

# Real-time profiling of organic trace gases in the planetary boundary layer by PTR-MS using a tethered balloon

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**Abstract.** A method for real-time profiling of volatile organic compounds (VOCs) was developed combining the advantages of a tethered balloon as a research platform and of proton transfer reaction mass spectrometry (PTR-MS) as an analytical technique for fast and highly sensitive VOC measurements. A 200 m Teflon tube was used to draw sampling air from a tethered aerodynamic balloon to the PTR-MS instrument. Positive and negative artefacts (i.e. formation and loss of VOCs in the tube) were characterised in the laboratory and in the field by a set of 11 atmospherically relevant VOCs including both pure and oxygenated hydrocarbons. The only two compounds that increased or decreased when sampled through the tube were acetone (+7%) and xylene (−6%). The method was successfully deployed during a winter field campaign to determine the small scale spatial and temporal patterns of air pollutants under winter inversion conditions.

## 1 Introduction

Tethered balloons have been used as research platforms to investigate boundary layer dynamics for a long time (see Stull, 1988, and references therein). Besides characterising the physical properties of the atmosphere, probing the chemical composition is of prime interest. The reduced payload capacity of the balloons, however, limits the set of monitorable compounds to species for which small sensors exist. Examples for such sensors are the miniature aerosol spectrometer (GRIMM 1.108 “Dustcheck”, 2.4 kg, GRIMM Labortechnik, 1996), which determines the aerosol mass for 15 different size bins (e.g. Maletto et al., 2003), or the widely used “ECC ozone sensor” developed by Komhyr and Harris (1971).

Volatile organic compounds (VOCs) are emitted in large amounts from both natural and anthropogenic sources and play an important role in tropospheric chemistry (Fehsenfeld et al., 1992). They are involved in the tropospheric ozone production (e.g. Monks et al., 2009) and in the formation of secondary organic aerosol (e.g. Monks et al., 2009; Hallquist et al., 2009). Some VOCs are known to have severe health effects (WHO, 2000). Proton-transfer-reaction mass spectrometry (PTR-MS) (Hansel et al., 1995; Lindinger et al., 1998) has become a powerful analytical technique for high time resolution (<1 s per compound) VOC measurements and has been successfully deployed on airborne platforms (de Gouw and Warneke, 2007, and references therein). For safety reasons, such aircraft measurements have a minimum flight altitude of 150 m above ground level (a.g.l.) over the continents. The lowest part of the planetary boundary layer is, however, of high interest because large gradients of VOCs may often occur there. Nearby sources and surface inversions, that are particularly strong in winter, often separate VOC-rich air from cleaner air aloft. Large differences in trace gas concentrations may occur within a few meters. One approach to probe the lowermost levels of the atmosphere is to place instruments on research towers (van Ulden and Wieringa, 1996; Popa et al., 2009). In principle, the gap between ground-based and aircraft measurements could also be bridged by helicopter-borne measurements (e.g. Eichinger Holder, 2009), which is a rather cost-intensive approach. Tethered balloons have been used to collect samples into bags or cartridges at different altitudes. However, the vertical resolution of this method is still poor and problems may appear during sampling and storing. Intercomparison measurements between Teflon bags and adsorbent cartridges showed large differences for some compounds (Greenberg et al., 1999).

In this paper, we present a method for VOC profiling that combines the advantages of a tethered balloon as a research platform and of PTR-MS as a fast and highly sensitive VOC



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sensor. While Jensen et al. (2002) proved the concept, by measuring acetone profiles in the Arctic using a PTR-MS and a tethered balloon lifting system, we have characterised and validated the method in both laboratory and field experiments. Data from a winter field campaign will be presented to illustrate the potential of this method to bridge the gap between ground-based and aircraft measurements.

