

Intercomparison of oxygenated volatile organic compound measurements at the SAPHIR atmosphere simulation chamber

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[1] This paper presents results from the first large-scale in situ intercomparison of oxygenated volatile organic compound (OVOC) measurements. The intercomparison was conducted blind at the large (270 m³) simulation chamber, Simulation of Atmospheric Photochemistry in a Large Reaction Chamber (SAPHIR), in Jülich, Germany. Fifteen analytical instruments, representing a wide range of techniques, were challenged with measuring atmospherically relevant OVOC species and toluene (14 species, C₁ to C₇) in the approximate range of 0.5–10 ppbv under three different conditions: (1) OVOCs with no humidity or ozone, (2) OVOCs with humidity added (r.h. ≈ 50%), and (3) OVOCs with ozone (≈60 ppbv) and humidity (r.h. ≈ 50%). The SAPHIR chamber proved to be an excellent facility for conducting this experiment. Measurements from individual instruments were compared to mixing ratios calculated from the chamber volume and the known amount of OVOC injected into the chamber. Benzaldehyde and 1-butanol, compounds with the lowest vapor pressure of those studied, presented the most overall difficulty because of a less than quantitative transfer through some of the participants' analytical systems. The performance of each individual instrument is evaluated with respect to reference values in terms of time series and correlation plots for each compound under the three measurement conditions. A few of the instruments performed very well, closely matching the reference values, and all techniques demonstrated the potential for quantitative OVOC measurements. However, this study showed that nonzero offsets are present for specific compounds in a number of instruments and overall improvements are necessary for the majority of the techniques evaluated here.

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1. Introduction

[2] Oxygenated volatile organic compounds (OVOCs) are of interest because of their key roles in atmospheric

photochemical processes. Sources of OVOCs include primary anthropogenic emissions (AP), primary biogenic emissions (BP), biomass burning (BB), and secondary photochemical formation from both anthropogenic (AS) and biogenic (BS) sources. Measurements of OVOCs are much less common than nonmethane hydrocarbon (NMHC) measurements, another VOC subset. This is because quantification of these species is, in general, more difficult than NMHCs and the importance of these species in atmospheric

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chemical cycles was not fully appreciated until well after the importance of NMHCs had been established.

[3] Once present in the atmosphere, OVOCs can react with free radicals such as OH, and NO_3 [Atkinson, 1994]. If the OVOC contains a double bond, such as methacrolein and methyl vinyl ketone, it can also react with ozone. Tropospheric mixing ratio ranges for OVOCs are highly variable [Riemer *et al.*, 1998; Singh *et al.*, 1994, 2000]. The aldehydes and ketones have relatively short lifetimes whereas saturated alcohols are the least reactive of the OVOCs and have the longest lifetimes; the alcohol, 2-methyl-3-butene-2-ol (MBO) has a relatively short lifetime because it is unsaturated. Among all of the OVOCs, methanol is present at the highest tropospheric mixing ratios [Singh *et al.*, 2000] and is distributed throughout the troposphere because of its long lifetime of 16 days at an OH concentration of 1×10^6 molec/ cm^3 .

[4] Through photochemical cycles similar to those involving NMHCs, OVOCs can participate in reactions leading to the formation of tropospheric ozone [Lloyd, 1979; Singh *et al.*, 1995]. Ozone is one of the key molecules in atmospheric chemistry because it is an important pollutant and a primary precursor to the formation of the OH radical, which is the major oxidizing agent of the atmosphere. Aldehydes and ketones may also photolyze at wavelengths less than 380 nm producing the radicals RO_2 , HO_2 and OH. In the drier parts of the atmosphere, this source of OH radicals, primarily from formaldehyde and acetone, can become the dominant source [Wennberg *et al.*, 1998]. Changes in OH directly impact the mixing ratios of radiatively important gases such as methane [Intergovernmental Panel on Climate Change (IPCC), 2007].

[5] In addition to the indirect impact of OVOCs on the radiation budget as a result of photochemistry, these species can participate in the production and modification of organic aerosols. Tropospheric aerosols pose one of the largest uncertainties in model calculations of climate forcing due to anthropogenic changes in the composition of the atmosphere. Recent studies have shown that secondary organic aerosol formation from gas-to-particle conversion is significant [IPCC, 2007, and references therein]. It is conceivable that photochemical processes could also serve as a source of aerosol-derived oxygenated compounds. However, more data are needed to fully understand the ultimate fate of OVOCs, their oxidation products, and their contribution to organic aerosol formation and modification.

[6] A variety of methods have been used for quantifying ambient OVOC mixing ratios, but it is commonly believed that OVOCs are difficult to measure with high accuracy. Vairavamurthy *et al.* [1992] present an early review on the subject of carbonyl measurements. Even at the time of this review, there were a number of competing techniques, ranging from liquid scrubbing chemical derivatization followed by liquid chromatography to gas chromatographic methods. Spectroscopic methods have been applied principally to the measurement of formaldehyde which, although it was one of the species compared in this study, is treated in a separate manuscript [Wisthaler *et al.*, 2008]. Silica gel cartridges impregnated with DNPH (Dinitrophenyl hydrazine) have been used for over two decades for carbonyl measurements [Fung and Grosjean, 1981]. This technique allows relatively easy sample collection in the field but

suffers from low time resolution and possible interferences. Gas chromatography (GC) has also been used to measure a number of OVOCs including alcohols, aldehydes ($>\text{C}_1$) and ketones [e.g., Goldan *et al.*, 1995; Lamanna and Goldstein, 1999; Leibrock and Slemr, 1997]. The most commonly used detectors for GC OVOC measurements have been the flame ionization detector (FID) and mass spectrometry (MS). Since the FID detector is nonspecific it is imperative that sufficient peak separation is accomplished through optimized chromatography to minimize the potential for coelutions of target and nontarget VOCs. Excellent examples of this technique are given by Schade *et al.* [2000] and Goldan *et al.* [1995]. GC-MS has become an increasingly popular technique for ground-based studies of OVOCs [e.g., Helmig and Greenberg, 1994; Yokouchi, 1994; Montzka *et al.*, 1993, 1995; Leibrock and Slemr, 1997; Biesenthal *et al.*, 1997; Starn *et al.*, 1998; Riemer *et al.*, 1998; Apel *et al.*, 2002, 2003] and recently has been deployed on an aircraft platform [Apel *et al.*, 2003]. Modern GC-MS systems are capable of detecting OVOCs with high sensitivity and excellent selectivity. The GC/Reduction Gas Detector (GC/RGD) [O'Hara and Singh, 1988] has been used for a number of years for aircraft-based studies [e.g., Singh *et al.*, 2000].

[7] Chemical ionization mass spectrometry (CIMS) has been used to detect a variety of OVOCs. The most common ionizing agent is H_3O^+ , which lends itself to the detection of species with proton affinities greater than water [e.g., Hansel *et al.*, 1995]. This technique (dubbed PTR-MS) has gained popularity and there are numerous studies in the literature [Hewitt *et al.*, 2003; de Gouw *et al.*, 2003a] documenting its use as a fast-response, continuous method for OVOC measurements. An FTIR spectrometer has been developed and deployed to study a number of species including OVOCs in biomass burning plumes [Yokelson *et al.*, 1999, 2003].

[8] There are pros and cons for each instrumental technique. GC-based methods have the potential for high sensitivity because large volumes of sample (air) can be preconcentrated but they generally require long cycling times (times between samples), often on the order of 0.5 to 1 h, which precludes them from observing short-term variability in air masses. Faster time response GC-based systems (2-min cycling time) have recently been developed (E. C. Apel *et al.*, Development of the trace organic gas analyzer, manuscript in preparation, 2008) but are not represented here. GC-FID systems are nonspecific and require good chromatographic characterization and separation. GC-MS instruments are selective as they discriminate with chromatography and mass. CIMS instruments are fast (typically 1–30 s) and require no sample preparation and, as a result, have perhaps less potential for artifact formation. However, they measure specific masses which are not always unique to one compound and thus have the potential for interferences from both known and unknown compounds. This problem is most pronounced in a complex urban environment. Differential Optical Absorption Spectroscopy (DOAS) [Brewer, 1973; Platt and Perner, 1983] is a completely noninvasive technique that allows for real time measurements but the number of species that can be measured is limited. FTIR has similar advantages to DOAS

Table 1. ACCENT OVOC Compound List With Letter Designation Used in Figures 5–8^a

Letter	Compound	Source	Relevance	Vapor Pressure ^b
a	1-butanol	AP	U	7
b	1-propanol	AP	U	20
c	2-methyl-3-butene-2-ol	BP	B	68 ^c
d	acetaldehyde	AS, BS, BB	R, U, O	1004
e	acetic acid methyl ester	AP	O	219
f	acetone	AP, BP, BB	R, U, B, O	245
g	benzaldehyde	AS	O	5 ^d
h	butanal	AS	R, O	120
i	ethanol	AP, BP, BB	U, B	60
j	hexanal	AS, AP	O	13
k	methacrolein (MACR)	BS	O, B	161
l	methanol	BP, BB, AP	U, B	130
m	methyl vinyl ketone (MVK)	BS	O, B	94
n	(MACR + MVK)	BS	O, B	N/A
o	toluene	AP	U, A	29

^aThe major source is indicated by anthropogenic primary and secondary (AP, AS), biogenic primary and secondary (BP, BS) and biomass burning (BB). The relevance is indicated by oxygenation processes (O), biogenic activity (B), urban tracer (U), radical cycling (R), and aerosol formation (A). The vapor pressures are given in hPa at 20°C except where indicated. N/A, not applicable.

^b<http://www.sigmaaldrich.com>.

^cVapor pressure (hPa) at 25°C.

^dVapor pressure (hPa) at 45°C.

