Linear unmixing of reactive organic pollutants in the atmosphere

Recently, factor analytical models have been applied to organic aerosol (OA) data (e.g., Lanz et al., 2007). Non-reactivity of the observed quantities is assumed within source-receptor models based on physical (linear) mixing processes (e.g., Positive Matrix Factorization, PMF) and is crucial to recover realistic source fingerprints of air pollutants from ambient datasets. However, it is well-known that organic aerosols (and gases) in fact do react in the atmosphere and air masses of different age arrive at measurement sites, complicating the issue of receptor-based source apportionments. This nonconformity has been tackled by using ambient measurements performed close to OA sources and interpreting the resulting factors as receptor profiles (i.e., secondary and differently aged OA) rather than source profiles. (In the case of organic gases, other strategies to account for reactivity have been
proposed: selecting species with similar atmospheric lifetimes, down-weighting the most reactive substances, excluding day-time samples etc.)
Irrespective of these precautions, it is nevertheless possible that the species were grouped to factors according to their reactivity rather than source origin in those studies: less reactive and secondary compounds exhibit a temporal variability pattern different from primary OA, leading to OA accumulation phases, seasonal cycles etc.. Different levels of variability (source activities, the species' stability in the atmosphere, age of the air arriving masses etc.) may interfere and it is often not clear which level has the strongest influence on the factor analytical results from receptor data.
As a first-guess approach a background estimate can be subtracted from the time series of each measured quantity before factor analytical modeling. We thereby assume that changes in the concentration of more persistent and secondary compounds occur on a larger time scale than primary emissions. The background estimates are based on iterative non-linear regression fits and low-pass filtering (Kolmogorov-Zurbenko) of the residuals as adapted from Novelli et al. (1998) and Thoning et al. (1989). Two data sets were investigated: an 8 year-long and 4 hourly-resolved record of volatile hydrocarbons at a high Alpine-site and 3-week OA data retrieved by aerosol mass spectrometry (AMS) at 2 minutes time-resolution (rural site).

Thoning et al., J. Geophys. Res., 94, 8549-8565, 1989.
Novelli et al., J. Geophys. Res., 103, 19015-19033, 1998.
Lanz et al., Atmos. Chem. Phys., 7, 1503-1522, 2007.