Real-Time Monitoring of Urban Organic Emissions in Bern, Switzerland With the Vocus CI-TOF

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Urban areas often suffer from poor air quality due to anthropogenic emissions of gases, including NO_x, SO_2, and volatile organic compounds (VOCs). These substances are chemical precursors to ozone and aerosol particles, both linked to adverse health effects and environmental damage. These key air pollutants are routinely monitored to ensure that they remain under legally defined limits. Limits in Switzerland are defined by the Swiss Ordinance on Air Pollution Control. Gasoline and diesel combustion engines are a significant source of VOCs in cities, despite reductions due to vehicle emission control technologies. VOCs originating from cooking, heating, solvents, paint, and cleaning agents are also gaining importance. Detailed knowledge of VOC pollution and emission sources over time and space is necessary to develop a successful strategy to minimize human exposure.

Standard analytical methods for the determination of VOCs in air include automatic sampling onto absorption traps, followed by gas chromatographic separation and detection by mass spectrometry using flame, photon, or electron ionization. These methods provide time-averaged data and are limited to certain classes of VOCs depending on the preconcentration/separation step and the choice of the detector. This makes them non-ideal for some important compounds and locations in which fast, continuous measurements are needed.

Fast, Continuous Measurements of Urban Organic Emissions

TOFWERK's Vocus CI-TOF mass spectrometer quantitatively measures VOCs at concentrations well below 1 ppbv (configured with PTR Reactor using H_3O^+ ionization). Air is sampled directly without trapping, so that time varying concentration of most urban VOC pollutants can be simultaneously reported with sub-second time resolution. The high mass resolving power of the Vocus provides accurate molecular identification of targeted species. Deployment of the Vocus CI-TOF in cities is advantageous when the averaged values from the conventional measurement methods are not sufficient and fast detection of transient pollutant plumes is required.

For this work, TOFWERK deployed a Vocus CI-TOF in the National Air Pollution Monitoring Network (NABEL) station at Bern-Bollwerk, which is one of sixteen NABEL stations in Switzerland. The stations are operated by the Federal Office for the Environment and the Swiss Federal Laboratories for Materials Science and Technology (Empa). The Bern-Bollwerk NABEL station is in the immediate vicinity of a Bern train station and experiences high emissions from road traffic. In addition to meteorological data, it routinely measures NO_x, CO_2, CO, SO_2, ozone, PM and operates a gas chromatograph (GC, Syntech Spectras Analyser GC955) for measurement of benzene, toluene, and ethylbenzene/xylenes (BTX).

Experimental Procedure

For the GC analysis, VOCs are enriched for 15 minutes on a sorption trap to reach the limits-of-detection (LODs) of the method. After fast thermal desorption using clean N_2 gas, the concentrated VOCs are separated by gas chromatography and analyzed by photoionization detection (GC-PID). The whole GC cycle takes 20 mins. During the GC separation, sample for the next GC cycle is collecting, resulting in a net 5-minute sampling dead time across successive measurements.

The Vocus CI-TOF mass spectrometer was run with proton transfer reactor ionization (PTR, H_3O^+ reagent ions), ionizing and detecting all VOCs having proton affinity greater than water. Data were continuously acquired with a save rate of 1 mass spectrum every 0.5 seconds. This corresponds to 1800 unique mass spectra during the duration of each GC measurement, and 600 mass spectra during the 5-minute dead time.

Results

For a first comparison, Vocus CI-TOF data were averaged (in post processing) over the 15-minute trapping times of the GC to produce a single mass spectrum per GC cycle. Vocus data acquired during the dead time of the GC were ignored. Figure 1 shows the resulting 12-day time series for BTX (benzene, toluene, and sum of xylenes and ethylbenzene) as measured by Vocus and GC. BTX are the most abundant aromatic volatile hydrocarbons in the urban atmosphere, of which benzene is known to increase the risk of cancer, cause damage to the immune system, or worsen respiratory problems. The averaged BTX concentrations reported by the Vocus CI-TOF and the GC agree very well. Note that the xylenes values reported by the Vocus CI-TOF represent a lower limit since the known fragmentation of

