

Milestone report MS 26 OVOC/terpenes side-by-side intercomparison

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1. Abstract

Volatile Organic Compounds (VOCs) include a wide range of species encountered in the atmosphere at very low concentrations. Especially Oxygenated Volatile Organic Compounds (OVOCs) are anthropogenic, biogenic, or photochemical activity tracers and constitute the major part of VOC at a global scale. Furthermore, terpenes are among the most reactive VOCs mainly emitted by the biosphere. Therefore, the long term measurements of these species are relevant due to their key role in atmospheric chemistry notably as precursors of secondary pollutants such as ozone and secondary organic aerosols. The general objective of an intercomparison is to demonstrate whether identical samples of simple to complex composition and of high to low mixing ratio are identically analyzed by collocated instruments. A first side by side intercomparison focussing on OVOCs was held at the Meteorological Observatory Hohenpeissenberg (MOHp) in 2013 within ACTRIS. This first experiment demonstrated how challenging the measurement of OVOCs are and raised many metrological issues (blank, artefacts, standard...) which have led to further method improvements.

This second exercise held at MOHp during two weeks focused on OVOCs and terpenes. It aimed at testing improved measurement methods using new standard mixtures.

6 partners including 3 candidate units of a future ACTRIS topical centre, took part in this side by side exercise by setting up 9 different methods/instruments including GC (Gas Chromatography), PTR-MS (Proton Transfer Reaction Mass spectrometry) and DNPH/HPLC (Dinitrophenyl Hydrazine, High Performance Liquid Chromatography). Most of the instruments worked properly to provide complete and promising datasets on synthetic mixture at various levels as well long series of ambient air. After the data submission, the data analysis is in progress in order to highlight the major outcomes and to come up with guidelines for long term observations of these crucial atmospheric constituents.

2. Participants and Instrumentation

Table 1: List of participants in the ACTRIS VOC s-b-s intercomparison with information about institution, operated sites, ACTRIS status, used method and position on the manifold. WCC, DWD, Empa and IMT are candidates to become units of the ACTRIS topical centre for reactive gases.

Institution	Sites	ACTRIS status	Participants	Method	Position Manifold, room
German Meteorological Service (DWD) Hohenpeissenberg Meteorological Observatory (HPB)	Hohenpeissenberg (MOHp)	partner	Anja Claude, Erasmus Tensing, Katja Michl, Dietmar Weyrauch	GC-MS/FID	#3, 402
				GC-MS/FID	#4, 402
IMT Lilli Douai, France (IMT)	National EMEP lab, La Tardière, Peyrusse-Vieille	associate	Stéphane Sauvage Thierry Leonardis	GC-FID	#14, 301
				GC-FID	#13, 301
				DNPH/HPLC-UV	#12, 301
Eidgenössische Materialprüfungsanstalt, Schweiz (Empa)	Rigi Beromünster Jungfrauojoch	partner	Matthias Hill	GC-FID/FID	#19, 301
Karlsruhe Institute of Technology (KIT) Campus Alpin, Germany WCC-VOC	WCC		Rainer Steinbrecher	PTR-MS	#16, 301
KIT, Germany	Airborne platforms: Caribic and Halo		Eric Förster Florian ...	PTR-MS	#2, 401
University of Utrecht, Netherlands (UU)	Laboratory studies and field campaigns		Kangming Xu	PTR-ToF-MS	#11, 301

All ACTRIS partners, associated partners and potentially interested European laboratories were asked for their interest to participate by email announcement. The institutions willing to participate were asked to fill questionnaires with information on their instrumentation, calibration, space and power requirements.

Finally, the six groups listed in Table 1 participated with five GC-, three PTR-MS-Systems and one off-line sampling method in the intercomparison. With the World Calibration Centre for VOCs (WCC-VOC), Empa, IMT Lille Douai (IMT) and MOHp, candidates to become units of the ACTRIS topical Centre for Reactive Gases in Situ Measurements (CiGas) were among the participating groups. Details about the systems are given in Tables 5 and 6 in the Appendix. Further information concerning the theory of operation, measurement principle, and so on can be found elsewhere, e.g. [1] and references here in.

3. Manifold and laboratory set-up

The side-by-side intercomparison was carried out in the guest laboratory and the VOC lab of the Hohenpeissenberg Meteorological Observatory (MOHp). All instruments were connected to a 1" PFA manifold, which runs through all laboratories (Figure 1).

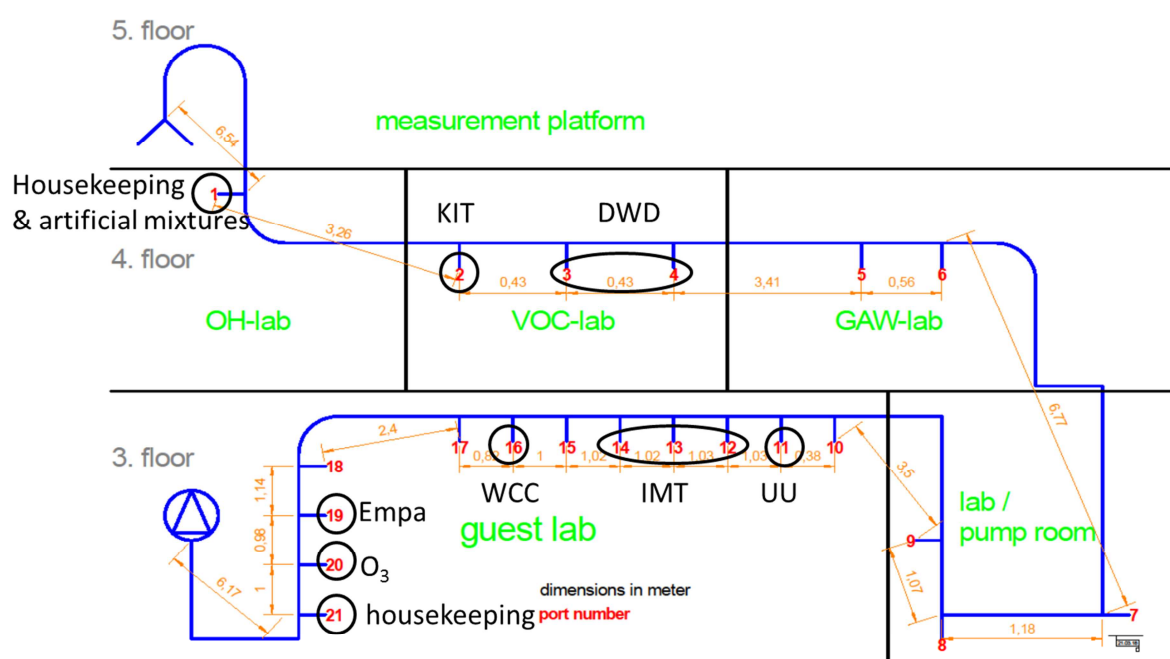


Figure 1: Scheme of the guest 1" PFA manifold. The manifold is shown in blue, port numbers in red. Port number of each instrument is highlighted with a circle and labelled with the group name or device information.

