

Project Full Name: Exploring the role of Semivolatile gas-phase vapors in Secondary Organic Aerosol Formation

## 1. FINAL PUBLISHABLE SUMMARY REPORT

### Overview of the project

Semivolatile organic compounds (SVOCs) are sticky and multiphasic, and largely responsible for Secondary Organic Aerosol (SOA) formation. But the quantification of semivolatiles in gas phase is an ongoing challenge. Recently, the Thermal desorption Aerosol Gas chromatograph (TAG) method (Williams et al., *Proc. Nat. Acad. Sci.*, **107**, 6676, 2010) was successfully applied to determine the gas/particle-phase partitioning of semivolatile compounds. In that method, the gas-phase portion of the semivolatiles were measured only on a relative scale and could not be quantified due to the lack of quantitative gas phase measurements. The measurement of multi-phase (gas and particle) concentrations of semivolatile organic compounds was the main task of this project. In this project, a sampler box containing three-denuders in series was constructed which was interfaced with TD-PTR-MS to quantify semivolatiles in an ambient aerosol mixture. The three-stage denuder-sampling device (bunch of DB-1 columns in 1<sup>st</sup> and 2<sup>nd</sup> denuder, and activated carbon in 3<sup>rd</sup> denuder) was effectively employed for sampling gas phase SVOCs in DB-1 denuders and VOCs in carbon denuder. A collection-thermal-desorption (CTD) cell in TD unit was used for collecting aerosol particles. The instrument was deployed in summer 2013 during the Southern Oxidant and Aerosol Study (SOAS) at the SEARCH ground site, Centreville, Alabama for first direct measurements of the bulk of SVOCs in the gas phase and the particle phase on 90 minutes time resolution.

### Results

(1) We developed a denuder sampler unit and successfully set up the unit with the existing TD-PTR-MS, which provides a sensitive and effective method for measuring low concentrations of highly oxidized organic compounds, possibly SVOCs in the gas phase. The instrument was developed as automated allowing for unattended sample measurements. The high mass resolution capabilities of ~5000, low detection limit (<0.05 pptv for gas species, <0.01 ng m<sup>-3</sup> for aerosol species) and good physical and chemical characterization of SVOCs with the TD-PTR-MS allows constraining both, the quantity and the chemical composition.

(2) We performed indoor measurements with the experimental set-up from where several hundreds aerosol species and semivolatile organic compounds including hydrocarbons, oxygenated hydrocarbons, organonitrates were identified (See Figure 1). A short- to long-term indoor measurement generated data about the indoor air quality.

(3) We deployed the instrument in SEARCH ground site, Centreville, Alabama, which was highly impacted by Biogenic Volatile Organic Compounds (BVOCs) and occasionally influenced by anthropogenic pollution. BVOCs and their oxidation products are capable of partitioning into the particle phase, so their simultaneous quantification in both phases using our instrumental set-up was used to determine the gas/particle-phase partitioning. These results give the valuable insights into sources

that reduce the current discrepancy in the global budget of Secondary Organic Aerosol (SOA). The partitioning results from the SEARCH site showed the expected diurnal variation based on the changes of air temperature for many species.

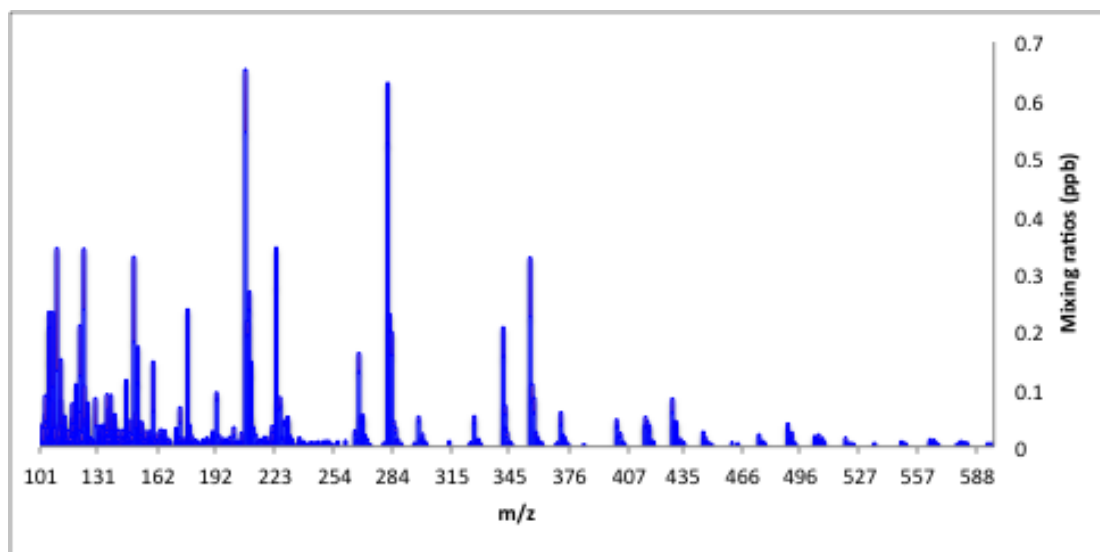


Figure 1: Mixing ratios of SVOCs ranging from  $m/z$  100 to  $m/z$  600 for 10L indoor sample