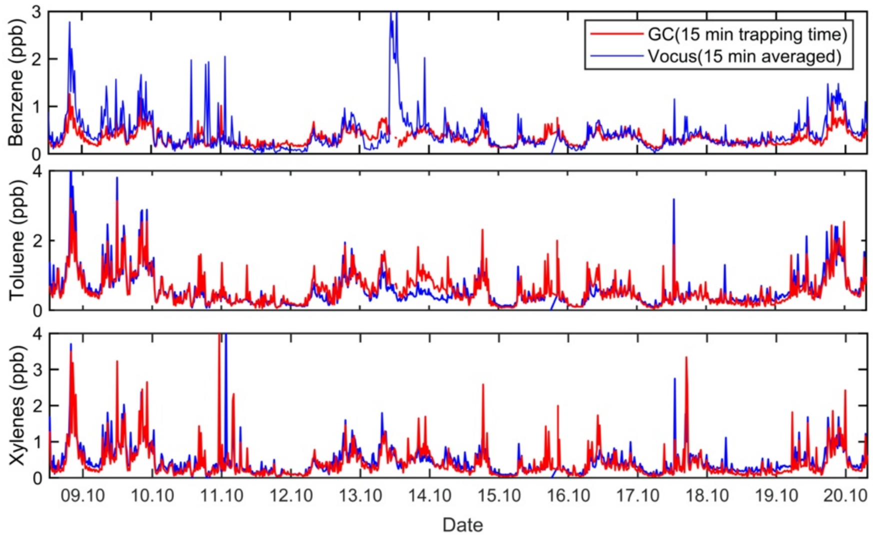

Figure 1. *Comparison of GC and averaged Vocus CI-TOF time series for three VOCs (Benzene, Toluene and Xylenes) in downtown of Bern measured in October 2020*

ethylbenzene was not taken into consideration.

In Figure 2 we show the concentration of toluene for two consecutive days as measured by the Vocus CI-TOF with 0.5 second time resolution (blue), the same data averaged to 15 minute time resolution to match the GC trapping time (green), and the GC measurements (red). 15 minute averaging is traditionally considered a short-term measurement and is used to indicate short term exposure limits (STEL). The high time resolution of the Vocus data reveals that the real peak concentrations reach up to 20 ppb, which is approximately twenty times higher than the 15 minute averaged peak values reported by the GC for toluene. Similar behavior was seen for the sum of xylenes, benzene, and tens of other potentially harmful VOCs. Averaging over longer time periods therefore leads to information loss. Fast Vocus CI-TOF measurements show that the VOC concentrations at this urban location are highly variable, indicating a huge difference in VOC emissions of individual vehicles on the road next to the sampling point. Exposure for pedestrians and cyclists may peak at even higher concentrations as they are closer to the emitting sources.

Figure 3 compares the time trends of BTX to the measurement of NOx, CO and total particle number with 1 minute time resolution. The Vocus data were also averaged to 1 minute. The daytime transient peaks reported by the Vocus CI-TOF are well-correlated with each of the key air pollutants shown in the Figure 3, indicating their similar origin and association with vehicular emissions dominating this location. Figure 4A shows the mass spectrum of a typical air plume detected by the Vocus CI-TOF in downtown Bern. The main peaks observed, such as benzene, toluene,

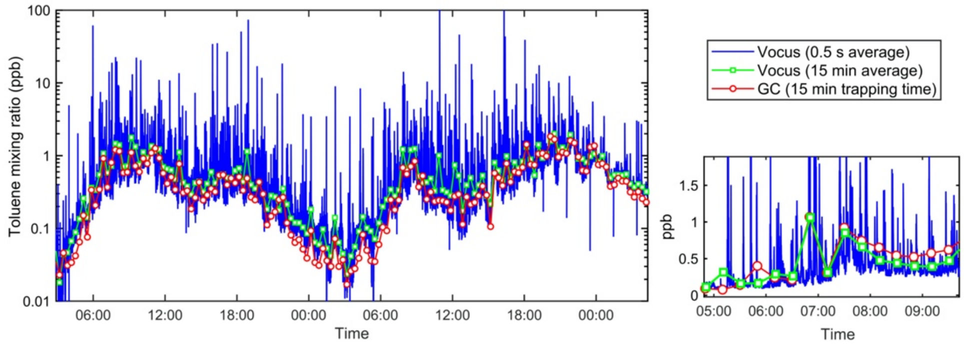

Figure 2. *Toluene concentration as measured by GC (red circles) and Vocus CI-TOF (blue) in downtown of Bern*