Previous to the intercomparison, the manifold had been modified. Originally, coming from the rooftop, the manifold had entered the building on the third floor and only served the guest laboratory. Since space is limited and in order to avoid moving in-house instrumentation into the guest lab, it was decided to extend the manifold into all GAW laboratories of the Observatory. Compared to previous campaigns this longer manifold resulted in an increased restriction and higher residence times. However, at flows of ~ 100 l/min the maximum residence time of the manifold was < 10 s and sufficient for the campaign. Table

2 shows residence times along the inlet for typical flow rates applied to the manifold. This new configuration has been validated in terms of residence time and possible lost/adsorption along the line.

Ambient Air mode:

Figure 1 depicts the manifold with port numbers, distances between the single ports and the positions of housekeeping and VOC instruments in ambient air mode. The air inlet of the manifold (Figure 2 left side) is situated on the SW rim of the measurement platform on the fifth floor of MOHp. Air is sucked through the manifold by a pump situated at the end of the manifold (Figure 2, right side). During the SbS2018 the manifold was flushed with ~90-100l/min during the ambient air phase.

Upstream of port 1, which was equipped with the housekeeping sensors (relative humidity, dew point, temperature), another inlet port is added where defined flows of high concentrated VOC mixtures can be applied (see below artificial mixtures). In regular ambient air mode this inlet was closed.



Figure 2 left: Air inlet of the guest manifold on top of the MOHp measurement platform. Right: pump set-up at the end of the manifold to enable ambient air flows up to 200 l/min.

Port positions:

Instruments were either situated in the VOC lab or the guest lab. Respective port positions are listed in Table 1 and shown in Figure 1. PRT-MS instruments with the high time resolution were distributed over the inlet line to have one at the first port and one close to the end of the line: PTR-MS - KIT was therefore on the first instrument port and PTR-MS WCC on the second last (due to space issues EMPA GC was on the last port). In this set-up any changes or problems on the inlet line either in time or along the line can be detected with a high time response time.

Table 2: Residence times in the guest manifold at different port positions.

Guest lab ring manifold		residence times at			
port no.:	Distance from inlet to port:	200	100	50	l/min
		8.77	4.38	2.19	m/s
1	6.54 m	0.75	1.49	2.98	s
2	9.80 m	1.12	2.24	4.47	s
3	10.23 m	1.17	2.33	4.67	s
4	10.66 m	1.22	2.43	4.86	s
5	14.07 m	1.60	3.21	6.42	s
6	14.63 m	1.67	3.34	6.67	s
7	21.40 m	2.44	4.88	9.76	s
8	22.58 m	2.58	5.15	10.30	s
9	23.65 m	2.70	5.39	10.79	s
10	27.15 m	3.10	6.19	12.39	s
11	27.53 m	3.14	6.28	12.56	s
12	28.56 m	3.26	6.51	13.03	s
13	29.59 m	3.37	6.75	13.50	s
14	30.61 m	3.49	6.98	13.96	s
15	31.63 m	3.61	7.21	14.43	s
16	32.63 m	3.72	7.44	14.88	s
17	33.45 m	3.81	7.63	15.26	s
18	35.85 m	4.09	8.18	16.35	s
19	36.99 m	4.22	8.44	16.87	s
20	37.97 m	4.33	8.66	17.32	s
21	38.97 m	4.44	8.89	17.78	s

Zero air/ artificial mixtures mode:

In the zero air mode, port one was modified in a way that it was disconnected from the inlet and connected to the in-house zero air as depicted in Figure 3. In this mode zero air is pushed through the manifold. Zero air is applied via three mass flow controllers (MFC) into the manifold. If MFC 1 is open zero air is flushed through a heated water bath. By setting flows through MFC 1 to 3 and the water bath temperature, the humidity level and the total flow into the manifold were controlled. Due to restrictions concerning the MFC dimensions and the envisaged VOC dilution levels (see below), the manifold was flushed with ~50l/min in zero air mode.

Zero air used for the campaign was the in-house zero air provided by an oil-free compressor system combined with a downstream adsorption dryer that worked with activated aluminium oxide (KAESER desiccant dryer DC 1.5) reducing the water content to ~ 1000 $\mu\text{mol/mol}$.

Dilution set up

Upstream of port 1, small but well-defined flows of high-concentrated VOC mixtures can be applied into the manifold (both in zero and ambient air mode). The VOC mole fraction in the manifold X can be determined, if the flow in the manifold flow_m , the flow of the VOC mixture flow_{VOC} and the mole fractions in the high-concentrated VOC mixture X_{ref} are known:

$$X = X_{\text{ref}} * \text{flow}_{\text{VOC}} / \text{flow}_m$$

Since especially OVOCs are sensitive to surfaces and often losses or artefacts are observed, we avoided using MFCs to control the flow_{VOC} of the VOC mixtures (larger inner surfaces, materials etc.). During SbS2013 already a very simple set-up using crimped tubings and long methyl-sil capillaries as so-called restrictions had been applied. The flow through the restriction is proportional to the pressure drop over the restriction. The latter was monitored constantly over the experiment. Though this set up had been

successful with regards to stability and (not observed) losses, it had suffered from no thermal stabilization and that it had to be configured and switched manually.