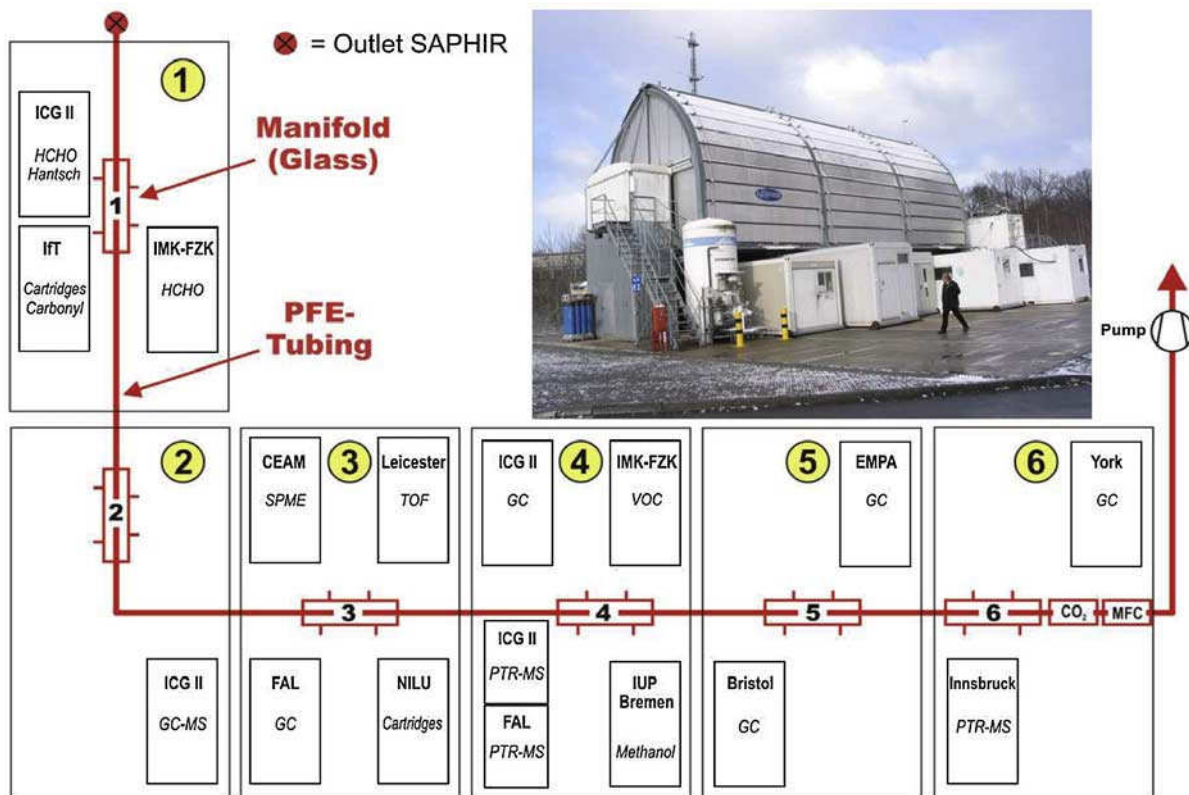
and in addition can measure a large number of species simultaneously, but suffers from relatively low sensitivity.

[9] There have been few instrument comparisons of OVOCs. *Apel et al.* [1998] reported on a ground-based comparison of GC-MS instruments with cartridge-based techniques for the measurement of carbonyl compounds.

Differences in the data of greater than a factor of two were common and it was noted that a more formal intercomparison of techniques would be desirable. A number of limited, informal comparisons have been reported. A CIMS technique and a GC-based technique simultaneously measured acetone aboard an aircraft over the North Atlantic free troposphere and lower stratosphere [Wohlfrom *et al.*, 1999]. A GC-MS technique was recently compared with a GC-RGD system aboard aircraft [Eisele *et al.*, 2003] and a GC-MS system was compared with a PTR-MS system aboard the *Ron Brown* Naval Vessel [de Gouw *et al.*, 2003b]. Two differently configured PTR-MS instruments were recently compared [de Gouw *et al.*, 2004]. Most recently, side-by-side measurements were made with a PTR-MS and a fast-response GC-MS aboard aircraft (E. Apel and T. Karl, private communication, 2007).

[10] The OVOC species targeted for this study are listed in Table 1 along with their major sources and relevance. The primary reason that these species were chosen was because of their acknowledged or potential importance in atmospheric chemical cycles; toluene was chosen because it is a common, relatively easily measured NMHC that is easily calibrated, especially with flame ionization detector-based techniques, and it could be measured by the majority of the instruments. It should be noted that measurements in the real atmosphere using nonspecific techniques such as PTR-MS present problems that are not present here in this simplified matrix. For example, benzaldehyde is detected at the same mass as the xylenes and ethyl benzene.

[11] This paper describes the results from this, the first large-scale controlled intercomparison study of OVOCs.

**Figure 1.** Setup of the instruments at the chamber. All instruments were connected via PFA tubing, and each portable laboratory had a glass manifold from which sample could be drawn.

This experiment was conducted as part of the ACCENT (Atmospheric Composition of the Atmosphere: the European Network of Excellence) program. Sixteen different instruments and one cartridge sampling system (Figure 1) were situated in trailers near the Simulation of Atmospheric Photochemistry in a Large Reaction Chamber (SAPHIR) environmental chamber. Included in these were a number of new techniques: proton transfer time-of-flight mass spectrometry (PTR-TOF-MS), solid phase microextraction (SPME), and a novel catalyst that allows for the conversion of methanol to formaldehyde and thus near simultaneous detection of formaldehyde and methanol via the Hantzsch method.

[12] The instruments were set up to simultaneously measure well-mixed SAPHIR synthetic air mixtures containing the 13 OVOCs, toluene, and formaldehyde at mixing ratios between 500 pptv and 10 ppbv, a range observed in moderately polluted ambient air. A separate manuscript [Wisthaler *et al.*, 2008] describes the results obtained from the measurement of formaldehyde, leaving 15 total instruments intercompared for OVOCs.

2. Experiment

2.1. SAPHIR Chamber

[13] This intercomparison was performed at the Atmosphere Simulation Chamber SAPHIR on Forschungszentrum Jülich campus in January 2005 (Figure 1). The SAPHIR chamber consists of double-walled Teflon FEP bag of cylindrical shape (length 18 m, diameter 5 m, effective volume 270 m³, surface/volume 1 m⁻¹) that is held by a steel frame. FEP film was selected because it is chemically inert and UV permeable. Typically, 80% of the outside actinic flux (290–420 nm) is available inside the chamber [Bohm *et al.*, 2005]. However, the experiments described here were performed in the dark with the roof of the chamber closed. In this case, less than 0.2% of the outside photolysis of NO₂ is observed inside the chamber.

[14] The inner tube is used as a reactor for simulation experiments. Its volume is 270 m³ and can be flushed with dry or wet synthetic air (purity 99.9999%) loaded with a variety of trace gases if required. The space between the inner and the outer tube (0.2 m) is permanently flushed with clean nitrogen to prevent diffusion of gases from outside. The inner volume is always held at 60 Pa pressure over ambient in order to keep the volume constant and the FEP film under tension. Leaks and gas extraction by instruments require a replenishment flow rate of 3–10 m³ h⁻¹ in order to hold the pressure constant.

[15] The SAPHIR chamber is equipped with a comprehensive set of sensitive instruments. For this campaign online measurements of ozone, humidity, temperature, and pressure were used. Technical details of the SAPHIR chamber have been described in previous studies [Rohrer *et al.*, 2005; Wegener *et al.*, 2007; Schlosser *et al.*, 2007].

2.2. Design of the Intercomparison

[16] The intercomparison was performed from 24 to 28 January (days 1–5) 2005. Although all days were originally planned to be included in the intercomparison, data from days 1 and 5 were excluded for technical reasons discussed briefly below. The experimental approaches for the three

remaining days were similar, as seen in Figure 2. Day 2 conditions are shown in the first column, day 3 in the second and day 4 in the third. The first row shows the ozone and water concentrations for each day, the second row shows the temperature information, the third row gives the SAPHIR dilution rate, and the fourth row shows the durations of the three daily segments labeled A, B, and C, along with the calculated concentrations for butanal. Figure 3 shows time series data similar to that shown in the fourth row of Figure 2 but with participants' experimental data superimposed. For all experiments the chamber was flushed overnight using high-purity synthetic air produced from liquid nitrogen (Purity = 99.99999%) and liquid oxygen (Purity = 99.99999%). After flushing the chamber with the clean synthetic air, mixing ratios of ozone, NO_x, and single VOCs were below 100 pptv, 20 pptv, and 10 pptv, respectively. Also water vapor pressure was reduced to levels less than 0.1 hPa, corresponding to dew points below -40°C. Predetermined amounts of OVOCs were injected, through a heated injector port, vaporized, and swept into the SAPHIR environmental chamber using the replenishment flow of clean synthetic air (approx. Ten m³ h⁻¹, Figure 2, third row). Each species was injected individually with a high-accuracy volumetric syringe (Hamilton, model 701, 10 μl). Initial values for OVOC mixing ratios were calculated on the basis of known injection volume, known chamber volume, and known state parameters. The mixing ratios decreased with time because of the continuous clean air refill of the chamber which maintained the chamber pressure at 60 Pa above ambient; the dilution rate of species in the chamber was approximately 3% h⁻¹. Flushing of the chamber by rates of up to 300 m³ h⁻¹ was done twice per day during the experiments to intentionally dilute the gas mixture in the chamber. Thus, each day consisted of three segments, A, B, and C as shown in Figure 2. The solid line in the fourth row represents the calculated values (here for butanal) obtained from considerations above.