## 2 Experimental

### 2.1 PTR-MS

Proton transfer reaction mass spectrometry (PTR-MS) (Hansel et al., 1995) is a chemical ionisation method for online measurements of VOCs.  $\text{H}_3\text{O}^+$ -ions are produced from pure water vapour in a glow discharge ion source. These ions are then injected into a drift tube which is continuously flushed with sampling air.  $\text{H}_3\text{O}^+$ -ions transfer protons to compounds that have a higher proton affinity than water ( $691 \text{ kJ mol}^{-1}$ ; i.e. most VOCs except alkanes). The protonated VOCs are then analysed and detected by a quadrupole mass filter secondary-electron-multiplier (SEM) detector system. de Gouw and Warneke (2007) have recently reviewed the deployment of PTR-MS for atmospheric measurements.

### 2.2 Tethered balloon lifting system

A tethered balloon ( $27 \text{ m}^3$ , Evolution GmbH, Stockach, Germany) filled with balloon gas (99% helium) was used to lift about 10 kg of payload. An electric winch (TS-3AW winch; A.I.R. Inc., Boulder, CO, USA) was used to raise and lower the balloon at variable speed (maximal speed  $1.8 \text{ m s}^{-1}$ ). The profiling system was deployable at ground wind speeds  $<5 \text{ m s}^{-1}$ . At higher wind speeds it was difficult to handle the balloon and the profiling altitude was limited due to the strong wind drag. Under such conditions, a parafoil kite could be a suitable alternative (Balsley et al., 1998; Jensen et al., 2002). A meteorological sonde (TS-3A-SP; A.I.R. Inc., Boulder, CO, USA) was mounted about one metre underneath the balloon. The basic meteorological parameters (temperature, pressure, humidity, wind speed and wind direction) were measured as 10 s mean values and radio transmitted to a ground based receiver (ADAS AIR-3A; A.I.R. Inc., Boulder, CO, USA). The wind direction was derived from the orientation of the streamlined balloon. The pressure information was used to derive the altitude of the balloon. This is more accurate than measuring the length of the tether because it is independent from the wind drag.

One end of a 200 m long thin wall PFA Teflon tube (Entegris Inc., Chaska, MN, USA; outer diameter: 6.35 mm, inner diameter: 4.826 mm) with a total weight of 6.08 kg was mounted next to the meteorological sonde. The tube was pressure controlled at the other end (500 mbar), using a pressure controller (Bronkhorst El-Press, Ruurlo, The

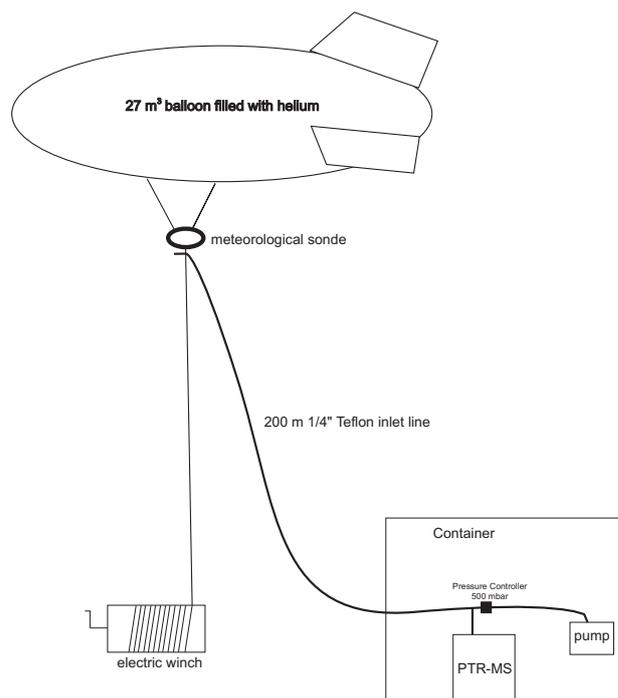


Fig. 1. Schematic drawing of the experimental setup.