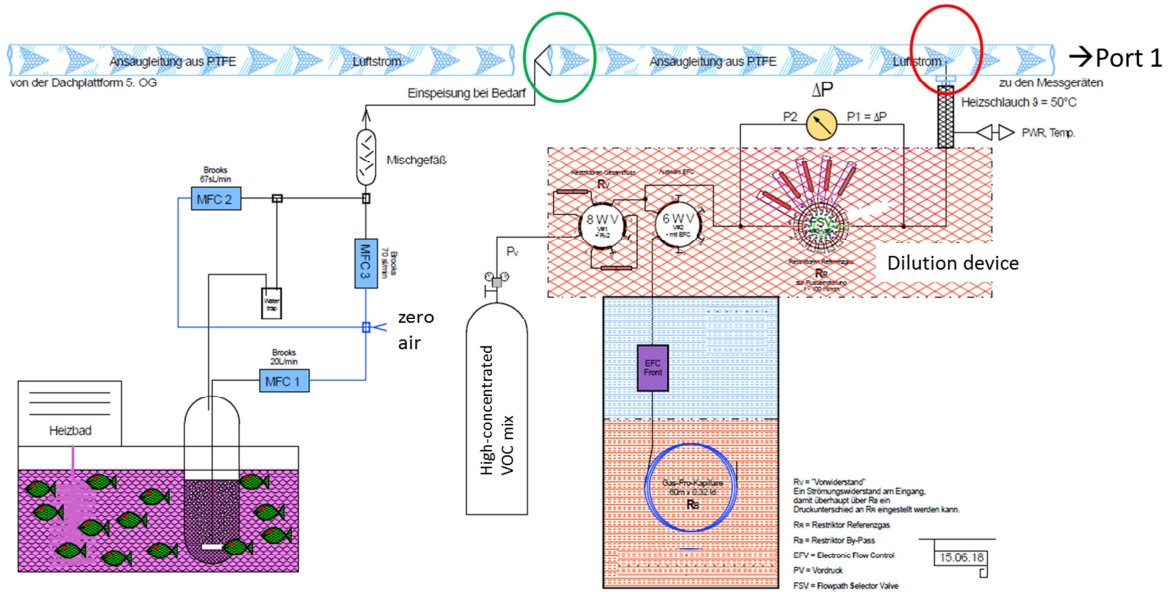


Figure 3: Set up to generate humidified synthetic VOC mixtures: zero air flow into the manifold (green circle) and the humidity level are controlled by mass flow controllers (MFC 1 to 3). With a dilution device a defined flow of a high concentrated VOC mixture can be applied into the zero air (red circle).

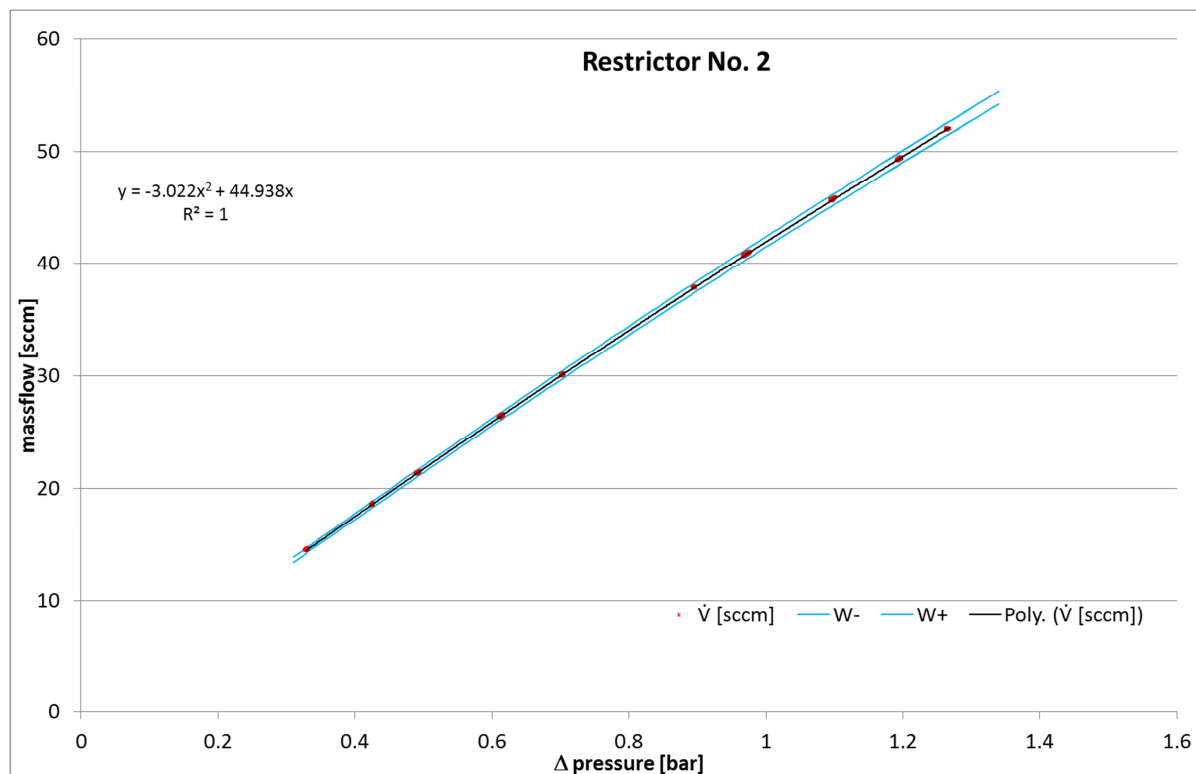


Figure 4: Example for a flow/pressure calibration curve for restriction no. 2 used in the dilution device. The blue lines show the confidential interval of the calibration curve.

In order to improve this, restrictors (again crimped Sulfinert® tubings) were installed into a heated (~70°C) box (dilution device in Figure 3). Different so-called dilution flows were set by using heated Valco® valves (stainless steel body with R-rotor) with small inner volume. An old GC system was used to control the valve switching automatically in time. The pressure drop Δp was monitored with a Δ -pressure sensor continuously during the experiments. Each restriction was calibrated regarding its p-flow characteristics previous the side-by-side campaign. Figure 5 shows an example for a calibration curve for one of the restrictions. Measured flows are plotted versus the measured pressure drop d_p over the restriction. A quadratic polynomial fit yields the calibration curve. The latter is used to calculate the flows over the restriction during the experiments. The pressure sensor has an uncertainty of 0.0015bar. Calculated flows are estimated to have an uncertainty of < 3% (final uncertainties to be determined).

Calibration gases / VOC mixtures:

Besides the individual calibration gases of each group listed in tables 5 and 6 in the Appendix, common gas standard were circulated among the groups for calibration and diluted into the manifold. Table 3 lists all respective gas mixtures. The calibration gases were circulated among the groups in the beginning and the end of the campaign for instrument calibration. This measure provides the possibility to refer all measurements to the same scale.

Table 3: Table of calibration gases (cal) and test mixtures (mix) used during the Side-by-Side intercomparison.