[17] The beginning of segment A represents the initial calculated mixing ratio in the chamber. The slope of the line in segment A corresponds to the dilution rate of the chamber (≈3% h⁻¹) but was calculated exactly from the measured replenishment flow rate. The steep slope between segments A and B represents the flushing rate of the chamber and so on through segment C. This pattern was repeated on each of the three intercomparison days but for each day, different initial mixing ratios were used along with different flushing rates. The concentrations of nonreacting species in SAPHIR are calculated by the following equation, describing the dilution in a well stirred reactor:

$$C(t) = C_0 \times \exp\left(-\frac{1}{V} \int_0^t F(t') dt'\right). \quad (1)$$

Here, $F(t)$ is the replenishment flow, C_0 is the initial concentration after injection (at $t = 0$) and mixing; V is the SAPHIR volume. All data from participating instruments in this paper are compared with values calculated using equation (1). This appears to be a reasonable approach but a brief discussion is warranted on the estimated accuracy of the calculated values. The accuracy of the calculated values is a function of the uncertainty in the SAPHIR volume and

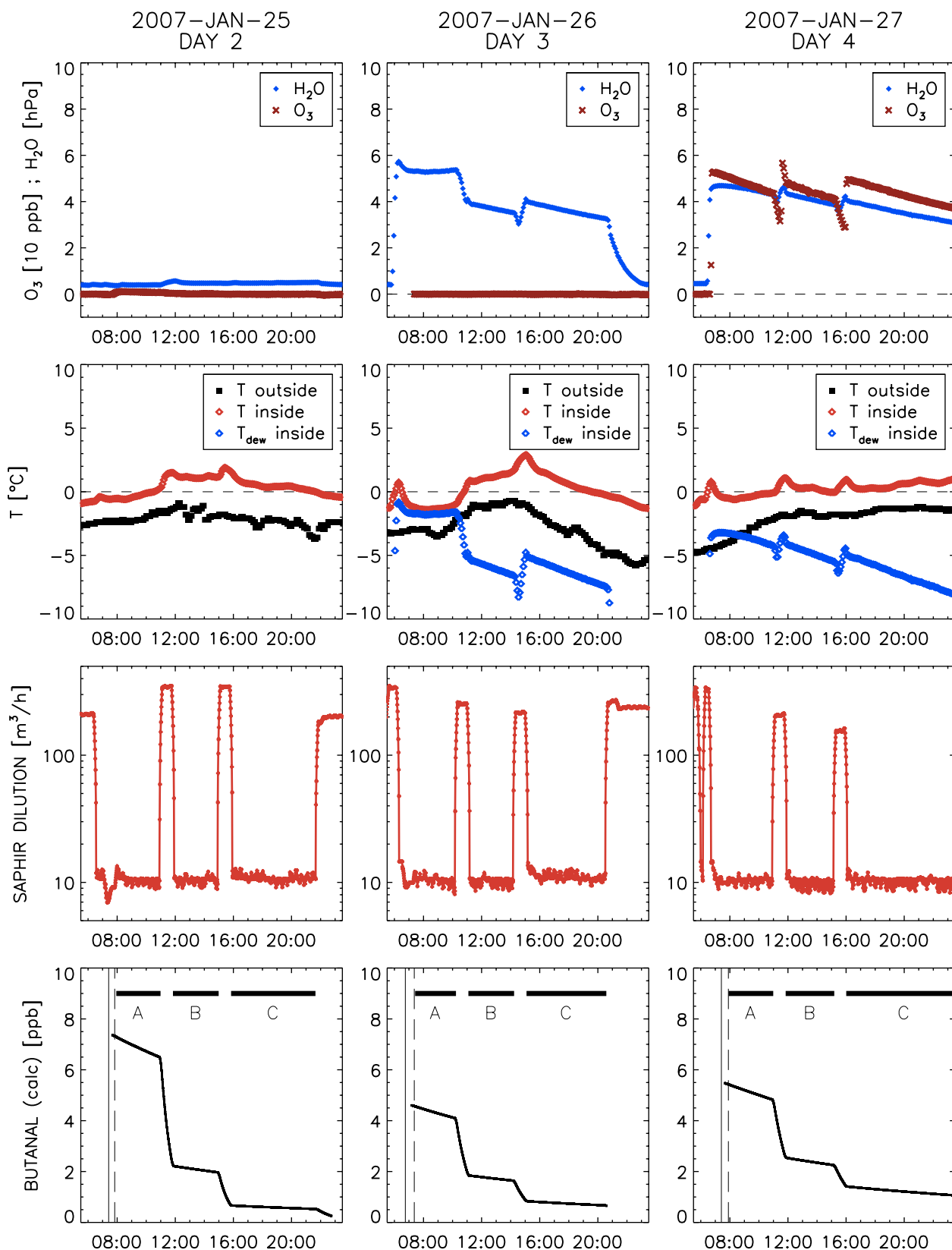


Figure 2. Diurnal profiles of ozone, water vapor partial pressure, inside, outside, and dew point temperatures, synthetic air gas flow, and calculated trace gas (butanal) concentrations for the experiment days 2–4. The horizontal bars in the fourth row indicate the experiment sections A, B, and C; the vertical solid lines indicate the beginning of the OVOC injection; and the dashed lines indicate the end. During this period a powerful fan was operated to achieve almost instantaneous mixing of the injected compounds.

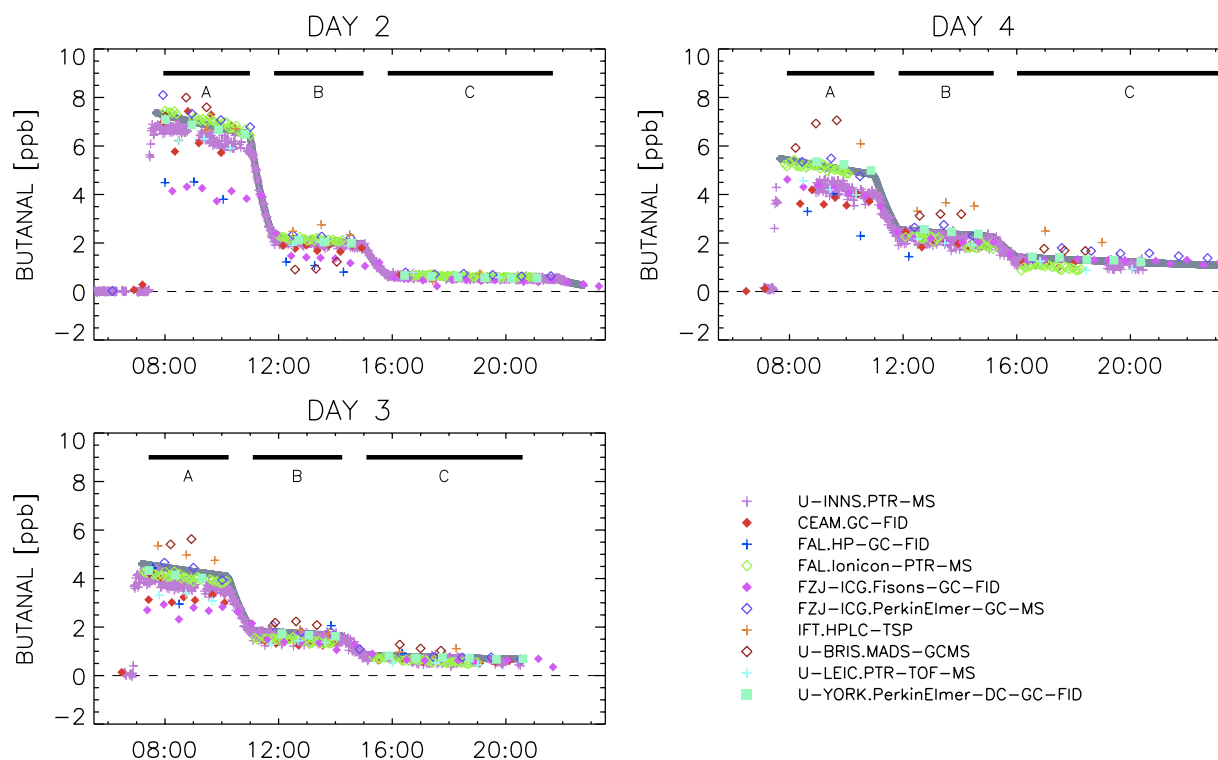


Figure 3. Experimental data superimposed on the calculated values for butanal for days 2, 3, and 4. Each day had three segments which are shown in the bars at the top of each panel.

the uncertainty of the syringe volume per injection. The syringe injection volume uncertainty is $\pm 5\%$ and the uncertainty in the chamber volume is 2%. Therefore, the total uncertainty or accuracy in the calculated concentrations is $\pm 7\%$, found by adding these two contributions. There are other potentially unknown uncertainties that could be associated with incomplete transfer of liquid through the lines into the SAPHIR chamber, the purity of the species injected, and adsorption of the species of interest on the walls of the chamber. On the basis of the data which will be discussed below, we believe that these uncertainties are small. The precision of the calculated values is very good since the mass flow controller employed for the replenishment flow has a less than 2% statistical error for a 1 min reading. Since the change in the concentration is small, the mass flow controller reading does not substantially contribute to the total error of calculated concentration.

[18] Instruments were challenged during day 2 with the full suite of OVOCs in dry synthetic air (Figure 2, left). For day 3, OVOC mixing ratios different from day 2 were added to the chamber; in addition, water vapor was added at relative humidity levels of approximately 60% in order to test whether water vapor had any effect on participants' results (Figure 2, middle). Day 4 presented the most challenging experiment as OVOC mixing ratios, different from either days 2 or 3, were introduced in synthetic air in which both ozone (60 ppbv) and water vapor (relative humidity $\sim 50\%$) were added (Figure 2, right). OVOC mixing ratios ranged from a low of 0.6 ppbv to approximately 10 ppbv and were different for each compound.

[19] Day 1 was a blank experiment: no OVOCs were injected into the chamber but water vapor and ozone were

added during the course of the day. Because there were a number of technical problems associated with both individual instruments and manifold leaks in the temporary laboratories, no data is reported for this day. During day 5, ambient air was drawn into SAPHIR and spiked with OVOCs to see the effect of a full air matrix on the instrument performance. Because of limited data coverage by a number of instruments, these data are not included in the intercomparison.

[20] Participants were given the list of compounds that were to be intercompared and the approximate range of expected mixing ratios before the experiment began; they were asked to not share their data with one another and to keep the experiment blind. The deadline for data submission was 30 April 2005 and the results were discussed during the data workshop (20–22 June).

