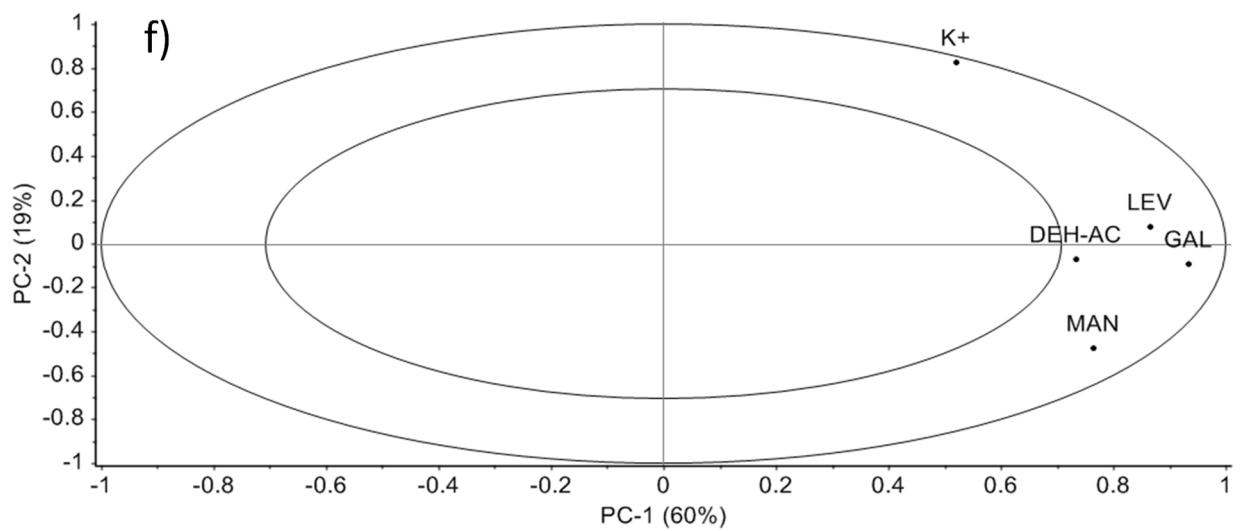
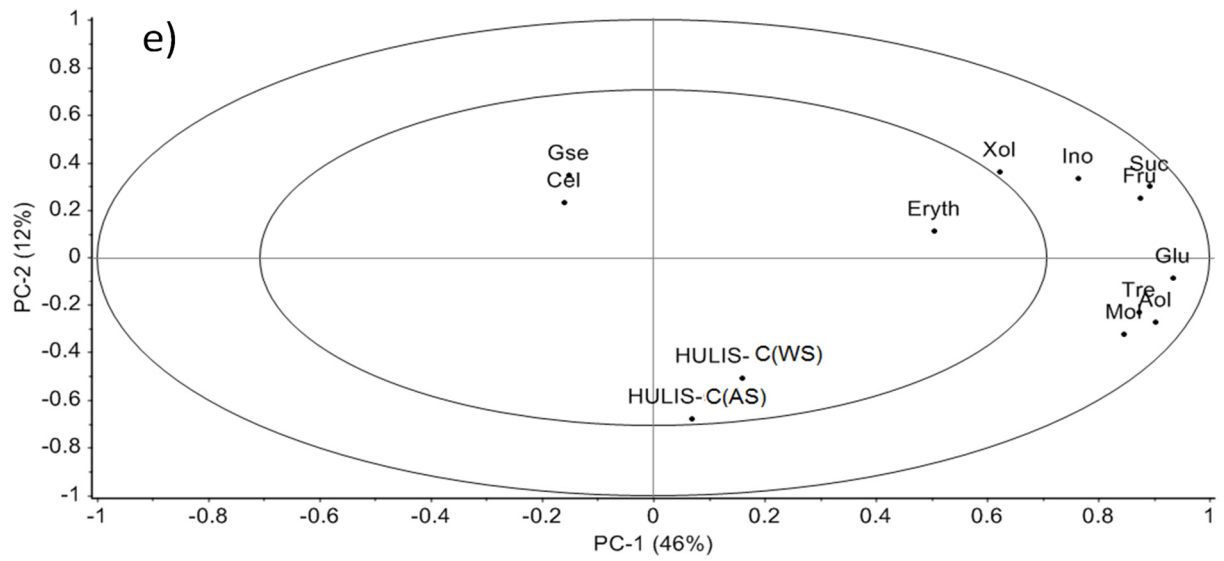


