Secondary organic aerosols (SOA) chemical characterization employing simulated NMR spectra of model compositions.

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Secondary organic aerosol (SOA) accounts for a significant fraction of ambient particulate matter and a detailed knowledge of the formation, properties and transformation of SOA is therefore required to evaluate its impact on atmospheric processes, climate and human health (Hallquist et al., 2009). Elucidation of the chemical and physical processes underlying SOA formation has been pursued using various experimental and modeling approaches of different degree of complexity. Most employed methods rely on the definition of volatility classes for the constituents of SOA as a function of precursor types and oxidation conditions. This kind of information can be achieved relatively easily in laboratory experiments and their application to field conditions is based on the hypothesis that the actual chemical processes involved in SOA formation occur at the same manner in smog chambers and in real ambient aerosol particles. In order to cope with the real complexity of the system, explicit gas-phase chemical models coupled to gas/particle partitioning models have been formulated (e.g., Johnson et al., 2006), Explicit chemistry models are much more complex and contain many more uncertain parameters then the approaches based on volatility distributions, but in turn, they can be constrained by the observations not only for total organic aerosol concentrations but also in respect to the actual chemical composition. For this reason, efforts aimed to identify good diagnostics extracted from chemical observations of ambient and laboratory SOA is a promising tool to reduce the uncertainty in SOA formation models in an effective way. In this context, molecular markers can provide unambiguous information of the occurrence of specific SOA types in ambient air, but their use as diagnostics for SOA composition is limited by the fact that molecular speciation methods show limited analytical recovery. Functional group methods have the clear advantage of targeting integral properties of the organic complex mixtures. In other words, molecular complexity can be reduced to a relatively small number of functionalities. The main caveat of functional group spectroscopic methods is that the individual techniques exhibit very different sensitivities to specific organic structures and that the spectra always present large peak overlaps. To cope with such complexity, *simulated* spectra can be generated starting from the modeled chemical composition so that models and observations can be compared directly using the spectral data.

This study examines the use of simulated H-NMR spectra as diagnostics for models of biogenic and anthropogenic SOA formation. Spectral fingerprints for selected SOA systems – ozonolysis and photooxidation of alpha-pinene and photooxidation of 1,3,5-trimethylbenzene (TMB) – were recorded for samples of SOA collected during reaction chamber experiments. The simulation of H-NMR spectra starting from model compositions was carried out using ACD-Labs algorithms tested against their ability to reproduce the spectra of standard compounds, including molecules possessing a complex stereochemistry like the oxidation products of alpha-pinene. Simulated spectra were recorded for model mixtures comprising compounds derived from literature studies of GC/MS and LC/MS characterization, as well as compounds expected to occur in SOA based on explicit gas-phase chemistry models for alpha-pinene and TMB. In particular, a set of chemical species from the Master Chemical Mechanism (MCM) was selected, based on simple assumptions about their expected volatility, to account for the uncharacterized fraction of SOA.

The results show that compounds bearing double bonds were very unlikely to occur in both alpha-pinene and TMB SOA samples. The analysis provides also candidate basic structures for the SOA fraction uncharacterized at the molecular level. These findings indicate that H-NMR spectroscopy can be used as a new, useful diagnostic tool for SOA formation models including explicit chemistry.

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