Netherlands; 13 SLMP, 0–1000 mbar), and pumped with a diaphragm pump (MD-4, Vacuubrand, Wertheim, Germany). The flow measured at the intake of the 200 m Teflon tube was typically 7 standard litres per minute (SLPM). The residence time was calculated to  $24 \pm 0.5 \text{ s}$ . This calculation includes the effect of a  $\sim 450 \text{ mbar}$  pressure drop along the tube. The inlet of the PTR-MS instrument was connected immediately upstream of the pressure controller. A schematic drawing of the experimental setup is shown in Fig. 1.

## 3 Results

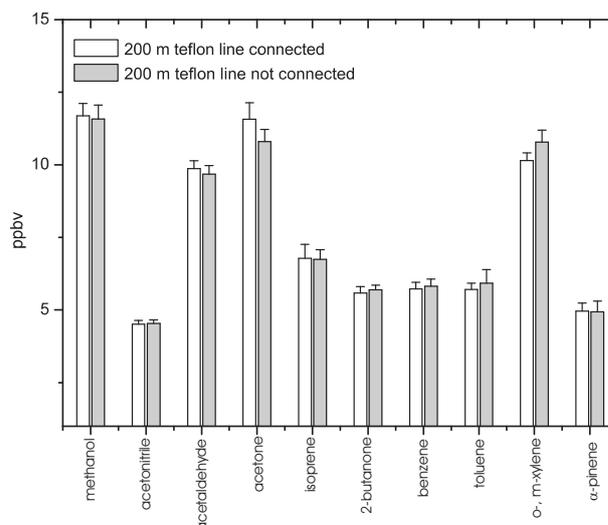
### 3.1 Characterisation of the inlet system

A series of tests was performed to investigate potential (positive and negative) VOC artefacts in the 200 m long Teflon tube. In a laboratory experiment, a gas standard (Apel-Riemer Inc., Denver, CO, USA), containing a set of VOCs (including both pure and oxygenated hydrocarbons), was spiked at a flow rate of 50 standard cubic centimetres per minute (sccm) into about 7 SLPM of air. Volume mixing ratios (VMR) of VOCs in the standard were a few ppmv (depending on the compound), resulting in VOC levels in the range of 4 to 12 ppbv. This analyte gas was either directly supplied to the PTR-MS or through the 200 m long Teflon tube. The Teflon tube was put outside the laboratory into the melting snow ( $\sim 0^\circ\text{C}$ ) to simulate the temperature conditions

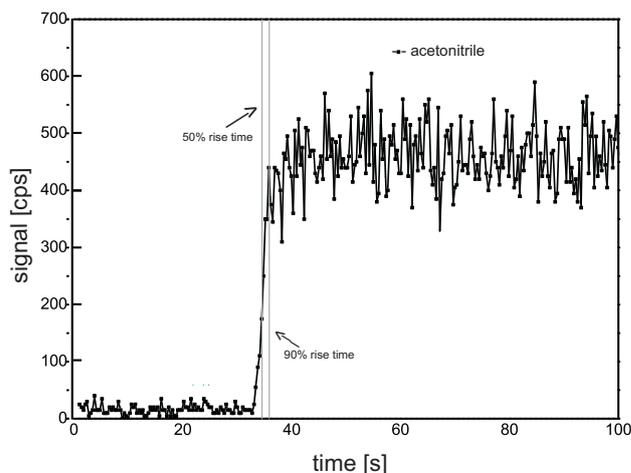
occurring during a winter field campaign. For most compounds, no statistically significant differences in concentrations, with and without the tube connected, were observed (Fig. 2). The ion signal at  $m/z$  59 which corresponds to protonated acetone showed a slight increase (+7%) when the tube was connected. Hereby,  $m/z$  denotes the dimensionless quantity formed by dividing the mass of an ion ( $m$ ) in unified atomic mass units by its charge number ( $z$ ). This finding indicates the presence of a minor source of acetone in the tube (e.g. from tube contamination, formation due to chemical reactions, or permeation through the Teflon tube). The ion signal at  $m/z$  59 may also partly arise from propanal or glyoxal, but literature data indicate that the PTR-MS  $m/z$  59 signal is usually dominated (>90%) by acetone (de Gouw and Warneke, 2007). Xylene levels were slightly lower (−6%) with the tube connected indicating some wall losses.