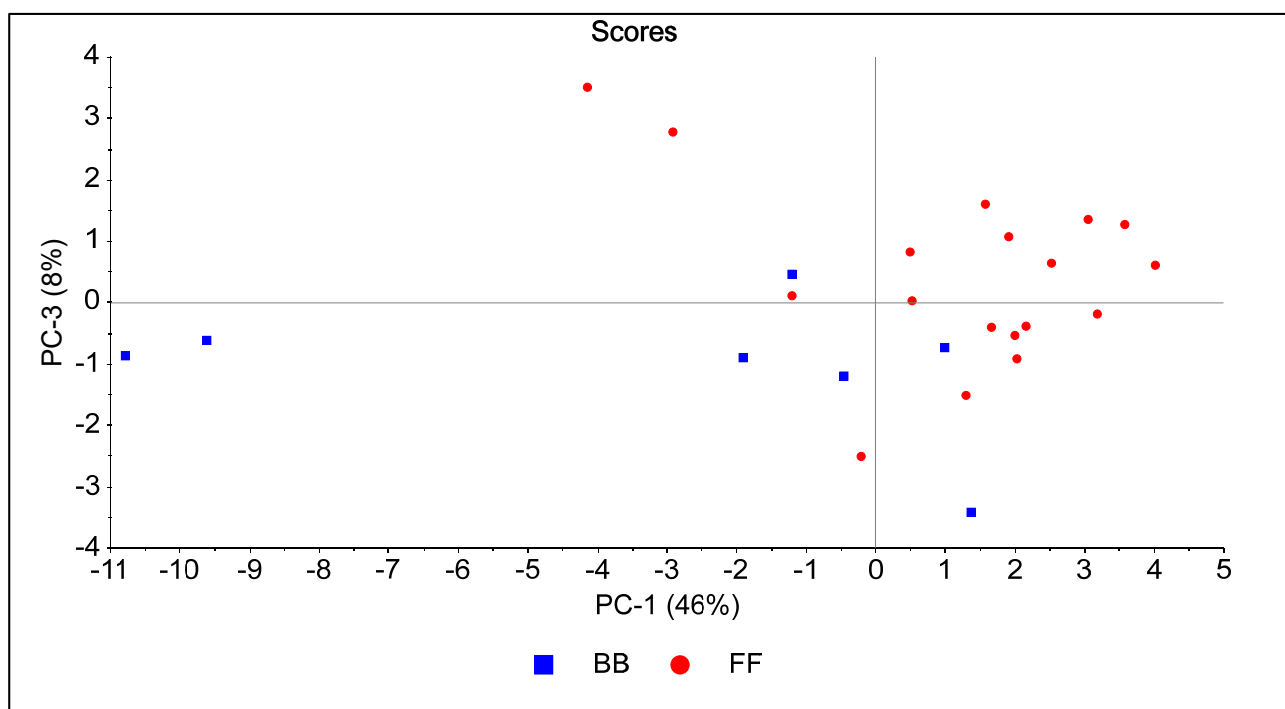
Fig. S5 Correlation loadings for a) PAHs, b) o-PAHS, c) hopans, d) alkanes, e) sugars and HULIS, f) BB markers, and g) ions.

### PCA with reduced number of compounds.

A number of variables taken in account for the final PCA was decreased in order to address the formal criteria of some statistical techniques that a number of variables should be less than amount of observations. In each family of organic compounds, from the groups of correlations only one representative was chosen. For PAHs, from 1<sup>st</sup> group (BaP, BgP, SumB, IND, ACE) two of them, namely IND and ACE, have been excluded. From Oxy-PAHS and hopans it is not possible to exclude any variables. From alkanes c20, c24, c25, c27, c32 were chosen, from sugars we include only Xol, Aol, Glu, Suc and we still keep 3 BB markers. From ions we have removed Ca<sup>2+</sup>. Total amount of variables was decreased to 29.