Name	Producer	Compounds	level	Mole fraction level [nmol/mol]	Uncertainty	Year of production
OVOC_VSL_WCC	VSL	methanol, ethanol, acetaldehyde, acetone, methacrolein, MEK, MVK, n-hexane and n-propane	cal	100	5%	2018
OVOC_NPL	NPL	acetaldehyde, methanol, ethanol, acetone, acetonitrile, MEK, n-hexane	cal	5000	5%	2012
Terpenes_NIST	NIST	a-pinene, 3-carene, limonene, 1,8-cineole and ?	cal	2	?	?
Terpenes_NPL	NPL	a-pinene, 3-carene, limonene, 1,8-cineole and n-octane	Cal	2	≤ 5%	2017
Terpenes_IMT	IMT	Isoprene, alpha-pinene, camphene, myrcene, beta-pinene, 2-carene, 3-carene, p-cymene, limonenen, 1,8-cineole, linalool, nopinone and toluene	mix *	10000-20000	10%	2018

* Used as a high-concentrated mixture for spiking and terpene dilution series

4. Experiments - Overview

Table 4: Final manifold schedule of the campaign. Hours of day (UTC) indicate the start of one hour (e.g. 02:00 stand for the hour from 02:00 a.m. to 03:00 a.m.). Dates are shown in the two left columns. Colours indicate the type of gas flushed through the manifold: ambient air in blue, zero air in green, synthetic mixtures in orange and spiked ambient air in red. Objectives of the individual experiment days are given in Table 3.

		hour of the day UTC																									
		00:00	01:00	02:00	03:00	04:00	05:00	06:00	07:00	08:00	09:00	10:00	11:00	12:00	13:00	14:00	15:00	16:00	17:00	18:00	19:00	20:00	21:00	22:00	23:00		
Friday	2018-06-15							Installation phase and set up													Installation phase and set up, ambient air on the manifold						
Saturday	2018-06-16							Installation phase and set up, ambient air on the manifold													Installation phase and set up, ambient air on the manifold						
Sunday	2018-06-17							Installation phase and set up/Zero and Calibration measurement (internal)													Installation phase and set up/Zero and Calibration measurement (internal)						
Monday	2018-06-18																										
Tuesday	2018-06-19																										
Wednesday	2018-06-20																										
Thursday	2018-06-21																										
Friday	2018-06-22							5ppb OVOC NPL																		2-3ppb OVOC	
Saturday	2018-06-23	2-3ppb OVOC VSL									1ppb OVOC VSL								500ppt OVOC VSL							100ppt OVOC	
Sunday	2018-06-24	100ppt OVOC VSL																									
Monday	2018-06-25													~700ppt Terpenes IMT													~100ppt terpenes IMT
Tuesday	2018-06-26						400 ppt Terpenes IMT		40ppt terpenes IMT					1.5ppb terpenes IMT													
Wednesday	2018-06-27								spiking with terpenes					spiking with terpenes + O3					with terpenes								Final calibrations
Thursday	2018-06-28	Final calibrations																									
Friday	2018-06-29	Final calibrations																									

In Table 4, the schedule shows which sample gas was flushed at which time through the manifold, Table 5 summarises the respective objectives of each experiment day. Each day, a short morning briefing was conducted at 7:30 UTC. If possible (depending on time and experiment status) an afternoon meeting was performed, providing the opportunity to present the individual measurement systems and discussing preliminary results.

After a set-up phase from Friday 15th, 2018, to Monday 18th, 2018, the intercomparison started with an ambient air phase. This was a deviation from the original plan where we had envisaged synthetic conditions in the beginning of the campaign. However, this change of plan was necessary in order to react to the weather conditions, which predicted a warm weather phase (and thus higher terpene and OVOC levels) only for the first few days of the campaign.

Table 5: Objectives of each experiment day

		GOAL
Day 1	2018-06-15	get all instruments up and running with defined calibration points and blanks
Day 2	2018-06-16	get all instruments up and running with defined calibration points and blanks
Day 3	2018-06-17	get all instruments up and running with defined calibration points and blanks
Day 4	2018-06-18	Ambient air intercomparison
Day 5	2018-06-19	Ambient air intercomparison
Day 6	2018-06-20	Ambient air intercomparison
Day 7	2018-06-21	Ambient air intercomparison
Day 8	2018-06-22	Ambient air intercomparison + manifold blanks, repeatability & Linearity of instruments, response times, memory effects
Day 9	2018-06-23	determine manifold blanks, repeatability & Linearity of instruments, response times, memory effects
Day 10	2018-06-24	manifold blanks, repeatability & Linearity of instruments, response times, memory effects + Ambient air intercomparison
Day 11	2018-06-25	determine manifold blanks, repeatability & Linearity of instruments, response times, memory effects
Day 12	2018-06-26	determine manifold blanks, repeatability & Linearity of instruments, response times, memory effects+ Ambient air intercomparison
Day 13	2018-06-27	Ambient air intercomparison + Artefacts, defined calibration points and blanks
Day 14	2018-06-28	defined calibration points and instrument blanks
Day 15	2018-06-29	defined calibration points and instrument blanks

On days 8-10, the manifold was switched to synthetic conditions and the manifold was flushed with humidified zero air. Into the zero gas OVOCs were added at different mole fraction levels ("dilution

series”). This provided the opportunity to check not only the linearity of the systems but also to look for memory effects or losses occurring in the systems. A similar dilution series with terpenes was performed from day eleven to twelve. In between the dilution series and afterwards the manifold was switched back to ambient air conditions. Day thirteen was used to perform some so-called spiking experiments with terpenes and O₃ in ambient air.

During the final days the manifold was kept in ambient air mode, providing on-going opportunities to perform parallel measurements, however the time most mostly used to get final calibration points and instrument blanks. Please, find a more detailed description of the individual experiments in Section 6 below.

5. Preliminary results

In the following all experiments will be shown in a chronological order. After a short description, some preliminary results are presented.

Day 1 to day 3: Instrument set-up and calibration points, blanks

Description:

Instrument set up requires 1-3 days, depending on the complexity and number of components of each individual system. While PTR-MS systems are more compact, usually GC systems comprise a number of components including traps (e.g. water, ozone), pre-concentration unit, the GC itself and the detector. For laboratory GCs, those components are often separate units and if a GC is moved they have to be dismantled and set up again. In any case, moving larger instruments creates potential problems like leakages or malfunctions.

IMT being a Co-organizer of this intercomparison, set up their instruments (2 GCs) already two weeks ahead of the campaign, in order to have a well-running and checked system. The decision to have an early set up was a result of SbS2013, when after the set up some leakages and problems were detected and resulting higher blanks led to problems during the first days of the SbS2013.

