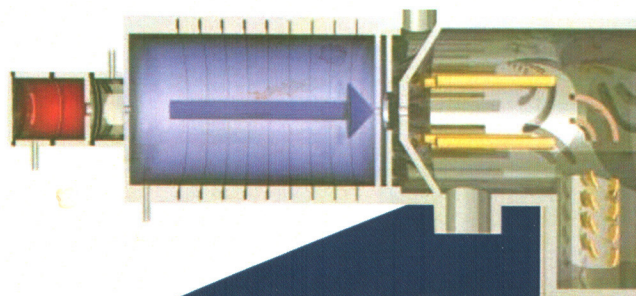


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Armin Hansel, Jürgen Dunkl

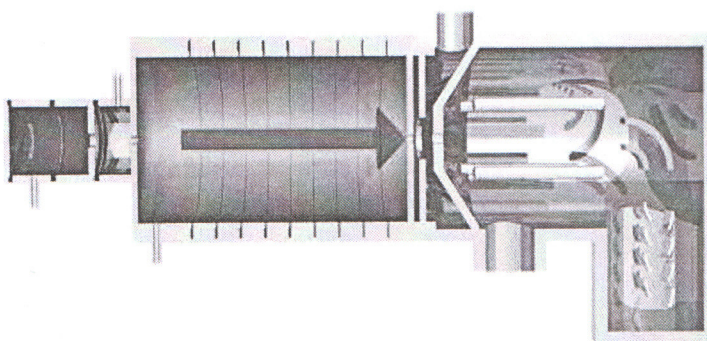
**Contributions**

5<sup>th</sup> International Conference on  
Proton Transfer Reaction  
Mass Spectrometry and its Applications



*innsbruck university press*

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## Contributions

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*January 26<sup>th</sup> – February 2<sup>nd</sup>, 2011*

## Ambient VOCs measurement in winter: Belgrade semi-urban area

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### Abstract

In order to assess the ambient levels and possible origin of volatile organic compounds (VOCs), concentrations of thirty one compounds were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) in a semi-urban site of Belgrade. Measurements were conducted in February 2010. One-hour mean values have been calculated and used for further analyze together with meteorological parameters. Unmix receptor model was used to identify the sources of VOCs.

### Introduction

As very important local and regional atmospheric pollutants, monitoring of volatile organic compounds (VOCs) and determination of their origin is significant. By affecting OH radical concentrations and the production of photochemical oxidants, VOCs play an important role in tropospheric chemistry. Chemical reactions with nitrogen oxides under sunlight lead to the production of secondary air pollutants, resulting in tropospheric ozone and secondary organic aerosols (SOAs) (Seinfeld and Pandis, 1998). Due to the adverse effects some of them have on human health, monitoring of VOCs in the urban area is very important (WHO, 2000).

VOCs sources in semi-urban areas can be both anthropogenic and biogenic. Major anthropogenic sources include vehicle exhausts, gasoline evaporation, solvent use, natural gas emissions, and industrial processes. Benzene and toluene are compounds associated with traffic emissions, but toluene is also released with the use of solvents (painting, printing, dry cleaning, etc.).

### Receptor modeling

Receptor models based on chemical composition have been used intensively for source apportionment. The fundamental principle of receptor modelling is that the mass conversation can be assumed and a mass balance analysis can be used to identify and apportion sources of VOCs. In order to obtain data set for receptor modelling individual chemical measurements can be performed at the receptor site by measuring VOCs concentrations. From a receptor point of view, pollutants can be roughly categorized into three source types: source known, known source tracers (i.e. pollutant is emitted with another well characterized pollutant) and source unknown what lead to main differences between models - the degree of knowledge required about the pollution sources prior to the application of receptor models. For sources that have known tracers but do not have complete emission profiles, factor analysis tools such as Principal Component Analysis (PCA), Unmix and Positive Matrix Factorization (PMF) can be used to identify source tracers. PCA attempts to simplify the description of a system by determining a minimum set of basis vectors that span the data space to be interpreted. The concepts underlying Unmix have already been presented in geometrical and intuitive manner (Henry, 1997) and mathematical details are presented elsewhere (Henry, 2003). In this study, the version of EPA Unmix 6, available from the US Environmental Protection Agency (U.S. EPA, 2007) have been used.

## Experimental Methods

VOCs concentrations were measured on-line using Proton Transfer Reaction Mass Spectrometer (PTR-MS) - Ionicon Analytik, Innsbruck, Austria; which allows real-time measurements in the air with a high sensitivity and a fast time response (Lindinger et al., 1998). The air to be analyzed is continuously pumped through a drift tube reactor where the fraction of VOCs is ionized in proton-transfer reactions with hydronium ions ( $\text{H}_3\text{O}^+$ ) - the soft ionization method, that generally does not lead to fragmentation of the product ions 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 product ions 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 quantity measured with PTR-MS is usually the intensity of a protonated compound on the mass of which information is obtained what does not directly allow the definite identification of isobars and isomers. The measurements were performed at 6 m above ground, at the platform of the Institute of Physics, ( $\phi = 44^\circ 51' \text{ N}$ ,  $\lambda = 20^\circ 23' \text{ E}$ , Hs = 92 m) Zemun, 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 ( $70^\circ \text{C}$ ), inner diameter 3 mm. The PTR-MS operated at standard conditions with average  $\text{H}_3\text{O}^+$  ion signal of  $3 \cdot 10^6$  cps with less than 2%  $\text{O}_2^+$ .