Figure S6 shows the score PC1 & PC3 plot, and PC1, PC3 loadings for a reduced number of variables. The intercomparison of reduced PCA with the full variable set results shows the losing of separation between BB-affected and FF daily chemistry, as was observed above. That means that the formal requirement of a small amount of compounds as variables can not provide the satisfactory data presentation.

a)





b)

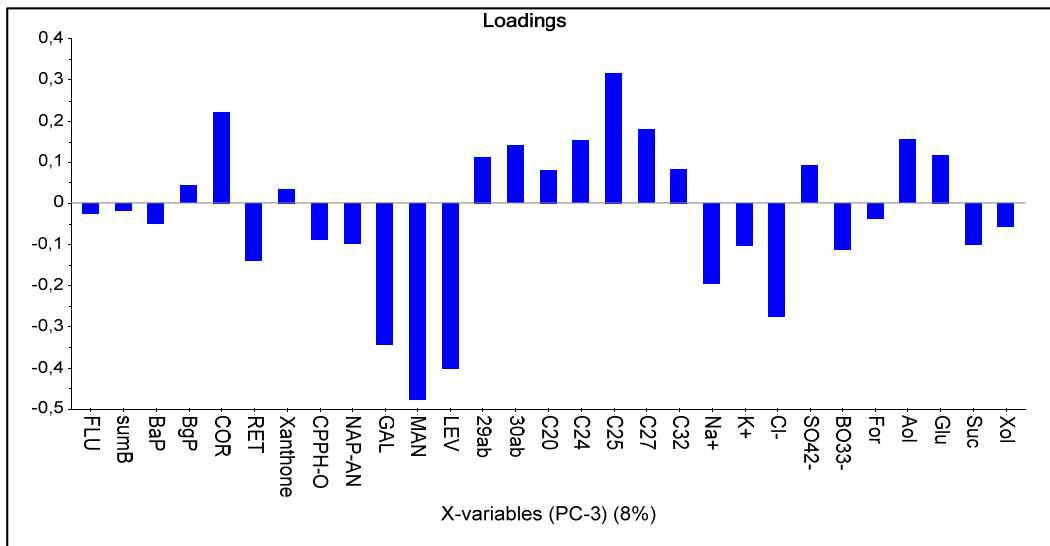
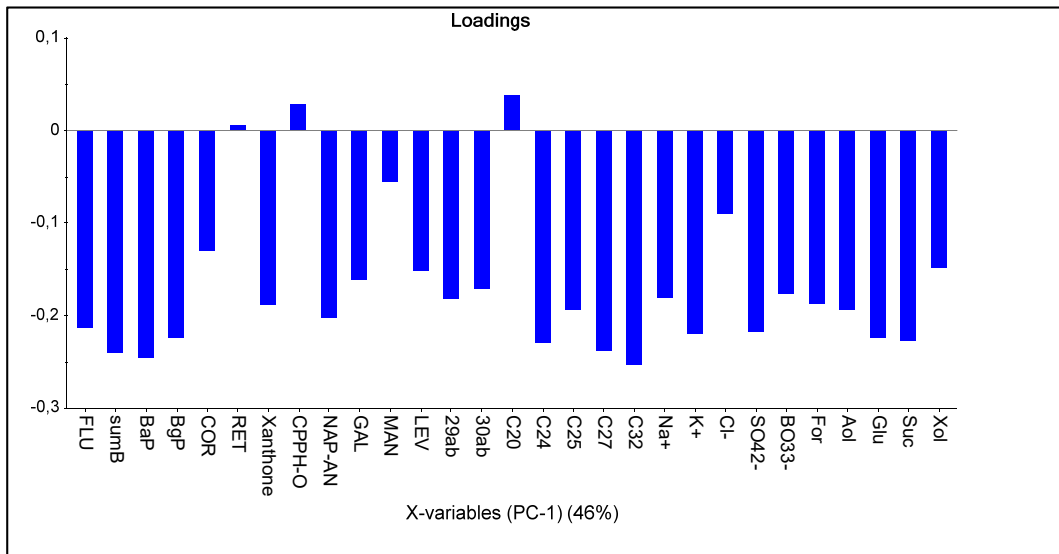


Fig.S6. a) Score PC1 & PC2 plot and b) PC1 and PC3 loadings for a reduced number of variables.