All other participating groups arrived at the Meteorological Observatory Hohenpeißenberg (MOHp) between Wednesday 14th and Friday 15th, 2018. After a successful set up the calibration gases listed in table 3 were circulated among the groups.

On Monday 18th of June, all instruments were up and running besides PRT-MS UU. On Monday the PTR-MS WCC had a minor mal function which was fixed on Tuesday 19th. However, the PTR-MS system by UU had a major problem and was down for the first week of the intercomparison until June 21st (afternoon). Due to a malfunction of the trap cooling device on June 24, the DWD GC-MS/FID system for OVCOs was offline during the artefact tests and terpene dilution series.

In the meantime DWD performed last tests of the functionality of synthetic gas addition to the manifold to approve its stability and correctness of the nominal values.

Day 4 to day 8, and sporadic periods later on: Ambient air measurements

Since the weather forecast showed a period of good weather for the first days of the intercomparison, the opportunity was taken to run ambient air measurements. In Figure 6, the meteorological parameters are shown. Maximum temperatures were rising from June 18 to June 21 from 17.7°C to 24.4°C. On June 20, a nice day with no cloud conditions was observed. In the evening of June 21, a cold front passed and on the 22nd, a maximum temperature of less than 13°C was recorded. A satellite image of the respective cold front is shown in Figure 7.

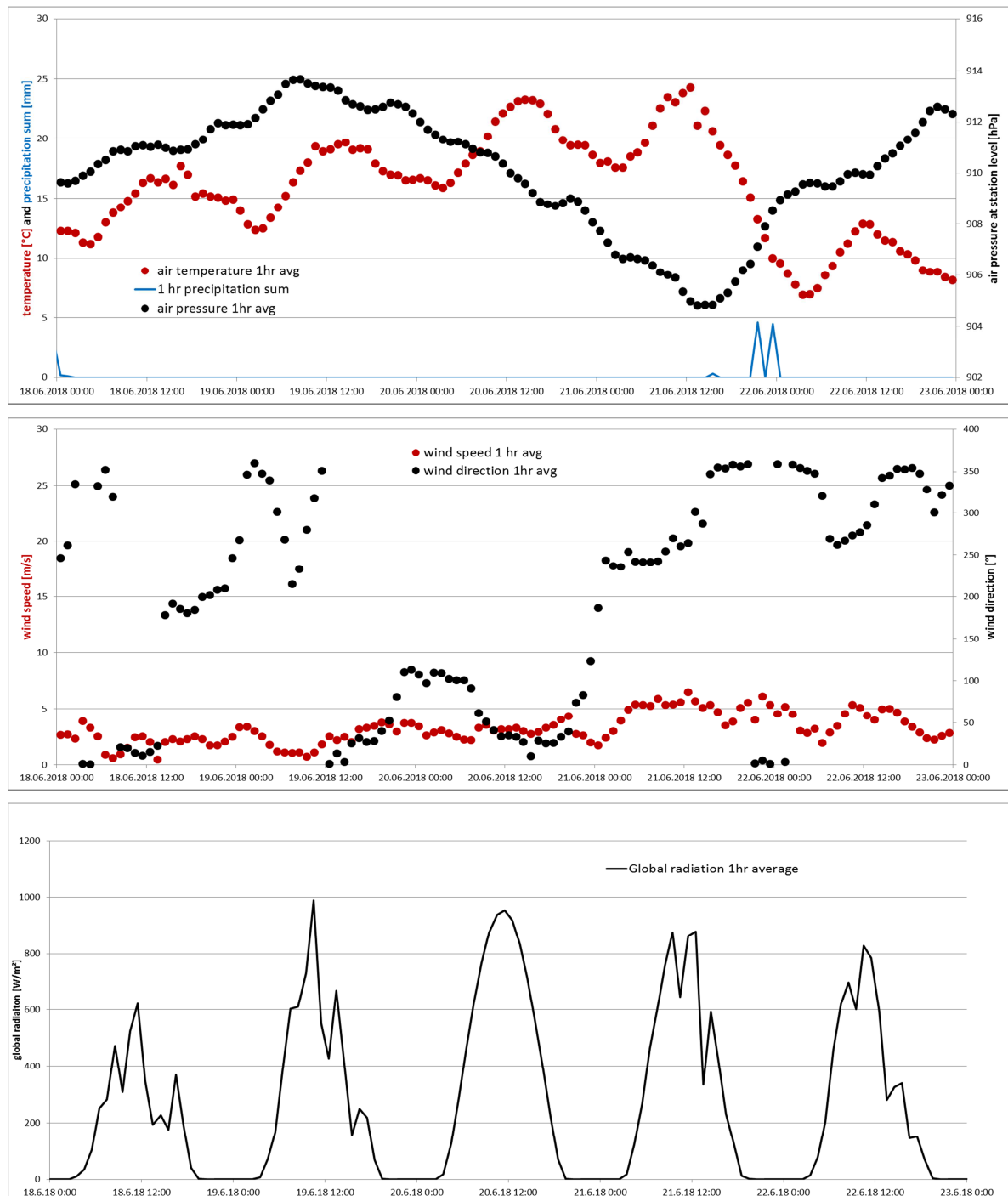


Figure 5: Meteorological parameters during the ambient air phase from June 18 to June 22, 2018. Upper panel: one hour averages of air temperature (red), precipitation sum (blue) and air pressure (black). Middle

panel: one hour averages of wind speed (red) and direction (black). Bottom panel: Global radiation in W/m^2 . All parameters were observed at the meteorological station of MOHp.