[21] This was not meant to be the most challenging OVOC experiment possible but was intended to obtain data to gain information on the state of OVOC measurements, particularly European ground-based measurements, and their comparability within a simulated air matrix. It should be noted that the air matrix for the experiment was simulated but certainly less complex than ambient air as there were no additional compounds that are or may be present in real air that could complicate the analyses.

2.3. Instruments

[22] The chamber enables the easy attachment of field instruments. In this case, 14 different instruments for OVOC measurements were located near the chamber and housed in six temporary laboratories (Figure 1); sample mixtures were provided via 10 mm ID heated (50°C) PFA tubing which

Table 2. List of Instruments Participating in the OVOC Campaign^a

ID	Institute Name	Instrument Identifier	Accuracy	Precision	Standard Used
A	CEAM	GC-FID	3–5%	N/A	in house
B	EMPA	MADS-GCMS	1–30%	1–5%	AiR, ^b USA
C	FAL	HP-GC-FID	20–50%	0.3–1 ppbv	AiR, USA
D	FAL	Ionicon-PTR-MS	10–20%	0.07–0.42 ppbv	calculated, AiR, USA ^c
E	FZJ-ICG	broadband-DOAS	3–5%	0.04 ppb benzaldehyde, 1 ppb else	line strength
F	FZJ-ICG	Fisons-GC-FID	4–19%	0.3–0.9 ppb	AiR, USA
G	FZJ-ICG	PTR-MS	4.2–23.3%	1.5–3.3%	diffusion source
H	FZJ-ICG	PerkinElmer-GC-MS	10–20%	3–15%	AiR, USA
I	IFT	HPLC-TSP	N/A	N/A	in house
J	IMK-IFU	BrukerFranzen-GC-MS	5%	10% for MBO, 10% for benzaldehyde, 5% for hexanal, 5% for toluene	Messer-Griesheim, Germ. (Δ_2 -carene), in-house diffusion source
K	U-BREM	Catalytic converter–Hantzsch	6%	2%	Messer-Griesheim methanol in N ₂
L	U-BRIS	MADS-GCMS	7%	0.16–1.4 ppb (compound specific)	AiR, USA
M	U-INNS	PTR-MS	$\pm 5\%$ ^d	$\pm 5\%$ ^d	AiR, USA
N	U-LEIC	PTR-TOF-MS	5–25%	10%	AiR, USA
O	U-YORK	PerkinElmer-GC-FID	7–11%	0.5–10%	AiR, USA

^aThe accuracy and precision (further discussion is given in the text on some technique precisions and accuracies) refer to the a priori defined values from independent calibration procedures.

^bAiR is a registered trade name for Apel-Riemer, Env. Inc.

^cFurther discussion is given in the text on some technique precisions and accuracies.

^dThe accuracy of the standard was $\pm 5\%$ for the OVOCs and $\pm 3\%$ for toluene. Within-run precision and day-to-day precision were calculated and varied with individual species, e.g., $\pm 4\%/\pm 3\%$ for methanol, $\pm 4\%/\pm 2\%$ for acetaldehyde, $\pm 7\%/\pm 20\%$ for ethanol, $\pm 2\%/\pm 2\%$ for acetone, and $\pm 3\%/\pm 6\%$ for toluene. The values given for the accuracy and precision in Table 2 are thus an oversimplification.

was routed from the chamber and through glass manifolds located in each of the temporary laboratories. Individual experimentalists connected their respective instruments to the glass manifold via one of 8 nipples that were located on each manifold. The sampling system was constantly flushed with 40 l min⁻¹ chamber air. An additional instrument (DOAS) measured in situ via an optical path within the chamber.

[23] Table 2 lists the instruments that participated in the intercomparison and their key measurement parameters. The accuracy and precision refer to the a priori defined values from independent calibration procedures. The letter designation for each respective instrument remains consistent throughout the paper and is used in the presentation of the data in sections 3 and 4. A description of each instrument follows.

2.3.1. Fundacion Centro de Estudios Ambientales del Mediterraneo (CEAM) GC-FID

[24] The technique used was solid phase microextraction (SPME). The limit of detection was 0.100 ± 0.003 ppb hexanal, 0.120 ± 0.003 ppb butanal, 0.240 ± 0.009 ppb benzaldehyde, and 0.88 ± 0.04 ppb toluene. The measurement frequency was one sample every 40 min (manual sampling). Background signal determination or zeroing procedure consisted of loading the derivatizing agent on fiber and sampling for 20 min from zero air (flushed chamber). Inlet material and temperature were Teflon tubing and ambient temperature, respectively. Typical applications were ground-based measurements (under development). The calibration procedure consisted of syringe injections in a Euphore chamber.

[25] Further details are as follows: A system for active sampling solid phase microextraction (SPME) was developed for this study (E. Gómez Alvarez and V. Moreno, manuscript in preparation, 2008). O-(2, 3, 4, 5, 6) penta-

fluorobenzylhydroxylamine hydrochloride (PFBHA) on-fiber derivatization [Koziel *et al.*, 2001; Martos and Pawliszyn, 1998] was employed in which the derivatizing agent is loaded in excess from the headspace of a high-concentration aqueous solution (17 g L⁻¹). The analytes are retained and derivatized when the tip of the SPME needle containing the agent is exposed for 20 min in a sample flow-through cell. The fiber is subsequently injected into a gas chromatograph (Hewlett-Packard Co., model 6890, Wilmington, DE, USA) equipped with an HP-5MS capillary column (cross-linked 5% PHME Siloxane, 30 m $\times$ 0.25 μ m $\times$ 0.25 μ m) which was coupled to an inlet liner with a narrow internal diameter, 0.75 mm i.d. predrilled Thermogreen (Supelco, Lund, Sweden) LB-2 septa for SPME, and a flame ionization detector (FID). The flow-through cell was connected to a pump and a flow controller at a flow rate set to 1.6 L min⁻¹ with calculated air speed inside the cell of 0.154 m s⁻¹, and to a thermostatic bath, set at 20°C. The chromatographic conditions were as follows: The injector was 270°C; the detector was 300°C; the oven was initially set at 80°C for 2 min, then ramped at 20.0°C min⁻¹ to 280°C and held for 3 min (total run time was 15 min); the column was constant pressure mode (1744 hPa); and the flow was 2.6 ml min⁻¹. Average velocity was 0.5 m s⁻¹. For the inlet, the pressure was 1.5 bar, and total flow was 14.6 ml min⁻¹. The heater was 260°C. The purge flow to the split vent was 9.1 mL min⁻¹ at 1 min.

[26] Calibration was carried out in EUPHORE, another high-volume simulation chamber having similar characteristics to SAPHIR, in two different experiments. In one of them, triple injections of equivalent amounts were performed in order to characterize the precision. In the second of the calibration experiments, known amounts of each of the carbonyls measured in the intercomparison plus toluene, were introduced via syringe injection in the EUPHORE

chamber at concentration levels of about 20 ppb. After a number of sampling steps, dilution was applied to bring the concentration levels to approximately 6, 2 and 0.6 ppb. Measurements leading to calibration were performed in these three plateaus.

2.3.2. Swiss Federal Laboratories for Materials Testing and Research (EMPA) Modified Adsorption/Desorption System (MADS) GC-MS

[27] The technique used was GC-MS. The limit of detection was 1–730 pptv and was compound-dependent. Measurement frequency was 25 min. Background signal determination or zeroing procedure consisted of zero air from zero air generator. Inlet material and temperature were Teflon and ambient, respectively. Typical applications were ground-based measurements. The trapping material was Haysep D. The calibration procedure consisted of sampling of certified calibration mixtures.

[28] Further details are as follows: The EMPA system consists of a preconcentration sampling unit coupled to an Agilent HP 6890–HP 5973N GC-MS. The main parts of the sampling unit are two traps, each filled with the Polydivinylbenzol (PVDB) Haysep D from Supelco. The first trap is filled with 0.6 g of the adsorbent material and is kept at room temperature during sampling. This allows most of the water to pass the trap, and the rest of the water is then removed with helium flushing. After initial trapping of a 350 ml sample, the compounds are subsequently desorbed onto a smaller trap which is also filled with Haysep D, but is cooled to -40°C by Peltier elements to increase the capacity. The compounds were rapidly desorbed from this trap (180°C) and transferred by a heated fused silica line onto the gas chromatograph. The chromatographic separation was performed on a $25\text{ m} \times 0.32\text{ }\mu\text{m}$ CP-Porabond U column (Varian Inc., USA) with $7\text{ }\mu\text{m}$ film thickness, using He as carrier gas with a flow of 1 ml/min. Initially the temperature was held at 40°C for 2 min, and then it was increased rapidly to 120°C at a rate of $20^{\circ}\text{C}/\text{min}$, and at a rate of $5^{\circ}\text{C}/\text{min}$ to 200°C , where it was held constant until the end of the run. Individual compounds were detected by running the mass spectrometer in single ion monitoring (SIM) mode, for improved signal-to-noise ratio. The compounds are identified by their mass spectra and quantified using a 24 compound OVOC standard gas mixture in the range 350–450 ppb (AiR Environmental, Inc., also known as Apel-Riemer Env., Inc, USA), and a 30 compound VOC standard gas mixture in the range 1–10 ppb (NPL, England). The valves are all VICI valves with Valcon E rotor material and all lines in contact with the sample are made of 1/16" Silcosteel[®] (Restek Corp., Bellefonte, PA, USA). The valves and lines are heated to 80°C . The sampling, calibration and analysis are done automatically without any need for user interaction.

2.3.3. Swiss Federal Research Station for Agroecology and Agriculture (FAL) Hewlett-Packard (HP) GC-FID

[29] The technique used was GC-FID. The limit of detection was not determined; GC is normally used as a front end for the FAL PTR-MS described in section 2.3.4 below. The measurement frequency was 55 min. Background signal determination or zeroing procedure consisted of sampling VOC-free air generated by ChromGas Zero Air Generator (model 1000, Parker Hannifin Co., Haverhill MA, U.S.). The inlet material and temperature were PFA

and 50°C , respectively. Typical application was operation in combination with PTR-MS, for qualitative separation of isobaric compounds. The trapping material was Tenax TA. The calibration procedure consisted of sampling of calibration mixtures diluted with VOC-free air (see above) by mass flow controllers.