Field tests in the Arctic and during a winter field campaign showed an up to 20% higher  $m/z$  45 signal when the Teflon tube was connected.  $m/z$  45 is commonly assigned to acetaldehyde and the observed signal increase corresponds to an acetaldehyde artefact in the range of 50–200 pptv. This artefact may be caused by acetaldehyde formation from the heterogeneous ozonolysis of non-volatile, unsaturated species accumulated on the tube walls (Northway et al., 2004). However, during the field tests, the ozone levels were very low, typically 5–15 ppbv.

In addition to artefact tests, we measured the response time of different VOCs through the 200 m Teflon tube kept at  $\sim 0^\circ\text{C}$ . The above described mix of VOCs was switched in and out of the air supply using a fast electronic valve (TEQCOM, Santa Ana, CA, USA). As an example, the time series of acetonitrile is shown in Fig. 3. At time 0 s the VOCs mixture was spiked into the 200 m long Teflon inlet. After about 30 s a sudden increase of the signal at  $m/z$  42 was measured with the PTR-MS. The 50%, and 90% rise and fall times are summarised in Table 1. The mean value for the 50% rise and fall times of the signal were 32.3 s and 30.9 s, respectively. Using the onset of the increase or decrease as starting points, a 90% increase and fall were reached within 1.9 and 3.1 s, respectively (on average). Some compounds showed a tailing at the fall. For toluene, we observed a 9 s difference between 50% and 90% signal fall, indicating that toluene partly adsorbs on the wall at  $0^\circ\text{C}$ . Note that the system was in use at even lower temperatures ( $-12^\circ\text{C}$ ) during the winter field campaign described in Sect. 3.2. When the whole tube was kept inside the laboratory ( $25^\circ\text{C}$ ), the difference between the 50% and 90% fall time for toluene dropped to 3 s (data not shown). The tube tests were performed during and after the winter field campaign, where no aging effect was observed. Overall, Teflon seems to be a suitable material in measuring the tested compounds through a long unheated inlet tube. However, the response time of the tube has to be taken into account when choosing the vertical profiling speed.



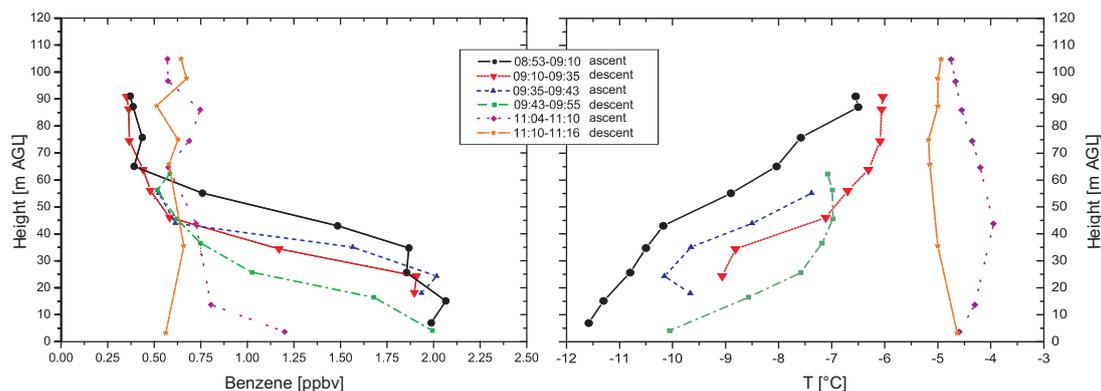
**Fig. 2.** VOCs from a gas standard measured with and without the 200 m Teflon tube. The error bars show the standard deviation of the 25 data points, each with 1 s integration time.



**Fig. 3.** The response time of the whole 200 m long inlet system when spiking acetonitrile into it (Integration time 0.33 s for one datapoint).

