Topic number: W1

PROTON TRANSFER REACTION MASS SPECTROMETRY: AMBIENT AIR VOCs MEASUREMENT IN BELGRADE SEMI-URBAN AREA

Andreja Stojić (*), Mirjana Perišić, Zoran Mijić, Slavica Rajšić

Institute of Physics, University of Belgrade, Belgrade, Serbia

(*)**andreja@ipb.ac.rs**

Volatile organic compounds (VOCs) are very important local and regional atmospheric pollutants playing an important role in tropospheric chemistry by affecting OH radical concentrations and the production of photochemical oxidants. Monitoring of VOCs in the urban area is important due to the adverse effects some of them have on human health (WHO, 2000). Benzene, associated with traffic emissions and 1,3-butadiene are considered to be the most toxic. In semi-urban areas, VOC sources can be both anthropogenic and biogenic. Major anthropogenic sources include vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions and industrial processes. Biogenic emissions, whose main sources are terrestrial plants, are globally the most important source of the VOCs found in the atmosphere.

In order to assess the ambient levels and possible origin of VOCs, concentrations of thirty-one compound were measured on-line in a semi-urban site of Belgrade using Proton Transfer Reaction Mass Spectrometer (PTR-MS) – Ionicon Analytik, Innsbruck, Austria. Measurements were conducted during thirty days episode in February, 2010. The one-hour mean values from on-line measurements have been calculated.

PTR-MS allows real-time measurements of VOCs in air with a high sensitivity and a fast time response (De Gouw and Warneke, 2007). The air to be analysed is continuously pumped through a drift tube reactor. A fraction of VOCs is ionized in proton-transfer reactions with hydronium ions (H_3O^+) – the soft ionization method that generally does not lead to fragmentation of the productions what simplifies the interpretation and the quantification of the mass spectra. The mass of the product ion equals the VOC mass plus one atomic mass unit. At the end of the drift tube the reagent and productions are measured by a quadrupole mass spectrometer combined with Secondary Electron Multiplier detector. The product ion signal is proportional to the VOC mixing ratio.

The measurements were performed at the height of 4 m above ground, at the platform of the Institute of Physics, 10 km northwest of Belgrade centre (Serbia), in the semi-urban area and 100 m far from the right bank of the Danube River. The air was conducted to a PTR-MS system through a 2 m heated Teflon tube, inner diameter 3 mm. PTR-MS was programmed to monitor 31 mass at 100 ms per mass.

Meteorological parameters including temperature, relative humidity, rainfall, wind direction and speed were provided by the local Meteorological Station positioned at the same platform.

The most abundant compound was propanol followed by methanol, propene, and acetaldehyde with mean concentrations of 23.45 ppb, 22.12 ppb, 13.38 ppb and 11.39 ppb respectively.

In order to find correlation between measured compounds and meteorological parameters, Pearson's correlation coefficients were calculated. The highest correlation coefficient ($p<0.05$) was observed between methanol and acetaldehyde ($r = 0.96$) and benzene and acetonitrile ($r = 0.96$). Methanol was also highly correlated with formaldehyde ($r = 0.94$), acetone, 1.3-butadiene and cyclohexane. The correlations between volatile compounds and meteorological parameters were not expressive.

Since one of the main difficulties in air pollution management is to determine the quantitative relationship between ambient air quality and pollutant sources, Unmix receptor

model has been used to analyse VOCs concentrations (Hopke, 2003). Model was run with 654 observations. Five factors were chosen as the optimum number for the model. The highest contribution has factor which has high loadings with compounds related to local production processes, followed by profiles related to biomass burning and traffic emissions. Time series plot and scatter-plots of observed and Unmix predicted concentrations of acetonitrile and benzene are shown at Fig. 1.

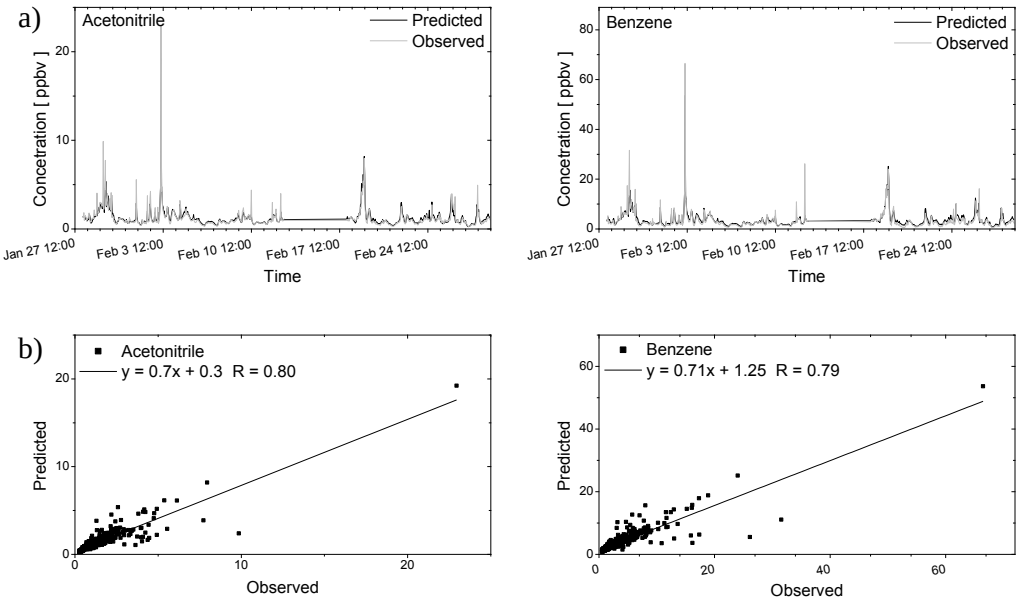

Fig. 1: a) Time series plot of observed and Unmix predicted VOCs concentrations b) Scatter-plots of measured and Unmix predicted VOCs concentrations

References

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