[30] Further details are as follows: This system consists of a Hewlett-Packard gas chromatograph (HP 5890, Series II plus) upgraded with an online thermal desorption system (TDS G, Gerstel, Germany) and a cool injection system (CIS 3, Gerstel, Germany) equipped with a liquid CO_2 cooling device. The compounds were separated on a DB-624 column ($30\text{ m} \times 0.32\text{ mm ID}$, $3\text{ }\mu\text{m}$, P/N: 125–1334, Agilent J&W) and detected by a flame ionization detector (FID). The helium carrier gas was controlled by electronic pressure control (EPC). SAPHIR chamber air was led from the sampling manifold by a 3 m long, heated 1/4" PFA-Teflon tube to the inlet of the GC-FID. There the compounds were adsorbed on a glass tube ($1/4" \times 12\text{ cm}$) filled with Tenax TA at a temperature of 5°C and a sample flow of 100 ml min^{-1} for 10 min (one liter total). After the adsorption, the glass tube was flushed for 1 min with Helium (50 ml min^{-1}) at a temperature of 5°C in the opposite direction of the adsorption flow to remove water. Then the compounds were thermally desorbed (temperature program of the TDS G: $60^{\circ}\text{C min}^{-1}$, hold at 260°C for 4 min) with a Helium flow of 50 ml min^{-1} and cryofocused in the CIS on a glass sleeve filled with Tenax TA at -70°C . The sample was then injected (temperature program of the CIS: $12^{\circ}\text{C s}^{-1}$, hold at 260°C for 4 min) on the column (oven program: 30°C hold for 5 min, $10^{\circ}\text{C min}^{-1}$ to 230°C , $70^{\circ}\text{C min}^{-1}$ to 30°C). The Helium flow on the column was held constant at 2.3 ml min^{-1} . The FID at the column's end had a temperature of 260°C . The total sampling and cryofocusing time was about 20 min, the GC run time 35 min, which corresponds to a total cycle time of about 55 min. Ethanol, 1-propanol, 1-butanol, 2-methyl-3-buten-2-ol, methacrolein, butanal, hexanal, benzaldehyde, acetone, methyl vinyl ketone, acetic acid methyl ester and toluene were detected. A gas phase standard provided by AiR Env., USA was used for calibration.

2.3.4. Swiss Federal Research Station for Agroecology and Agriculture (FAL) Ionicon PTR-MS

[31] The technique used was PTR-MS. The limit of detection was 5–120 ppt and was compound-dependent. The measurement frequency was 20 s. Background signal determination or zeroing procedure consisted of sampling VOC-free air generated by ChromGas Zero Air Generator (model 1000, Parker Hannifin Co., Haverhill MA, U.S.). Inlet material and temperature were 2 m long 1/8" PFA-Teflon tube, 50°C , and 30 cm of 0.25 mm ID Silcosteel[®] capillary. Typical applications were ground-based (flux) measurements. The calibration procedure consisted of sampling of calibration mixtures diluted with VOC-free air (see above) by mass flow controllers.

[32] Further details are as follows: This system is a commercially available proton transfer reaction mass spectrometer (PTR-MS, IONICON GmbH, Innsbruck, Austria) [Lindinger et al., 1998]. This PTR-MS version corresponds to the PTR-MS-HS type, featuring three turbo pumps for increased sensitivity and a drift tube (equipped with Teflon rings) optimized for fast time response and minimal surface

interactions [Spirig *et al.*, 2005]. A 2 m long 1/8" PFA-Teflon tube was used to connect the sampling manifold of the container to the inlet of the PTR-MS instrument. This inlet line was permanently heated to 50°C. Within the PTR-MS instrument, sample air is directed to the drift tube in a 0.25 mm Silcosteel[®] capillary, also kept at a temperature of 50°C. The sampled VOCs are ionized in the drift tube at a pressure of 2.1 mbar: the reaction between $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0,1}$ ions (generated by electrical discharge of pure water vapor) and VOC molecules produces VOCH^+ ions. In principle, any VOC with a higher proton affinity than water can be ionized in this way. These charged compounds are then analyzed with a quadrupole mass filter (at a pressure of 2.4×10^{-5} mbar) in conjunction with an ion multiplier (secondary electron multiplier, Mascom, MC-217, R-217). The accuracy value obtained for the instrument depends on the way the mixing ratio is calculated: by means of a semitheoretical calculation or using a gas phase standard for calibration [Ammann *et al.*, 2004]. Methanol, 1-butanol, 1-propanol, 2-methyl-3-butene-2-ol (all alcohols), butanal, acetic acid methyl ester and benzaldehyde were calibrated via theoretical considerations with an accuracy on the order of 50%. The accuracy of the calibrated compounds (determined with gas-phase standards) which include acetaldehyde, acetone, methacrolein and methyl vinyl ketone (mass 71) and toluene, are given in Table 2 (AiR Env., Inc.) The system was operated in selected ion measurement mode, with dwell times of 0.5 to 1 s for each ion mass resulting in measurement cycles of 20 s. Final data were provided as 5 min averages. Detection limits were calculated as two standard deviations from zero air measurements in the same mode.

2.3.5. Forschungszentrum Jülich–Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) Broadband DOAS

[33] The technique used was DOAS. The limit of detection was 0.12 ppb (benzaldehyde) and 3 ppb (toluene). The measurement frequency was 15 s. Background signal determination or zeroing procedure consisted of reference spectra taken before and after the experiments. There was no inlet. Typical applications were ground-based measurements. The calibration procedure was absolute.

[34] Further details are as follows: The instrument has been described in detail [Bossmeier *et al.*, 2006; Brauers *et al.*, 2007] therefore only a short description follows. A Xenon short arc lamp (OSRAM, XBO 75W/2) serves as the light source and is placed in a lamp housing outside the chamber. The light is transferred to the chamber via mirrors and an optical fiber. During the OVOC campaign, an edge filter (Schott, U-330) was used to block excess light. Entering and exiting the chamber through a quartz window at one end, the light passes SAPHIR along the axis of its cylindrical volume. In order to obtain sufficiently long light paths, a modified version of a White-type multiple reflection system is employed. The optical components of the White cell are integrated at the north and south end, respectively, into the SAPHIR setup at a distance of 20 m. Having passed the White cell, the light is guided via an optical fiber assembly into a Czerny–Turner type spectrograph (Jobin Yvon, HR 460) equipped with a photo diode array (Hamamatsu, S3904) with 1024 pixels covering a

spectral range of 44 nm. The spectral resolution is 0.17 nm full width at half maximum. Data are acquired through a controller (Hoffmann Messtechnik, DOAS Controller) connected to a PC. Formaldehyde, benzaldehyde and toluene were detected with the DOAS instrument. (The experiment describing formaldehyde result is reported separately [Wisthaler *et al.*, 2008]). Since benzaldehyde and toluene absorb in a different spectral regime than formaldehyde, the two required spectral intervals (260...300 nm; 310...350 nm) and light paths (320 m; 960 m) were alternated. The precisions were about 0.04 ppb, and 1 ppb and the accuracies were 5% and 3% for benzaldehyde and toluene, respectively. The specified accuracies reflect the error of the absorption cross sections obtained from Etzkorn *et al.* [1999]. As the cross section is a fundamental property of any absorber, no in situ calibration is required.

2.3.6. Forschungszentrum Jülich–Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) Fisons GC-FID

[35] The technique used was GC-FID. The limit of detection ranged from 8 ppt (toluene) to 40 ppt (1-propanol). The measurement frequency consisted of sampling 10 min every 30 min. Background signal determination or zeroing procedure consisted of measurement of high-purity synthetic air. Inlet material and temperature were Teflon (PFA) at 40°C. The trapping materials were Tenax TA and Carboxpack X. The ozone scrubber consisted of the addition of 0.6 ppm nitrogen monoxide. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[36] Further details are as follows: This system is composed of a gas chromatograph (GC 8000, Fisons Instruments, Mainz, Germany) equipped with a flame ionization detection (FID) system (MD 800, Fisons Instruments), a thermal desorption device (Aerotrap 6000, Tekmar, Cincinnati, OH, USA), and a cryofocus module (Cryo 820, Fisons Instruments). The VOCs are sampled in the Aerotrap 6000 on a glass tube with 50 mg Tenax TA (60–80 mesh, Macherey-Nagel, Dueren, Germany) and 150 mg Carboxpack X (20–40 mesh, Supelco, Bellefonte, PA, USA) at 30°C. Sampling was done at a flow rate of 50 ml min⁻¹ (at -30°C) for 10 min (500 ml sample). The desorbed VOCs are refocused twice and transferred into the GC (chromatographic column Optima-5-MS, 30 m x 0.25 mm I.D., 0.5 µm film thickness, Macherey-Nagel). Compound separation on the column is aided with a temperature program. The initial temperature of the GC oven is held at 40°C for 3 min and then ramped to 160°C at a rate of 15°C min⁻¹. Helium is used as carrier gas at a flow rate of 2.1 ml min⁻¹. The system was calibrated with a certified 50 compound standard mixture of OVOC in nitrogen (AiR Env., Inc.). OVOC mixing ratios in this standard mixture ranged from 50 to 1000 ppbv, which were dynamically diluted for calibration. Calibrations and zero air measurements were performed both under dry and humid conditions without observable effects of the humidity.

2.3.7. Forschungszentrum Jülich–Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) PTR-MS

[37] The technique used was PTR-MS. The limit of detection was 20–400 pptv and was compound-dependent.

The measurement frequency was 13 min. Background signal determination or zeroing procedure consisted of dry high-purity synthetic air. Inlet material and temperature were Teflon (PFA, 4 m I.D. 4 mm) and 50°C, respectively. Typical applications were ground-based measurements and simulation chamber measurements. The calibration procedure consisted of a diffusion source operated in the low ppb mixing ratio range. An outside air standard was routinely measured by the PTR-MS to check for constant operating conditions during the intercomparison campaign.

