

Applying multivariate statistical methods to Herbivore induced plant volatile measurement data

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Volatile organic compounds (VOC) are constantly emitted from terrestrial plant life. Emissions of plant volatiles are dependent on physiological conditions, and changes in these conditions could rapidly induce emissions or alter emission dynamics. Herbivore induced plant volatiles (HIPVs), are a class of VOCs produced by plants mainly to provide direct and indirect protection against herbivores. In order to study the HIPV formation and the subsequent secondary organic aerosol (SOA) formation and growth an intensive measurement campaign was organized in our research facilities during summer 2015.

To study HIPV emission dynamics Scots pine saplings were exposed to four bark feeding-pine weevils. The emitting compounds were monitored continuously before and after treatment by proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) and the online measurements were supplemented with cartridge samples, which were analyzed offline via thermodesorption-gas chromatography-mass spectrometry (TD-GC-MS). SOA formation was monitored with High resolution-aerosol mass spectrometer (HR-AMS), and scanning mobility particle sizer (SMPS).

The advanced online monitoring techniques used in this study produce large sets of complex and highly detailed data on the chemical and physical quantities of the emissions. Wyche et al. (2015) used principal component analysis (PCA), hierarchical cluster analysis (HCA) and positive least-squares discriminant analysis (PLS-DA) to address the need for advanced data analysis methodology in the analysis of the large datasets produced in their chamber measurements. Using multivariate statistical methodology to mass spectrometry data is not totally new approach, as positive matrix factorization (PMF), introduced by Paatero and Tapper (1994), is the de facto method for the analysis of AMS measurement data. In addition, Wyche et al. lists several other recent papers using similar methodology for other aerosol composition data. This inspired us to apply similar methodology to our HIPV and SOA formation data.

The data was pre-treated in the same manner as described in Wyche et al., including using Mann-Whitney test to find the signals in individual mass channels which were significantly differing from the signals measured during a blank experiment. The multivariate methods were for the significant signals in order to detect similarities and differentiating patterns between different mass fractions.

Our preliminary results indicate that we can identify different phases of the experiment (pre-treatment, active feeding and post-treatment) with canonical discriminant functions (Fig 1.) by using only 16 of the AMS mass signals.

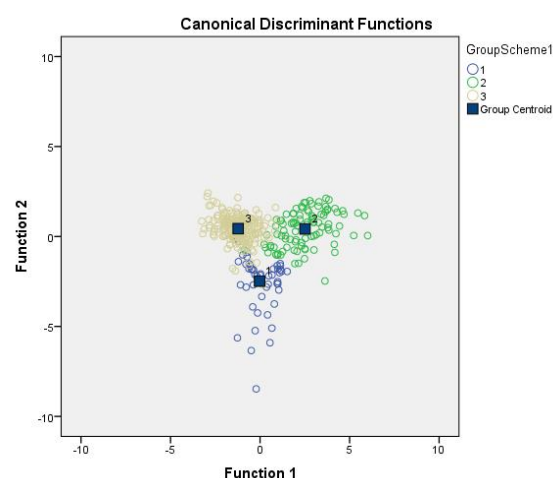


Figure 1. The phases of the experiment (1=pre-treatment, 2=active feeding, 3=post-treatment) separated with DA

We applied principal component analysis to AMS measurement data in order to separate different chemical compounds from the data. The first PCA results indicate that the masses do not separate very clearly between the components. However, some shapes in the dividing of the different compounds could be seen and additional analysis is needed to see all significant patterns in the AMS data. PCA is expected to work better for PTR-ToF-MS data as Wyche et al. were able to give clear mapping for gas-phase composition in their analysis.

The preliminary results showed that pine weevils had a large impact on VOC emissions emitted by Scots pine and subsequent SOA formation. We were able to detect the different phases of the experiments with the multivariate methodology and to construct three principal components out of the AMS measurement data. Subsequent analysis is needed for gaining full insight to the HIPV emission dynamics within our measurement.

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Paatero and Tapper. *Environmetrics*, 5, 111–126, 1994.
Wyche et al. *Atmos. Chem. Phys.*, 15, 8077–8100, 2015.