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**Real-time profiling of  
organic trace gases**

R. Schnitzhofer et al.

# A method for real-time profiling of organic trace gases in the planetary boundary layer

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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## 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 5 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. Potential positive and negative VOC artifacts of the inlet line were characterized in the laboratory and in the field and were found to be insignificant for most compounds. The method was successfully deployed during a winter field campaign to determine the small scale spatial 10 and temporal pattern 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. Besides the physical properties of the atmosphere, the chemical composition is of prime interest. The limited payload of the balloons, however, 15 constrains the monitored compounds to species for which small sensors exist. One example is the miniature aerosol spectrometer (GRIMM 1.108 "Dustcheck", 2.4 kg, GRIMM Labortechnik, 1996), which determines the aerosol mass for 15 different size bins (compare Maletto et al., 2003).

Volatile organic compounds (VOCs) are emitted in large amounts from both natural 20 and anthropogenic sources and play an important role in tropospheric chemistry (Fehsenfeld et al., 1992). Proton-transfer-reaction mass spectrometry (PTR-MS) (Hansel et al., 1995; Lindner 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 (see de Gouw and Warneke, 2007, and 25 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

AMTD

2, 1771–1782, 2009

---

## Real-time profiling of organic trace gases

R. Schnitzhofer et al.

---

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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 separate VOC-rich air from cleaner air aloft. Large differences in trace gas concentrations often occur within a few meters. One approach 5 to probe the lowermost levels of the atmosphere is to place instruments on different heights (or on elevators) of research towers (e.g. Corsmeier et al., 2005; Grabmer et al., 2004). With this rather expensive approach, measurement heights of 50 m AGL are seldom exceeded. Tethered balloons have been used to collect samples into bags or cartridges at different altitudes. However, the vertical resolution of this method is still 10 poor and problems appear during sampling and storing. An inter-comparison 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 15 VOC sensor. While Jensen et al. (2002) have given the proof-of-principle, we have characterized 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 fill the gap between ground based and aircraft measurements.

## 2 Experimental

### 20 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 25 to compounds that have a higher proton affinity than water (i.e. most VOCs). The protonated VOCs are then analysed and detected by a quadrupole mass spectrometer.

## Real-time profiling of organic trace gases

R. Schnitzhofer et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



## 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 meter underneath the balloon. The basic meteorological parameters (temperature, pressure, humidity, wind speed and wind direction) were measured as 10 s mean values and radiotransmitted 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 line was pressure controlled at the other end (500 hPa), using a pressure controller (Bronkhorst El-Press, Ruurlo, The Netherlands; 13 SLMP, 0–1000 mbar), and pumped with a diaphragm pump (MD-4, Vaccuubrand, Wertheim, Germany). The resulting flow through the 200 m line was about 7 standard liters per minute (SLPM). The inlet of the PTR-MS instrument was connected immediately upstream of the pressure controller.

## Real-time profiling of organic trace gases

R. Schnitzhofer et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



### 3 Results

#### 3.1 Characterisation of the inlet system

A series of tests was performed to investigate potential (positive and negative) VOC artifacts in the 200 m long Teflon line. 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 into about 7 SLPM of air 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 line. The Teflon line was put outside the lab 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 line connected were observed (Fig. 1). The signal at mass-to-charge ratio 59 ( $m/z$ ) showed a slight increase (+7%) when the line was connected indicating that acetone (or propanal/glyoxal which are also detected at  $m/z$  59) is produced in the line (line contamination, formation due to chemical reactions, permeation through the Teflon line). Xylene levels were slightly lower (−6%) with the line connected indicating some wall losses.

Field tests showed up to 20% higher  $m/z$  45 signal when the Teflon line was connected.  $m/z$  45 is commonly assigned to acetaldehyde and the observed signal increase corresponds to an acetaldehyde artifact in the range of 50–200 pptV. This artifact may be caused by acetaldehyde formation from the heterogeneous ozonolysis of non-volatile, unsaturated species accumulated on the line walls (Northway et al., 2004).

In addition to artifact tests, we measured the response time of different VOCs through the 200 m Teflon line 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). The PTR-MS was connected to the Teflon line and determined the 50%, and 90% rise and decay times as summarised in Table 1. The mean value for the 50% rise and decay times of the signal were 32.3 s and 30.9 s, respectively. 90% increase

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



and decay were reached after 1.9 s and 3.1 s, respectively (on average). Some compounds showed a tailing at the decay. For toluene we observed a 9 s difference between 50% and 90% signal decay indicating that toluene partly condenses on the wall under low-temperature conditions. When the whole line was kept inside the lab (25°C),  
5 the difference between the 50% and 90% decay time for toluene dropped to 3 s (data not shown). Overall, Teflon seems to be a suitable material to measure the tested compounds through a long unheated inlet line. However, the response time of the line has to be taken into account when choosing the vertical profiling speed.

### 3.2 Exemplary data from a winter field campaign

10 The described vertical profiling system for VOCs was successfully deployed during the INNOX (NO<sub>x</sub>-structure in the Inn valley during high air pollution) field campaign conducted near Schwaz, Tyrol, Austria in January and February 2006. The tethered balloon profiling system was used to fill the gap between ground based (PTR-MS) and aircraft (GC) VOC-measurements. Results from the whole field campaign can be found  
15 in Gohm et al. (2009); Harnisch et al. (2009); Lehner and Gohm; Schnitzhofer et al. (2009). 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 m s<sup>-1</sup>. The PTR-MS measured  
20 7 different VOCs at 10 s time resolution giving a minimum of 3 data points every 10 m. In Fig. 2 VMRs of benzene are shown together with temperature data. The data were averaged over 10 m.