[38] Further details are as follows: This instrument is a commercially available high-sensitivity proton transfer reaction mass spectrometer (PTR-MS) manufactured by IONICON (Innsbruck, Austria). The technique is extensively described in the literature [e.g., *Lindinger et al.*, 1998]. Here we refer only to some important aspects. In a drift tube held at an E/N ratio of 124 Td (E electric field strength, N buffer gas number density, 1 Td = 10^{-17} cm² V molecule⁻¹), chemical ionization of VOCs is achieved by proton transfer as described under instrument D above. The protonation of VOCs often result in $(M + 1)$ - m/z -signals (M being the molecular mass of the VOC), although for some compounds fragmentation occurs in the drift tube. Fragmentation sometimes enlarges the number of ions and may interfere with the single compound quantification. We therefore evaluated only m/z -signals with little or no interference from other compounds present in the VOC mix. The following compounds were measured: 1-butanol, benzaldehyde, hexanal, 1-propanol, 3-methyl-2-buten-2-ol, acetone, acetic acid methyl ester, methanol, toluene, and the sum of methacrolein and methyl vinyl ketone (compounds with the same molecular mass often cannot be distinguished in the PTR-MS and are measured as a sum signal). A calibration of the PTR-MS was carried out by means of a diffusion source operated in the low ppb mixing ratio range. All data signals were background corrected against dry synthetic air. An outside air standard was routinely measured by the PTR-MS to check for constant operating conditions during the calibration and the intercomparison campaign. The sampling flow rate was 400 ml (STP) min⁻¹.

2.3.8. Forschungszentrum Jülich–Institute for Chemistry and Dynamics of the Geosphere (FZJ-IGC) PerkinElmer GC-MS

[39] The technique used was GC-FID. The limit of detection ranged from 10 ppt (toluene) to 200 ppt (methanol). The measurement frequency was 30 min sampling every 50 min. Background signal determination or zeroing procedure consisted of measuring high-purity synthetic air. Inlet material and temperature were Silcosteel[®] at 50°C. Trapping materials were Tenax TA and Carbopack X. The ozone scrubber consisted of the addition of nitric oxide at 0.6 ppm. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[40] Further details are as follows: This system consisted of a dual-column gas chromatograph (Autosystem XL, PerkinElmer, USA) equipped with two flame ionization detectors, a cryofocus module (Automatic thermal desorber ATD 400, PerkinElmer, USA), and a mass spectrometer (PerkinElmer Turbomass E8411001). All transfer lines were made of Silcosteel[®]. Sampling was done at a flow rate of 50 ml min⁻¹ (at -30°C) for 30 min (1500 ml sample).

Water was removed by a cold trap (Silcosteel[®] tube, length 600 mm × 4 mm i.d.) at 223 K. OVOCs were trapped at 243 K in a narrow glass tube filled with 36 mg Carbopack X and 18 mg Tenax TA. After desorption at 523 K, the sample was transferred onto a DB5 column (60 m × 0.32 mm i.d., 0.25 μm film thickness, 4 ml min⁻¹ flow rate). Compounds eluting from the DB5 column within the first 13 min were directed to a PORABOND Q column (50 m × 0.53 mm i.d., film thickness 10 μm, 4 ml min⁻¹ flow rate) by means of a Deans' switch. Later eluting compounds were transferred to a second FID and to the mass spectrometer. Helium was used as carrier gas. The GC oven had an initial temperature of 328 K which was ramped at 3 K min⁻¹ to 493 K. The system was calibrated with a certified 50 compound standard mixture of OVOCs in nitrogen (AiR Env., Inc., USA). OVOC mixing ratios in this standard mixture ranged from 50 to 1000 ppbv which were dynamically diluted for calibration. Losses of OVOCs in the cold trap were observed at zero humidity. To cope this problem, a small amount of humidity was added upstream of the cold trap all the time together with the flow of NO for ozone titration.

2.3.9. Institut für Troposphärenforschung (IFT) HPLC-TSP (Thermospray)

[41] The technique used was HPLC. The limit of detection was dependent on compound and sampling volume, during the OVOC campaign: 30 ppt for formaldehyde, acetaldehyde and acetone; 50 ppt for butanal, hexanal and benzaldehyde; and 100 ppt for methacrolein. The measurement frequency was 60 min, typically 60–180 min. Background signal determination or zeroing procedure was as follows: During every sampling period one tube was analyzed as field blank (chamber air). Inlet material and temperature were 2 m 1/4" PTFE at room temperature. Typical applications were ground-based measurements. The calibration procedure consisted of in-house liquid DNPH standards.

[42] Further details are as follows: The sampling of carbonyl compounds was performed by using custom in-house prepared glass cartridges (100 × 10 mm i.d.) filled with approximately 1 g silica gel (Merck, Darmstadt, 125–200 μm sphere diameter) spiked with phosphoric acid and 2, 4-dinitrophenylhydrazine (DNPH) [Müller, 1997]. The collection of the carbonyl compounds was carried out by an automated 25 channel sampler developed at the Leibniz-Institut für Troposphärenforschung (IfT). At the sampler inlet a copper tube coil impregnated with potassium iodide (KI) was used as an ozone scrubber (Cu-tube: 1 m × 4 mm i.d.) to prevent a possible ozone influence [Arnts and Tejada, 1989] on the measurements. A quartz fiber particle filter was installed in front of the valve unit to prevent contamination of the valves. Every glass cartridge was located between two stainless steel valves. The airflow was regulated by an MKS mass flow controller at 2 l min⁻¹. All sampling parameters were controlled and recorded by a LabVIEW[®] program.

[43] The separation was carried out at 45°C in a Thermoquest AS3000. The detector was a UV3000HR. Carbonyl compounds were analyzed at 360 and 380 nm, respectively. At a flow rate of 1.5 ml min⁻¹ a ternary gradient of acetonitrile: water: tetrahydrofuran was used in a WATERS RP18 column (300 × 3.9 mm, 4 μm, 60 Å). Calibration was performed using three in-house prepared cross-calibrated

gravimetric standards (liquid phase) which contained a total of 29 compounds.

2.3.10. Institute for Meteorology and Climate Research (IMK-IFU) BrukerFranzen GC-MS

[44] The technique used was GC-MS. The limit of detection was 0.18 ppb. The measurement frequency was 25 min. Background signal determination or zeroing procedure consisted of chamber air samples collected prior to the injections of the target compounds. Inlet material and temperature were Teflon and ambient. Trapping materials were Tenax TA and Carbotrap X. There was no ozone scrubber. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted calibration mixture using a certified Δ^2 -carene gas mixture and diffusion source.

[45] Further details are as follows: This system is a coupled thermodesorption GC with mass selective (MS) detection (Quadrupole, TD-GC-MS EM 640, Bruker). Pre-concentration was accomplished using a mixed bed trap filled with 100 mg TENAX[®] in a deactivated glass tube followed by 100 mg Carbotrap X. The total sample volume collected, at a flow rate of flow rate of 170 ml min⁻¹, was 2.5–10 L, depending on the expected mixing ratio range. After a 10 s purge (for oxygen and water) with He at a flow rate of 50 ml min⁻¹, analysis commenced with a desorption cycle (4 ml min⁻¹ flow (He), 260°C, 60 s). The chromatographic conditions were as follows: Oven initial temperature was 40°C for 4 min, 10.0°C min⁻¹ to 220°C, 20.0°C min⁻¹ to 260°C, held for 1 min (total run time was 25 min). Column was HP-5MS, 30 m, and 500 hPa. The MS was operated in two modes: (1) total ion chromatogram (TIC) 40 to 220 u and (2) single ion monitoring (SIM) with the main mass of the target compound. Calibration (internal standardization) was performed with a commercially available gas standard containing Δ^2 -carene (SAID, Austria) as well as with in-house prepared standards by the diffusion technique [Schnitzler *et al.*, 2004]. Liquid standards were placed into small glass vials (2 ml) sealed by a Teflon coated septum. Diffusion of compounds to air was achieved by puncturing the septum with uncoated silica glass capillaries (i.d., 0.1 mm; length depends on volatility, 2–5 cm). These vials were placed into a diffusion system for preparing gas standards (Kintec, AeroLaser, Garmisch-Partenkirchen, Germany). The weight of the vessels was determined monthly and the observed weight loss was used to calculate the gas concentrations of the target compounds. For calibration, the outlet gas flow of the diffusion system was diluted 1:200 with purified air (Aadco 737, Aadco, Cleves, Ohio, U.S.).

2.3.11. University of Bremen (U-BREM) Catalytic Converter–Hantzsch

[46] The technique consisted of a selective catalytic converter followed by Hantzsch reaction conversion of formaldehyde with subsequent semicontinuous detection of pyridine product via photometry. The limit of detection was 0.1 ppb methanol for 1 min average. The measurement frequency was variable; see below. Background signal determination or zeroing procedure consisted of zero air. Inlet material and temperature were glass/PFA Teflon and SS for converter and cooler. Typical applications were ground-based measurements. The calibration procedure

consisted of gas phase formaldehyde from permeation source.

[47] Further details are as follows: The selective catalytic converter coupled formaldehyde detector is a new measurement technique for atmospheric methanol measurements [Solomon *et al.*, 2005]. The air sample is pumped at a constant flow rate of 1.7 L min⁻¹ using a Teflon-coated pump (KNF Model N86 KTDC B) into one of two pathways using a three-way PFA Teflon valve (Metron Technologies, Germany); one stream passes through a heated, chemically selective catalyst, which converts the methanol to formaldehyde for semicontinuous measurement of methanol plus formaldehyde [Solomon *et al.*, 2005]; the alternate stream bypasses the catalyst for formaldehyde-only analysis. In either case formaldehyde was detected with a commercial, continuous flow analysis system (Methanalyser, Alpha Omega Power Technologies, Model MA-100) by subsampling at 1.5 L min⁻¹ to the Nafion diffusion scrubber inside the methanalyzer to a counter flow of water. The aqueous formaldehyde is then reacted with NH₄⁺ and acetyl acetone (Hantzsch reaction) inside the liquid reactor forming the fluorescent product 3, 5-diacetyl-1, 4-dihydrolutidine (DDL). Gas phase calibration to check the response of the methanalyzer to formaldehyde was performed using a KIN-TEK (LaMarque, Texas, USA) gas standard generator and the methanol response (conversion efficiency) was assessed by diluting a 20.4 μ mol mol⁻¹ certified methanol standard in N₂ (Messer Griesheim, Germany). Optimal methanol to formaldehyde conversion (>95% efficiency) occurred at a catalyst housing temperature of 345°C and an estimated sample-air/catalyst contact time of <0.2 s. The output of the methanalyzer instrument was collected using a PCMCIA data collection card (NI DAQ 6024E, National Instruments Inc.). During all days, the instrument measured continuously and data were averaged into 2-min intervals. Within 1 h the sum of methanol and formaldehyde was observed for 40 min, then formaldehyde alone for 20 min.