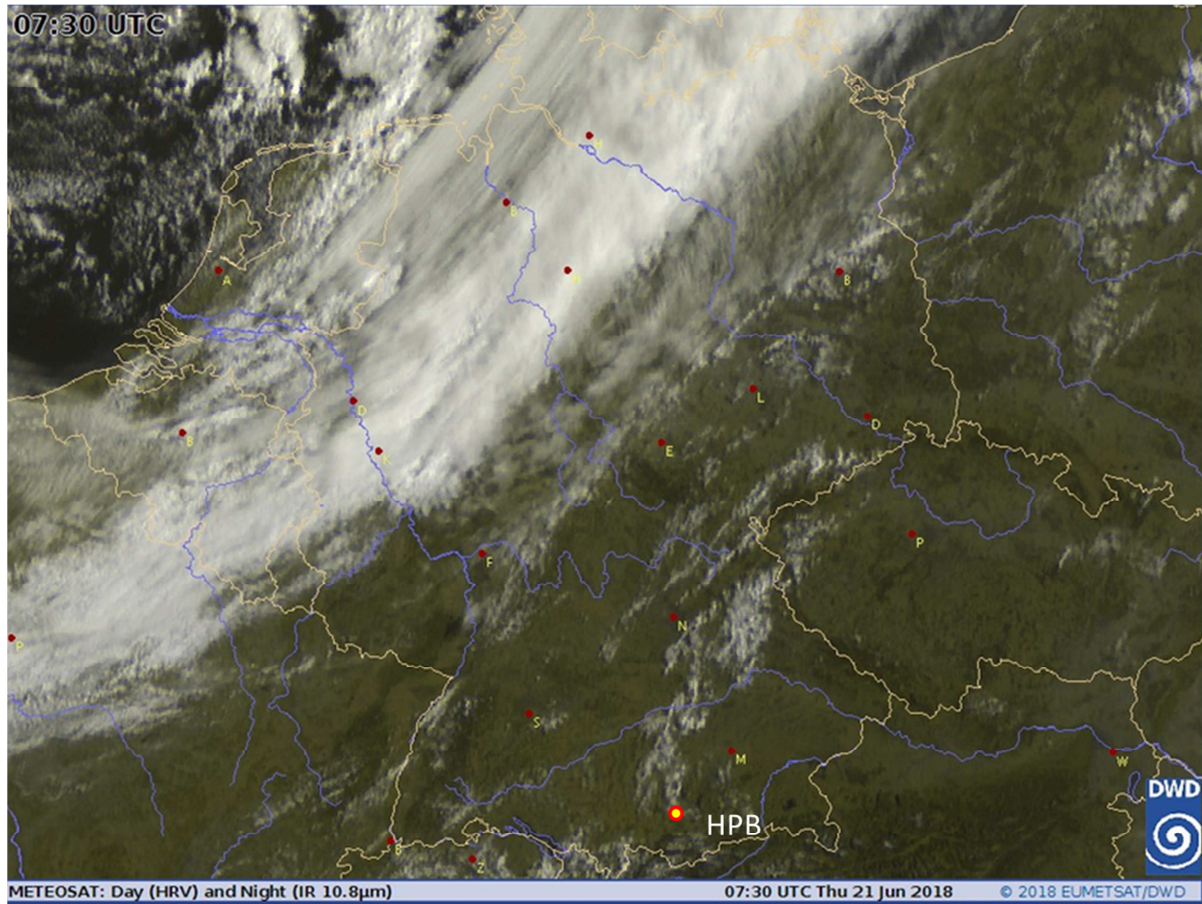


Figure 6: Meteosat picture (high resolution visible, HRV) on June 21, 2018 at 7:30 UTC. A cloud band clearly marks the passage of a cold front. The location of Hohenpeißenberg marked with a red/yellow circle.

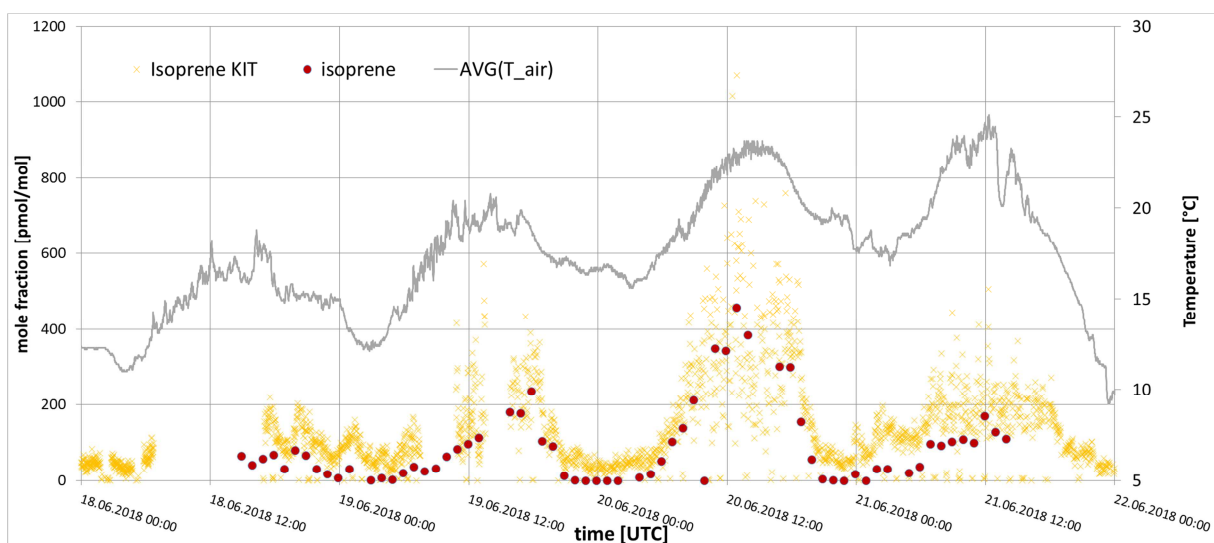


Figure 7: Time series of temperature and isoprene measured in ambient air from the 15/06 to the 22/06

As an example for this ambient air phase, Figure 7 presents time series of quick look data for isoprene in ambient air. Like expected, isoprene mixing ratios display a diel cycle related to biogenic emission and weather conditions. These first preliminary results (final data are still under validation) show the consistency between two different measurement methods namely a PTR-MS and a GC/MS.

Day 8 to day 13: OVOC & terpene dilution series

Two dilution series with OVOCs and terpenes, respectively, were performed between day 8 and 13 in order to check linearity and memory effects of the VOC systems. Figure 8 reflects the response [mole fraction in nmol/mol] of the GC/MS-FID system by MOHp to the dilution of NPL and VSL standard mixture including OVOCs and n-hexane. Apart for a short episode during the first dilution level when a pressure issue occurred (elevated red points) mixing ratios are very stable even for the zero air phases in between. The very good dilution and stability in the manifold will allow an interesting comparison of the instruments.