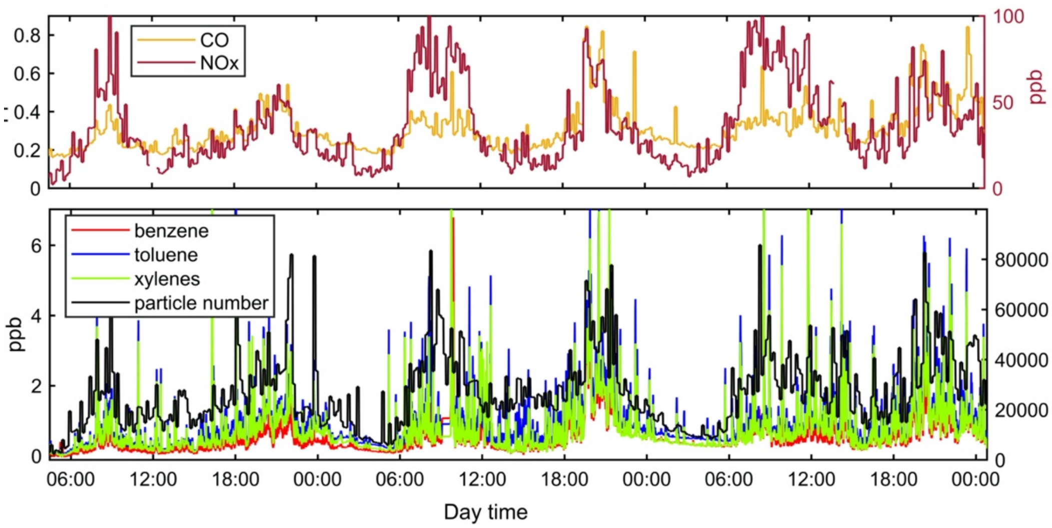

Figure 3. *(Upper) Measurement of CO and NOx during the measurement campaign in Bern Bollwerk. (Bottom) Concentration of BTX measured by Vocus CI-TOF and total particle number measured by CPC.*

trimethylbenzene or phenol, can be easily associated with traffic emission and direct car exhaust.

Figure 4B presents the difference between the time trends in the sum of these main VOC pollutants during a week and a weekend day. A clear rush-hour pattern and generally elevated concentrations during the weekday can be observed. A solid understanding and accessible presentation of these patterns could help people minimize their exposure to harmful pollutants. For example, people exercising outdoors could avoid pollution hotspots, and people with sensitive health conditions could manage their routines to avoid exposure at the worst times of day [1].

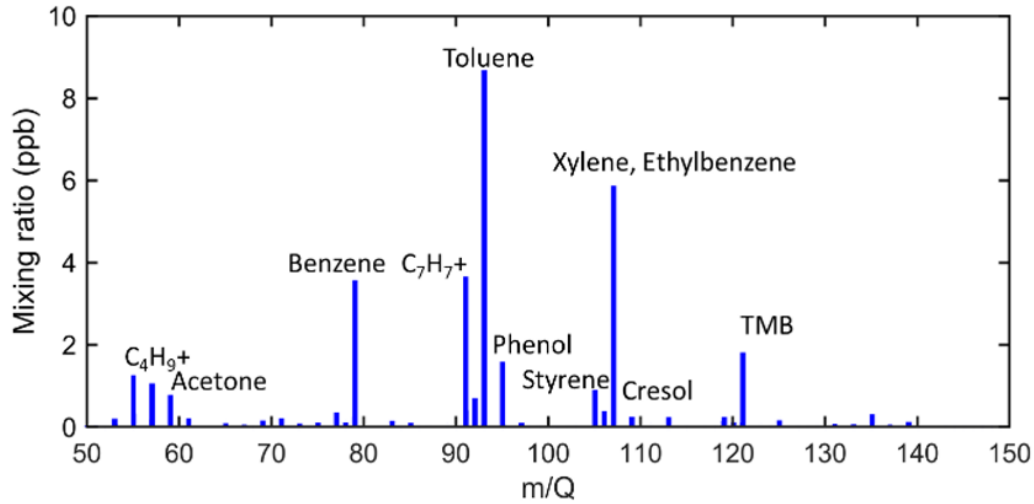

Figure 4A. *Typical mass spectrum of a traffic air plume downtown Bern measured by Vocus CI-TOF.*