2.3.12. University of Bristol (U-BRIS) Modified Adsorption/Desorption System (MADS-GCMS)

[48] The technique used was GC-MS. The limit of detection was 1–800 pptv and was compound-specific. The measurement frequency was 45 min. Background signal determination or zeroing procedure consisted of sampling of zero air from catalytic converter system. Inlet material and temperature were PFA Teflon and room temperature, respectively. The trapping materials were HiSiv 3000 and HayeSep D. There was no ozone scrubber. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[49] Further details are as follows: The Bristol MADS (Modified Adsorption/Desorption System) instrument is a dual trap preconcentration unit developed in house and utilizes an Agilent 6890 GC and 5973 MS detector. The inlet is composed of four valves (Valco) with purged housings maintained at 70°C. Samples are drawn through the system at 25 ml min⁻¹ using a double-chamber diaphragm pump (KNF) and a sample size of either 150 or 300 ml is obtained. After sampling, the trap is flushed with ultraclean, dry helium for 5 min at 10 ml min⁻¹ in the same direction as sample collection to remove residual water from

the trap (15 mg of HiSiv 3000, UOP). The sample is then desorbed by heating to 330°C for 10 min with 10 ml min⁻¹ of helium counter-purging the sample onto a cooled refocusing microtrap. The microtrap contains HayeSep D (15 mg) held at -30°C using two three-stage Peltier units (Thermo Electric Devices) with air cooled heat sinks. The microtrap is then counter-purged and the sample transferred directly to a GC column by resistively heating to 140°C in 3 s and holding for 30 s. GC analysis is carried out using a PoraBOND U column (Varian, 25 m, 0.32 mm i.d., 7 µm film) with a flow rate of 2 ml/min with detection utilizing the SIM capability of the MS. The column temperature is held at 40°C for 12 min to allow residual water to pass into the MS and be pumped away. The oven is ramped rapidly at 50°C/min to 80°C, then reduced to 10°C/min up to 140°C where it is held isothermal for 3 min. A further ramp at 10°C to 200°C and then up to 220°C at a rate of 20°C/min is performed with a final isothermal time of 3.6 min. A 250 µl loop enables the injection of aliquots of high concentrations (≈500 ppb) of an OVOC standard from a cylinder (AiR, Env, Inc., Denver CO) into a zero air stream. Air samples are calibrated by obtaining a ratio to bracketing standard samples. Standard is injected onto the HiSiv trap using wet zero air obtained from a zero air generator that cleans the air with a hot (450°C) palladium catalyst. System blanks, sampling zero air, are also performed regularly to allow subtraction of those compounds that appear to be present as contamination in the system, acetaldehyde, acetone and benzene being the main compounds.

2.3.13. University of Innsbruck (U-INNS) PTR-MS

[50] The technique used was PTR-MS. The limit of detection was 0.03–0.44 ppbv, depending upon compound. The measurement frequency was 2 s per compound every 75 s. Background signal determination or zeroing procedure consisted of periodic diversion of the inlet flow through a VOC scrubber (platinum coated quartz wool, T = 350°C). Inlet material and temperature were Teflon[®] PFA and Silcosteel[®] and 60°C, respectively. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[51] Further details are as follows: A commercial PTR-MS instrument (PTRMS-FDT-s, Ionicon Analytik GmbH, Innsbruck, Austria) was interfaced to the sampling manifold through a 2 m long Teflon[®] PFA tube (1/8" OD) pumped at a flow rate of 0.25 l min⁻¹ (STP). A flow of ≈150 STP cm³ min⁻¹ was branched off to the inlet of the PTR-MS instrument, which consisted of a 1 m long pressure-controlled Silcosteel[®] tube (1/16" OD). An effective sample flow of ≈20 ml min⁻¹ (STP) was fed to the PTR-MS drift tube, with the overflow being discarded. All inlet lines were heated to 60°C. To determine the instrumental background signals the sample flow was periodically diverted through a VOC scrubber (platinum coated quartz wool, T = 350°C) capable of removing VOCs with >99.9% efficiency.

[52] At PTR-MS standard operation conditions (E/N = 120–140 Td) some of the OVOC intercomparison target molecules (e.g., ethanol) undergo fragmentation upon protonation. The Innsbruck PTR-MS instrument was thus operated at E/N ~ 75 Td with H₃O⁺(H₂O)_{n=0,1} being the primary chemical ionization reagent ions. The various implications of nonstandard PTR-MS operation are described in

detail by *de Gouw et al.* [2003a] and *Hewitt et al.* [2003]. The PTR-MS was run in the selected ion monitoring (SIM) mode with a single ion dwell time of 2 s and a total SIM cycle time of 75 s.

[53] The Innsbruck PTR-MS was calibrated on site using a calibration gas standard (Air Env., Denver, CO) containing ~1 ppmv of methanol, acetaldehyde, ethanol, acetone, and toluene, respectively. The standard was dynamically diluted to ppb levels with dry and humidified zero air. The accuracy of the standard was ±5% for the oxygenates and ±3% for toluene. A multipoint calibration was performed on the first day of experiments. Within-run precision and day-to-day precision were calculated and varied with individual species, e.g., ±4%/±3% for methanol, ±4%/±2% for acetaldehyde, ±7%/±20% for ethanol, ±2%/±2% for acetone, and ±3%/±6% for toluene. The values given for the accuracy and precision in Table 2 are thus an oversimplification.

2.3.14. University of Leicester (U-LEIC)

PTR-TOF-MS

[54] The technique used was chemical ionization reaction time-of-flight mass spectrometry (CIR-TOF-MS), operating in proton transfer reaction mode (i.e., PTR-TOF-MS). The limit of detection was compound-specific, but typically ~4–26 ppbV min⁻¹ [see *Wyche et al.*, 2005]. The measurement frequency was 1 min. Background signal determination or zeroing procedure consisted of chamber air; when conducting observations of ambient air, an instrument baseline is typically obtained at regular intervals during measurement by passing the sample gas first through a hydrocarbon trap to filter out the trace species of interest. Inlet material and temperature were 1/4" diameter Teflon tube at 40 (±1)°C. Typical applications were atmospheric monitoring of gas phase organic compounds in urban and remote locations and smog chamber experiments investigating secondary organic aerosol formation mechanisms. Nonatmospheric applications include use in medical and forensic sciences. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[55] Further details are as follows: The chemical ionization reaction mass spectrometer used in this work has been described in detail elsewhere [Blake *et al.*, 2004; Wyche *et al.*, 2005, 2007]. The basic elements of the University of Leicester CIR-TOF-MS are an ion source, a drift tube, an ion transfer region, and a reflectron time-of-flight mass spectrometer. The ion source and drift tube assembly is similar to that described recently by *Hanson et al.* [2003]. Briefly, the ion source uses a 1.2 mCi, strip of ²⁴¹Am in a stainless steel cylinder. The alpha particles emitted are employed to generate an excess of reagent ions. In this instance water vapor was ionized to produce hydronium (H₃O⁺) ions. The ion source is held at a high positive potential of about 2.7 kV relative to ground. The drift tube is 10 cm in length and constructed of stainless steel guide plates separated by static dissipative Teflon cylinders, with Viton O rings between the two. The sample to be analyzed is continuously injected at a flow rate of 275 ml min⁻¹ (STP) into the upstream end of the drift tube, which is typically maintained at a constant pressure of ~8 mbar. Positive reagent ions from the ion source are drawn by a voltage gradient into the drift tube, in which ionization of the sample occurs. In the case of hydronium, ionization of the sample is facilitated by proton exchange reaction as the

gas mixture proceeds along the drift tube. Throughout the OVOC intercomparison the drift tube was typically operated with an electric field to gas number density ratio (E/N) of around 150 Td. The CIR(PTR)-TOF-MS was calibrated using three separate multicomponent gas mixtures (AiR, Env., Inc., Denver, CO) containing compounds of known concentration. Two separate phases of calibration were conducted, first during and then following the intercomparison, from which an instrument sensitivity was determined for each of the target OVOCs. However, as no calibration standard was available for acetic acid methyl ester, a calculated sensitivity was employed.

2.3.15. University of York (U-YORK) PerkinElmer GC-FID

[56] The technique used was GC-2 $\times$ FID. The limit of detection was species-specific, ranging from 1 pptv for NMHCs and acetaldehyde to 30 pptv for methanol. The measurement frequency was 1/h. Background signal determination or zeroing procedure was as follows: High-purity 6.0 N₂ gas was passed through a heated metal getter catalyst, and then humidified to ambient level by passing over the headspace of distilled water. Inlet material and temperature were $\frac{1}{4}$ " Teflon tubing heated to 55°C. Trapping materials were Carboxen and Carbotrap B. There was no ozone scrubber. Typical applications were ground-based measurements. The calibration procedure consisted of a dynamically diluted certified calibration mixture.