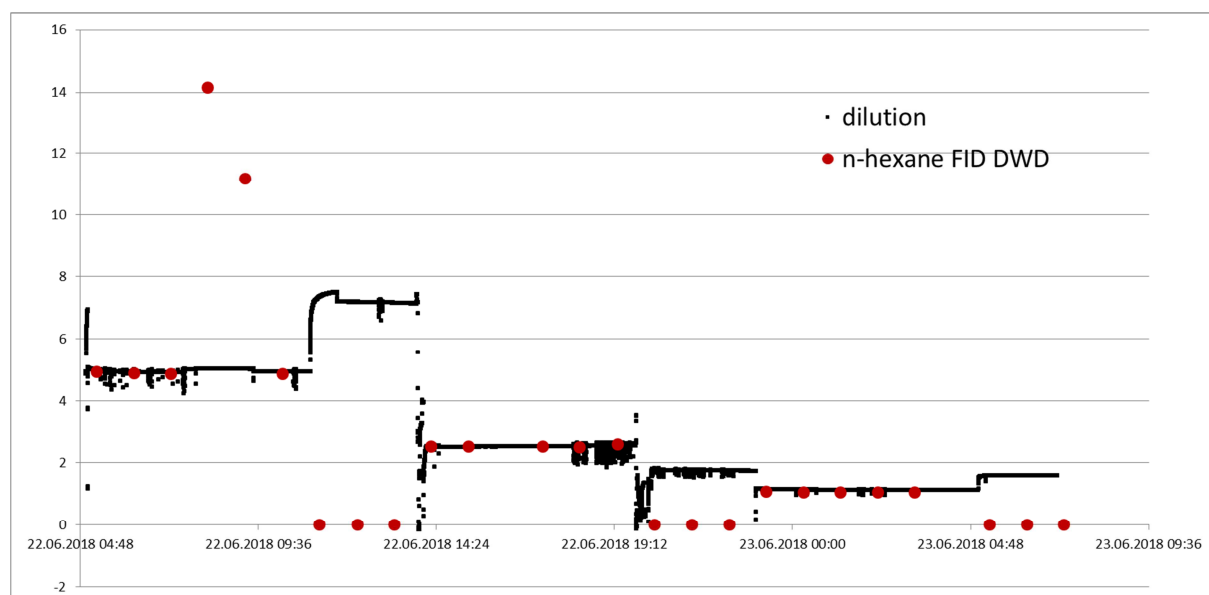


Figure 8: Preliminary data for n-hexane [nmol/mol] MOHp's GC/MS-FID system (red points) measured during the OVOC dilution series. Plotted in black is the expected mole fraction calculated from the dilution flow.

Day 13: Artifacts

OVOCs and terpenes are subject to fast reaction with ozone especially in the sampling part of the instrument (sampling line, pre-concentration trap of the GC, etc.). Especially for the GC system, an ozone scrubber can be used to tackle this artefact. The experiments held the day 13 consisted in adding ozone in ambient air in order to test the potential effect of ozone on the instruments.

Day 14+15: Final calibrations and dismounting

Before being switched off, all participants performed end of experiment calibrations and blank tests.

6. Outlook

This second intercomparison experiment on OVOCs and Terpenes held in Hohenpeissenberg has been successful and provide promising datasets. After check and validation of their data, participants are expected to submit their data to the organizers by the end of September 2018.

A First meeting is planned during the ACTRIS2 technical meeting in Lille (16-18 Oct 2018) in order to discuss the status of the submitted data and to define the workplan for the data analysis. A workshop of 1 day will be held in January 2019 at HPB in order to present the main results and to list the major highlights of this experiment. Subsequently, Stéphane Sauvage will stay at HPB as guest Scientist with the objective to draft a paper on the outcomes of this intercomparison and the workshop.

7. Appendix

Table 6 Gaschromatography systems used during SbS2018.

	DWD GC-FID/FID-MS	DWD GC-FID/MS	Empa GC-FID/FID	IMT GC-FID/FID	IMT GC-FID/MS	IMT DNPH tubes – LC/MS
Sampling system	On-line, custom-made sampling unit	On-line, custom-made sampling unit	On-line, Air server-Unity-xr (Markes International, UK)	to be up-dated later	On-line, Air server-Unity I (Markes International, UK)	to be up-dated later
Sampling line	1/16" e-polished SS, 70°C, 2 m	1/16" Silcosteel® (Restek), 150°C, 1.50m	1/4" PFA, 3 m		1/16" (ID 0.96 mm), Silcosteel® (Restek), unheated, 2,5 m	
Inlet filter	None	Silcosteel® (Restek) particle filter, 0.5 µm pore size	SilcoNert® 2000 (Swagelok) particle filter, 0.5 µm pore size		None	
O₃ trap	1/16" e-polished SS, 70°C, 2 m				None, except of heated 1/16" stainless steel lines	
H₂O management	Cold trap: 1/8" (ID 2.1 mm) Sulfinert® (Restek) 16 cm, -35°C, reconditioning at 110°C between runs	none	Kori-xr (Markes International, UK) @ -25°C, additional cold trap: Glass vessel (120 ml), -42°C, no reconditioning between runs		Sample dilution with dry zero air by DWD (50:50), hydrophobic adsorbents at 12.5°C, dry purge	
Materials used in sample gas path	1/16" UltiMetal™ (Varian), Silcosteel® (Restek) or Sulfinert® (Restek), deactivated fused silica capillaries, all 50°C	Silcosteel®, ultimetal, deactivated fused silica capillaries at room temperature or at 150°C; SS and VALCO valves at 150°C	1/16" Silcosteel® (Restek) and PFA, both unheated		1/8" PFA, 1/16" stainless steel at 140°C	
Flushing of lines with sample gas prior to sampling	10 min, 20 ml/min, includes water trap	10 min, 80 ml/min (air sample) or 50ml/min (working standard)	25 min, 50 ml/min, includes water trap			
Adsorbent trap	1/8" (ID 2.1 mm) Sulfinert® (Restek), 6 cm, 75 mg Carbopack™ X, 5 mg Carbopack™ B	1/4" fritted glass tube (Supleco), Tenax TA 100 mg, Carbopack X 120 mg, Carboxen 569 120 mg	MARKES Ozone Precursors trap ^a		1.9 mm ID quartz tube, 6 cm, 75 mg Carbopack™ X, 5 mg Carbopack™ B	
Dry purge of adsorbent trap	4 min, 10 ml/min helium	7 min, 10 ml/min, helium	1 min, 25 ml/min helium		4 min, 10 ml/min helium	None