25 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 ~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

---

### Real-time profiling of organic trace gases

R. Schnitzhofer et al.

---

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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.

AMTD

2, 1771–1782, 2009

## 5 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 m<sup>3</sup> tethered aerodynamic 10 balloon at one end and to a PTR-MS on the other end. Potential positive and negative VOC artifacts of this long inlet line 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 pattern of air pollutants under winter 15 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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Real-time profiling of organic trace gases

R. Schnitzhofer et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[|◀](#)

[▶|](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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---

Real-time profiling of organic trace gases

R. Schnitzhofer et al.

---

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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---

**Real-time profiling of organic trace gases**

 R. Schnitzhofer et al.
 

---

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[|◀](#)
[▶|](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


## Real-time profiling of organic trace gases

R. Schnitzhofer et al.

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

compound ( <i>m/z</i> )	50% rise (s)	90% rise (s)	50% decay (s)	90% decay (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
o-,m-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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

|◀

▶|

◀

▶

Back

Close

Full Screen / Esc

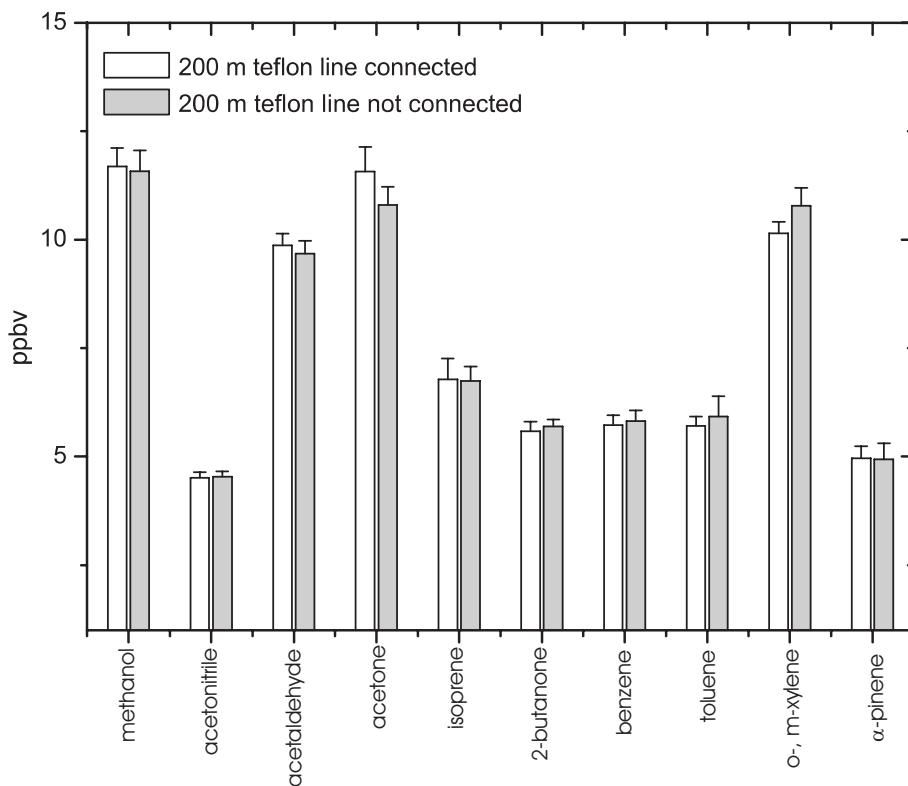
Printer-friendly Version

Interactive Discussion



**Real-time profiling of organic trace gases**

R. Schnitzhofer et al.



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

[Title Page](#)  
[Abstract](#) [Introduction](#)  
[Conclusions](#) [References](#)  
[Tables](#) [Figures](#)

[◀](#) [▶](#)  
[◀](#) [▶](#)  
[Back](#) [Close](#)

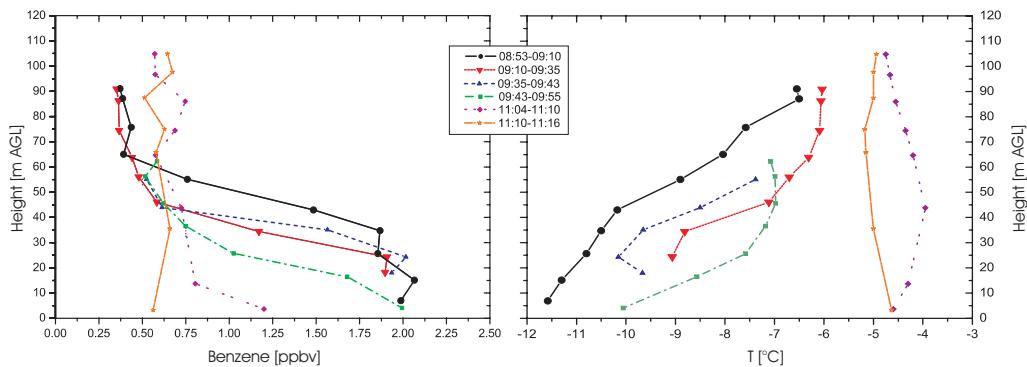
[Full Screen / Esc](#)

[Printer-friendly Version](#)  
[Interactive Discussion](#)



## Real-time profiling of organic trace gases

R. Schnitzhofer et al.



**Fig. 2.** 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 morning hours of 16 January 2006.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[|◀](#)[▶|](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)