### 3.2 Exemplary data from a winter field campaign

The described vertical profiling system for VOCs was successfully deployed during the INNOX ( $\text{NO}_x$ -structure in the Inn valley during high air pollution) field campaign conducted near Schwaz, Tyrol, Austria in January and February 2006 (Gohm et al., 2009; Harnisch et al., 2008; Lehner and Gohm; Schnitzhofer et al., 2009). During wintertime, the main pollution sources at this location are residential heating and traffic on the A-12 motorway ( $\sim 750$  m distance from



**Fig. 4.** Temporal evolution of benzene VMR (left panel) and temperature (right panel) in the lowest 120 m a.g.l. near the town of Schwaz during the morning hours of 16 January 2006.

**Table 1.** Experimentally determined rise and fall times (50%, 90%) of different VOCs in the 200 m long Teflon tube and the short PTR-MS inlet system.

compound ( $m/z$ )	50% rise (s)	90% rise (s)	50% fall (s)	90% fall (s)
methanol (33)	33.5	35.5	30.7	31.4
acetonitrile (42)	34.3	36.0	28.9	32.0
acetaldehyde (45)	31.4	33.4	31.1	33.9
acetone (59)	30.5	31.9	31.1	33.1
isoprene (69)	33.7	35.8	30.7	31.4
2-butanone (73)	32.7	35.1	32.3	35.8
benzene (79)	34.4	35.1	30.8	35.2
toluene (93)	34.1	36.5	31.0	40.0
<i>o</i> -, <i>m</i> -xylene (107)	30.0	32.4	31.4	35.8
$\alpha$ -pinene (137)	28.1	30.2	30.7	31.7
mean value	32.3	34.2	30.9	34.0

the measurement site;  $\sim 52\,000$  vehicles per day). The tethered balloon profiling system was used to bridge the gap between ground-based (PTR-MS) and aircraft (GC) VOC-measurements. It is important to point out that the profiling experiments had to be closely coordinated with air traffic control of Innsbruck airport.

Here, we only show exemplary data from 16 January 2006 which was at the end of an extended period of cold, fair winter weather with strong nighttime inversions. A low level jet eroded the highly polluted surface inversion layer through the course of the day. The vertical speed of the balloon was  $0.3\text{ m s}^{-1}$ . The PTR-MS measured 7 different VOCs at 10 s time resolution giving a minimum of 3 data points every 10 metres. In Fig. 4, VMRs of benzene are shown together with temperature data. The data were averaged over 10 m.

During the first ascent between 08:53 and 09:10 UTC, the benzene VMR was 2 ppbv in the lowermost 40 m a.g.l. Above a thin transition area between 40 and 60 m a.g.l. with a very strong vertical temperature gradient, the benzene VMR was only  $\sim 0.3$  ppbv. In the following descent between 09:10 and 09:35 UTC, the strong inversion layer that trapped the

pollutants was about 15 m lower. The next ascent showed a little increase of the pollution layer thickness. Throughout the whole morning, the low level jet continued to erode the pollution layer. At 10:00 UTC it was only 15 m thick and at 11:15 UTC the lowermost 110 m a.g.l. were completely mixed with a benzene VMR of about 0.6 ppbv. This set of data nicely illustrates the potential of our method to obtain altitude profiles of VOCs with high vertical resolution.

## 4 Conclusions

A method, for detailed investigations of the vertical VOC distribution in the lowest atmospheric layers, has been presented. It combines the advantages of a tethered balloon as a research platform and of PTR-MS as a tool for fast and highly sensitive VOC measurements. A 200 m Teflon tube was connected to a  $27\text{ m}^3$  tethered aerodynamic balloon at one end and to a PTR-MS on the other end. Potential positive and negative VOC artefacts of this long inlet tube were characterized in the laboratory and in the field and were found to be insignificant for most compounds.

The method was successfully deployed during the INNOX-2006 field campaign to determine the small-scale vertical and temporal patterns of air pollutants under winter inversion conditions. The described tethered balloon system works under calm and moderate wind conditions. With higher wind speeds, a parafoil kite can be used alternatively.

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