OVOC trap adsorption (ads.) and desorption (des.)	Ads.: -20°C, 20 ml/min for 10 min; Des.: 300°C, 15 ml/min helium for 6 min	Ads.: 30°C, 20 min, 80 ml/min; Des.: 200°C 7.5 min, 10 ml/min	Ads.: -30°C, 25 ml/min for 20 min; Des.: 320°C, 20 ml/min helium for 5 min		Ads.: 12.5°C, 13.5 ml/min 50:50 dry zero air:sample gas for 40 min; Des.: 200°C, helium for 15 min	
	DWD GC-FID/MS	DWD GC-FID/FID-MS	Empa GC-FID/FID		IMT GC-FID/MS	IMT DNPH tubes – LC/MS
Sample volume [ml]	200 ml	1560 ml (manifold), 400ml (calibration)	400-500 ml		540 ml	
Refocus/Cryofocus and temperatures	No refocus	Methyl Silicone capillary @ -180°C, desorp. @ + 60°C	No refocus		No refocus	
Carrier gas	Helium 5.0 cleaned with Supelpure-O (Supelco), molsieve and charcoal	Helium 5.0 cleaned with Supelpure-O (Supelco), molsieve and charcoal	Helium 6.0		Helium cleaned with charcoal cartridge	
GC model	Agilent 7890A	Agilent 6890	Agilent 7890B		Agilent	
GC column(s)	Semi-polar PoraBOND U (Agilent) PLOT, 25 m x 0.32 mm x 7 µm and Al ₂ O ₃ /Na ₂ SO ₄ PLOT (Varian), 50 m x 0.53 mm x 10µm for C2-C9 NMHC (no used during intercomparison) with Deans' Switch	SGE BPX-5, 50m x 0.32 mm x 1µm	Deans switch: Al ₂ O ₃ /Na ₂ SO ₄ PLOT (Varian), 50 m x 0.53 mm x 10µm for C2-C7 NMHC, high polar GS-OxyPLOT (Agilent) PLOT, 30 m x 0.53 mm x 10 µm for OVOC and some NMHC		High polar CP-LOWOX (Varian) PLOT, 30 m x 0.53 mm x 10 µm	
Column flow and oven temperature programme	2.5 ml/min; start 40°C, 20°C/min to 120°C, 5°C/min to 200°C, hold 15 min (Standby 150°C)	2.5 ml/min; start 10°C for 5 min, 6°C/min to 240°C	20 ml/min for each column for 6 min, 7 ml/min for 20 min, 21 ml/min for 27 min; start 40°C for 5 min, 6°C/min to 135°C, hold 4 min, 6°C/min to 200°C, hold 20 min		7 psi (19 ml/min); start 45°C, 5°C/min to 150°C, hold 2 min, 3°C/min to 250°C, hold 10 min	
Injection type	Splitless	Splitless	Splitless		Splitless	
Detectors	2 Agilent FIDs and Agilent MS 5975C (ei/quadrupole), split between FID and MS 64:36	Agilent FID and Agilent MS 5975B inter XL (ei/quadrupol), split 1:1.5 to MS:FID	2 Agilent FID, one for each GC column		Agilent FID and MS, split 80:20	
Calibration standard	Laboratory standards: VSL-OVOC 7 component mix @ 100nmol/ml (OVOC) and NPL-30 O ₃ precursors in N ₂ , @ 4nmol/mol (NMHC)	Laboratory standards: NPL-30 O ₃ precursors in N ₂ , @ 2nmol/mol (NMHC, terpenes) and VSL-OVOC 7 component mix @100nmol/mol; working standard: dilution of laboratory standard (working standard)	NMHC NPL, 4 nmol/ml		PRAXAIR 25-component mix (France, 2011), 3 µmol/mol	

	DWD GC-FID/MS	DWD GC-FID/FID-MS	Empa GC-FID/FID		IMT GC-FID/MS	
Calibration method	Direct supply of standard, one series of 3 measurements/week	Direct supply of standard standard and working standard (during intercomparison one WS every 6 th to 12 th sample).	OVOC calibration by concept of effective carbon numbers		Standard diluted with humidified zero air to 4 nmol/mol	
Limit of detection	7 – 44 pmol/mol	1-10 pmol/mol	4 – 10 pmol/mol		2 – 96 pmol/mol	
Determination of system blanks	Dry helium (5.0) cleaned with charcoal cartridge goes same paths like sample gas	Dry helium (5.0) cleaned with charcoal cartridge goes same paths like sample gas	Parker Zero air generator (dry and wet)		Not determined	
Frequency of samples	67 minutes	1 hour	1 hour		90 minutes	

Table 7 PTR-MS systems used during SbS2018

	WCC-VOC PTR-MS	KIT PTR-MS	UU PTR-TOF/MS
PTR-MS model/type	Ionicon QMS 500	Homebuilt instrument by KIT equipped with Pfeiffer quadrupole mass spectrometer	Ionicon TOF1000 MS
Sampling line	Silcosteel® (Restek), OD 1/16", 2 m, ambient Temp,	1/8", Silcosteel®, unheated, 2.5 m	1/8" PFA, 3m
Sample flow rate	125 ml	1000 nml/min	100 ml/min
PTR flowrate	125 ml	160 nml/min	100 ml/min
Materials used in sample gas path	Silcosteel® (Restek), Teflon, stainless steel	Silcosteel®, PEEK®, PFA®	1/8" PFA
Reaction Temperature	80 °C	65 °C	60 °C
Reaction Pressure	2.15 mbar	2.2 hPa	3.1 mbar
GD pressure	557 mbar		
E/N	120 Td	142 Td	120 Td
Calibration standard	Laboratory standards: VSL-OVOC 7 component mix @ 100nmol/ml (OVOC) and NPL-30 O ₃ precursors in N ₂ , @ 4nmol/mol (NMHC)	APEL-RIEMER ENVIRONMENTAL, IN, yop: 2016, Multi-component calibration mix, ~ 500 ppb VOCs	Apel-Riemer standards: 16 components mix @ 1000 nmol/mol (with acetaldehyde believably drops to 600 nmol/mol)
Calibration method	Direct supply of standards	Standard diluted with synthetic air to concentrations between 1 and 3 ppb	Standards diluted with humidified/dry zero air/N ₂ up to 50 nmol/mol
Limit of detection	10 to 50 pmol/mol	16-600 ppt	<10 ppt
Determination of system blanks	Zero-air	Sample air is scrubbed with a heated catalyst (300 °C) every 30 min for 5 min	Zero-air
Time resolution	2 to 3 min	122 s	Real time display

References

- [1] WP4- NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides, Deliverable D4.9: Final SOPs for VOCs measurements, http://fp7.actris.eu/Portals/97/deliverables/PU/WP4_D4.9_M42_v2.pdf , 2014.