## Results

PTR-MS was programmed to monitor 31 masses at 100 ms per mass with average measurement cycle was around 4 s. Monoterpenes concentration was estimated as the concentration of ions with protonated mass 137 divided by 0.46, because a certain fractionation of non-oxygenated monoterpenes occurs during ionization in the drift tube resulting in masses 67, 81 and 95. The most abundant was compound with protonated mass  $m/z$  61 (propanol, acetic acid) with mean concentration 23.44 ppbv and peak value of 565.31 ppbv, followed by  $m/z$  33 (methanol) with mean concentration 22.08 ppbv and peak value of 352.96 ppbv,  $m/z$  43 (propylene) with mean concentration 13.39 ppbv and peak value 186.54 ppbv,  $m/z$  45 (acetaldehyde) and  $m/z$  47 (ethanol).

In this study the Unmix model has been used to analyze 1-hour averaged VOCs concentrations during 30 days measurement episode for source apportionment purpose. The analysis generated source profiles and overall percentage source contribution estimates for source categories.

Unmix receptor model was run with 656 observations of 31 input variables. Compounds  $m/z$  54 (acrylonitrile),  $m/z$  63 (dimethyl sulfide) and  $m/z$  87 ( $\text{C}_5$  aromatics) had a large signal-to-noise ratio and therefore were excluded because efforts to incorporate more species led to no feasible solution. Five factors were chosen as the optimum number for the Unmix model, details of which are discussed as follows.

## Discussion

The first profile extracted by Unmix is the gasoline evaporation related to traffic (unburned vehicle emissions) and, probably, evaporation from gas station situated nearby (about 300 m), having high loadings of compounds with protonated masses  $m/z$  61 (propanol, acetic acid) and  $m/z$  89 (MTBE, 4 dioxane). This source has average contribution of 7%. The second Unmix profile has high loadings of compounds with protonated masses  $m/z$  91 (diethyl sulfide) and  $m/z$  120 (chloroform) and can be interpreted as local solvent use with average contribution of 7%. The third profile extracted by Unmix is the vehicular exhaust having the high loadings of compounds

with protonated masses  $m/z$  93 (toluene),  $m/z$  107 (xylene,  $C_8$ aromatics),  $m/z$  121 ( $C_9$ aromatics) and medium high loadings of compounds with protonated masses  $m/z$  55 (1,3 butadiene) and  $m/z$  57 (acrolein, butene). Its average contribution is 19%. The fourth Unmix profile has high loadings of compounds which can be related to biomass/ biofuel burning with average contribution of 33%. The fifth Unmix profile has high loadings of compounds which can be interpreted as industrial solvent and painting sources with average contribution of 34%. The identified source time series plots are presented on Figure 1.

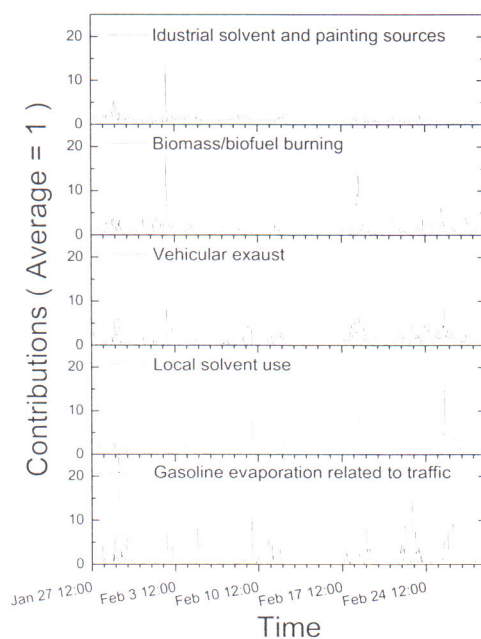


Figure 1: Unmix resolved source contributions time series

#### Diurnal patterns of source contributions

The average diurnal patterns of source contributions estimated by the two models are shown in Figure 2. The total VOC concentrations were higher in the day than at night since the most sources are related to human daytime activities. The first and third factors were related to traffic and showed typical morning and afternoon rush hours peaks. The second factor associated with solvent use, showed no pronounced peaks during working hours, which may point to constant evaporation from some warehouse. The fourth factor related to biomass/biofuel combustion showed morning peak and in the late afternoon, mostly reflecting traffic density. The maximum was extended late in the evening as a result of the use of various biofuels for individual heating units. The compounds grouped in fifth factor had higher concentrations during daytime.

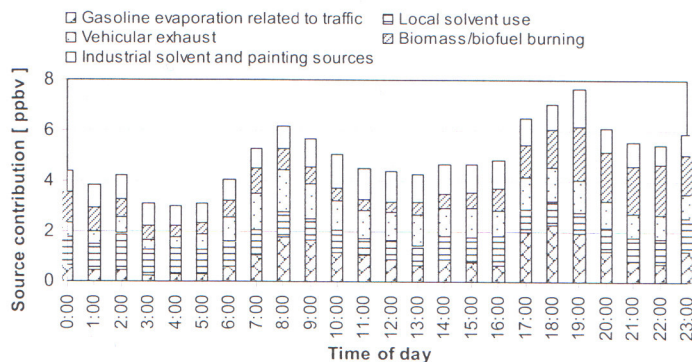


Figure 2: Diurnal patterns of source contributions estimated by Unmix

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ISBN 978-3-902719-88-1



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