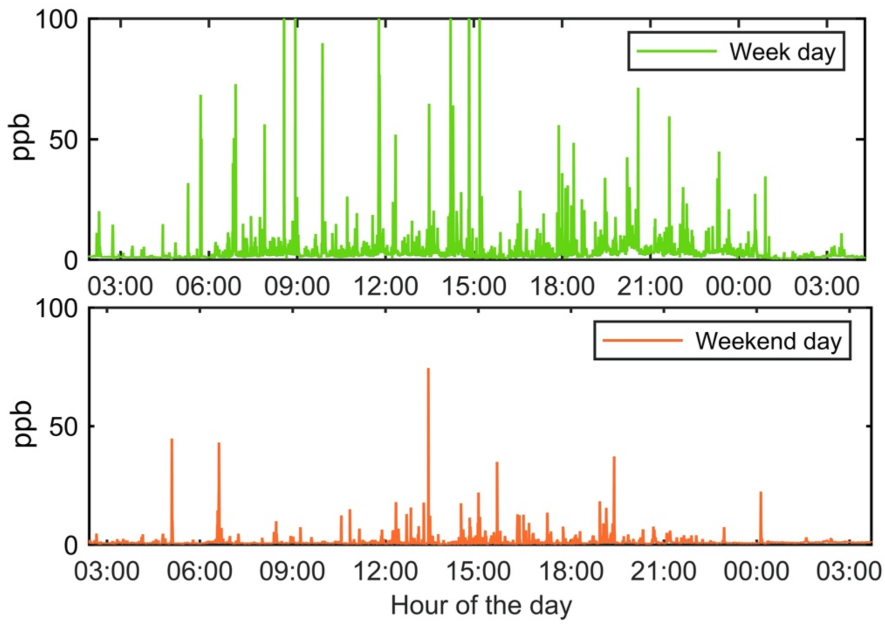

Figure 4B*. Summed time series of the main volatile aromatic hydrocarbons (benzene, toluene, xylenes and trimethylbenzene) observed in the air during week and weekend days.*

Conclusion

Measuring peak pollution concentrations near sources in high-traffic regions requires techniques with time resolution on the order of seconds. These measurements with the Vocus CI-TOF at the Bern-Bollwerk NABEL station demonstrate that peak concentrations of BTX can be more than an order of magnitude higher than what is reported by current "short-time" measurements.

According to current short-term exposure limits (STEL = 15 min), traffic emissions should not present a health risk. However, these 15-minute averaged concentrations can be much lower than peak concentrations. Air pollution epidemiology, studies of exposure to toxic chemicals, and European regulatory authorities recognize that both short-term exposure to high concentrations and long-term exposure to lower concentrations can negatively affect health, and for certain chemicals the peak concentrations may be more important than the average exposure [2,3,4,5]. More research is required for linking health effects to peak exposure in addition to average exposure to VOCs.

The Swiss Ordinance on Air Pollution Control states that its purpose is to protect not only from harmful pollution but also from annoying pollution. Annoyance is much more related to peak values than to time-averaged values. This same effect is currently in discussion with Swiss noise regulation, where legal noise levels are reduced by time-averaging and therefore may no longer present a valid measurement for annoyance.

Finally, the measured BTX peak concentrations cannot explain the annoyance of traffic related smells. The odor threshold for benzene is 1.5 ppmv, which is far higher than the measured peak concentrations. There must be other compounds responsible for the bad odors. Those compounds may occur in much lower concentrations, as BTEX are usually the most abundant substances in traffic pollution. More research is required for linking bad odors to their compounds of origin and their emission sources.

Acknowledgements

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References

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