### Conclusion

A new analytical approach that combines the strengths of TD-PTR-MS with multi-denuder gas phase SVOCs sampling has been developed and then deployed at the SEARCH ground site, Centreville, Alabama. The improved sensitivity of the instrument with high mass resolution capabilities of  $\sim 5000$  and the enhanced detection limit of the instrument with moderate sample volume allows to quantify the degree of oxygenation of low concentration of organic compounds and to elucidate the chemical processes that transform fresh compounds to highly oxidized compounds. The results from this study give valuable insights into sources and processing of Secondary Organic Aerosols (SOAs) that can be used to improve parameterization algorithms in regional and global climate models.

### Socio-Economic impacts of the project

(1) SVOCs are derived from natural as well as from human activity and are thus important aerosol precursors. All of these compounds are important for air quality and climate. The measurements of these compounds generate data about air quality. So, this project has a key impact in European science, management, and policy.

(2) A better understanding of the sources of SOA and their physicochemical processing is very important for policymakers of European countries due to associated health issues, climate change, and economic implications. The project addresses these issues with an innovative and powerful analytical approach through quantification of SVOCs and identification of unknown organic aerosols.

(3) The measuring-modelling integrated approach give the better understanding of the effects of SOA on the biosphere and human health, their radiative impacts, and their climate effects.

## 2. USE AND DISSEMINATION FOREGROUND

A qualitative and creative contribution to the development of SVOCs analytical measurement techniques and the application of these measurements in Southern Oxidant and Aerosol Study (SOAS) has been made for solving scientific problems in the field of atmospheric aerosol research. The project's result is important to this field because it transfers knowledge to this community in publications, presentations, and assessment of technical development. Two posters (one as a lead author and the other as a co-author) from the research project's result were already presented in AGU (American Geophysical Union) Fall Meeting 2013 held at San Francisco from December 9 to December 13. An oral presentation (outcome of the project) was delivered in the host institute (Institute of Marine and Atmospheric Research, Utrecht University). It is expected to participate a workshop on data from SOAS campaign, which will be held at the NCAR Boulder, CO, USA from March 31 to April 2, 2014. The outcome of the project has been a common interest for other groups (e.g., Prof. Allen Goldstein's group at UC Berkeley and Prof. Jose Jimenez at University of Colorado-Boulder), which establishes a stronger collaboration with the US scientists and will produce a number of joint publications. Three manuscripts (one on analytical technique and two on measurement data from SOAS) are in preparation stage, which will be published in reputed peer reviewed journal by the end of the year 2004.

### International Conferences

- (1) **Khan, M.A.H.**, Holzinger, R., Quantification of Semi-Volatile gas-phase Organic Compounds (SVOCs) and Organic Aerosol Species, AGU2013 Fall Meeting, Poster no-A13A-0153.
- (2) Thompson, S., Yatavelli, L.R., Stark, H., Kimmel, J., Krechmer, J., Hu, W., Palm, B.B., Jost P.C., day, D.A., Isaacman, G.A., Goldstein, A.H., **Khan, A.**, Holzinger, R., Lopez-Hilfiker, F., Mohr, C., Thornton, J.A., Jayne, J.T., Worsnop, D.R., Jimenez, J.L., Comparison of the composition and gas/particle partitioning of organic acids in monoterpene and isoprene dominated environments, AGU2013 Fall meeting, Poster no-A13A-0176.
- (3) Holzinger, R., **Khan, A.**, Oyama, B., Timkovsky, J., Chemical composition of organic aerosol explored by novel TD-PTR-MS, ACCENT-plus symposium, Urbino, 17-20 September 2013.

### List of papers (in preparation)

- (1) **Khan, M.A.H.**, Holzinger, R., Development of denuder sampling device interfaced with PTR-MS to quantify semivolatile gas-phase organic compounds, Preparing to submit in Atmospheric Measurement Techniques.
- (2) **Khan, M.A.H.**, Holzinger, R., Aerosol/gas partitioning of semivolatile organic compounds explored by denuder sampler-TD-PTR-MS from Southern Oxidant and Aerosol Study, Preparing to submit in Atmospheric Physics and Chemistry.

- (3) Thompson, S., Yatavelli, L.R., Stark, H., Isaacman, G.A., Goldstein, A.H., **Khan, M.A.H.**, Holzinger, R., Jimenez, J.L., Comparison of the composition and gas/particle partitioning of organic acids in monoterpene and isoprene dominated environments.