[57] Further details are as follows: Samples were dried prior to analysis by passing through a glass condensation tube, which was immersed in a 50:50 ethylene glycol: water mixture held at -30°C . The air from the chamber was continually flushed through all of the tubing in the system, including the condenser. The dried sample was passed onto a multibed, Peltier-cooled (-20°C), adsorbent trap containing Carboxen 1000 and Carboxen B, at a flow rate of 100 ml min⁻¹ for ten minutes (one liter sample). After sampling, the temperature of the adsorbent trap was maintained at -20°C for three minutes, during which the trap was flushed with the carrier gas, helium. This served to remove methane from the trap, which would otherwise obscure the peaks of interest. The trap was then heated at approximately 16°C/s to a final temperature of 350°C. The resultant collected compounds were injected into the GC. The mixture was split in an approximately 50:50 ratio between a 50 m aluminum oxide (Al₂O₃) porous layer open tubular (PLOT) column (Na₂SO₄ deactivation) and two 10 m LOWOX columns in series. Eluent from each column was detected by two independent FIDs [Hopkins *et al.*, 2003]. The oven program after thermal desorption was as follows: 40°C for 3 min then heated at a rate of 12°C/min to 110°C, then 7°C/min to 200°C, then isothermal at 200°C for 20 min before cooling back to 40°C for the next sample. A constant carrier gas He flow rate of ~ 15 mL/min through each column was used, with equality in flow through the shorter LOWOX column maintained through use a 50 μm restrictor at the head of that column.

[58] Calibration of the system was performed before and after the series of experiments using a 74-component mixture of NMHCs (including n-butane and toluene, supplied by AiR Env., Inc., Denver, CO) at the low parts per billion level. No significant change in detector response was observed. Calibration of OVOCs was performed after the

series of experiments using a 14-component mixture (supplied by AiR Env., Inc., Denver, CO) containing all of the compounds that had been injected into the chamber during this intercomparison. The OVOC standard (initial concentration ~ 500 ppb) was dynamically diluted using a 3–5 ml min⁻¹ flow rate of OVOC standard into a high flow (100–300 ml min⁻¹) of humidified nitrogen. These were thoroughly mixed then drawn through the condenser at a flow rate of 100 ml min⁻¹ using a vacuum pump. The excess was vented away. Total uncertainties in the measurement were generally less than 10%, except for ethanol, propanol and butanol which were all higher (23%, 32%, and 17% respectively) because of variability in response during calibration.

3. Results

3.1. Overview of Analysis

[59] Fourteen compounds were intercompared with 15 different instruments on three separate days in this study. The compounds are listed in Table 1 along with their identifier letter designation. In addition to individual compounds, the sum (MACR+MVK) is identified as well (letter n) since the PTR-MS instruments cannot distinguish between these compounds. These identifiers will be used throughout sections 3 and 4.

[60] The following procedure was applied to all the different data sets:

[61] 1. The calculated data (1 min time step) were averaged on measurement intervals of each instrument. If the data were recorded at shorter sampling intervals than one minute, the calculated data were linearly interpolated to assign a calculated value to each measured data point.

[62] 2. The Pearson correlation coefficient, r , was calculated; the square of the correlation coefficient, r^2 , denotes the portion of the measured values that changes with the calculated values. N represents the total number of measurements.

[63] 3. The data were fit to a straight line: $y = a + bx$. The error weighted fit, using errors in both coordinates, estimates a slope and an intercept, and the respective errors $\sigma(a)$ and $\sigma(b)$. The errors are calculated from the error propagation of the input data, mainly the measured data errors. For further discussion please see Press *et al.* [1992] or Brauers and Finlayson-Pitts [1997]. χ^2 and q are calculated as well to gauge the goodness of fit of the model approximation to the data.

[64] 4. The slope forced through the origin, $b(0)$, is calculated by the unweighted ratio of averaged x and y values, x_m and y_m . The error of the slope comes from the scatter around the calculated line.

[65] Figure 4 shows an example for one compound (butanal) and one instrument (GC-MS, FZJ, instrument H) of how the data were processed. The calculated values are plotted on the x axis and the reported values are plotted on the y axis. The parameters a , b , $\sigma(a)$, $\sigma(b)$, χ^2 , and q are given for the fit described under item 3 above. A full suite of 141 viewgraphs like Figure 4 is available as auxiliary material¹ (Figure S1). Throughout Figures 4 and S1, day 2

¹Auxiliary materials are available in the HTML. doi:10.1029/2008JD009865.

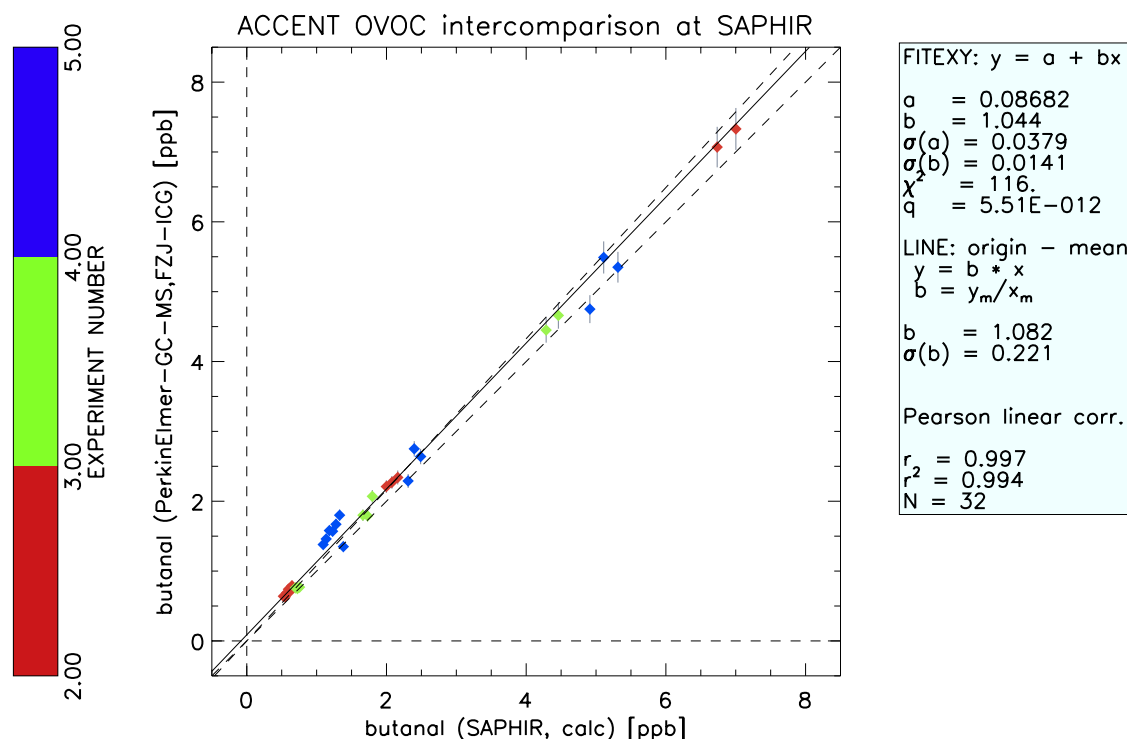


Figure 4. Example showing statistical analysis of data. The calculated data (for butanal in this case) are plotted against the data provided by instrument H. The slope of the fitted line is shown weighted by the errors in both coordinates. Also shown are the Pearson linear correlation coefficients.

is color coded red, day 3 is color coded green and day 4 is color coded blue. Table S1 gives a summary of how well each instrument performed as determined by a comparison with the calculated values. Listed in Table S1 are the parameters r , $b(0)$ (slope forced through origin), $\sigma(b(0))$, a , $\sigma(a)$, b (slope), and $\sigma(b)$. The original and evaluated data are available from the SAPHIR archive through the Eurochamp web site at <http://www.eurochamp.org>.

[66] Figures 5–7 are general overview graphs which provide a summary of the overall performance of participating laboratories. Figure 5 shows the correlation coefficient (left axis, blue symbols) and number of data points (right axis, red symbols, log axis) for each experimental data set (total = 141). In Figure 5 (top), the results are displayed versus compound (a–o in Table 1; note also that the sum MVK + MACR is identified) for each instrument and, in Figure 5 (bottom), results are shown versus instrument (A–O in Table 2) for each compound. Each group's measurements showed a significant correlation with the calculated values. For some instruments, e.g., instrument O, a very strong (r near unity) correlation was found for each compound measured. Please refer to the auxiliary material for additional details.

[67] Figure 6 shows the error-weighted slope (left log axis, blue symbols) and intercept (right linear axis, red symbols) for each experimental data set (total = 141). Similar to Figure 5, in Figure 6 (top) the results are displayed versus compound (a–o in Table 1) for each instrument, and in Figure 6 (bottom) results are shown versus instrument (A–O in Table 2) for each compound. Some instruments measured all or most of the full suite of compounds. For example, instruments L (U-BRIS MADS-

GCMS) and O (U-YORK PerkinElmer-DC-GC-FID) measured every individual compound and instrument M (U-INNS PTR-MS) measured all compounds but without resolving methacrolein and methyl vinyl ketone individually; The U-BREM catalytic converter–Hantzsch method (K) measured only methanol. The data for each instrument will be discussed in more detail below.

[68] Figures 5 and 6 and Table S1 will be referred to periodically in the discussions below about individual instrument results.

3.2. Individual Instruments

3.2.1. Fundacion Centro de Estudios Ambientales del Mediterraneo (CEAM) GC-FID

[69] The CEAM measurements matched very well with the calculated values for hexanal (slope = 1.06) and with an excellent correlation ($r = 0.997$). The slopes for benzaldehyde, butanal, and toluene were 0.83, 0.80, and 0.71, respectively with correlation coefficients all greater than 0.9. For the remainder of the species measured, the CEAM results were significantly low compared to reference values. Methacrolein and methyl vinyl ketone showed the furthest deviation from calculated values with slopes of 0.02 and 0.33, respectively. This low bias was not unexpected on the basis of the investigator's previous experience with yields from the derivatization with PFBHA. This is also documented in previous studies [Reisen *et al.*, 2003; Temime *et al.*, 2007]. However, one would assume that the yield could be characterized by using high-quality calibration standards. The inadequacy of the methodology to sample small carbonyl compounds (formaldehyde, acetaldehyde and acetone) due to strong backgrounds coming from the

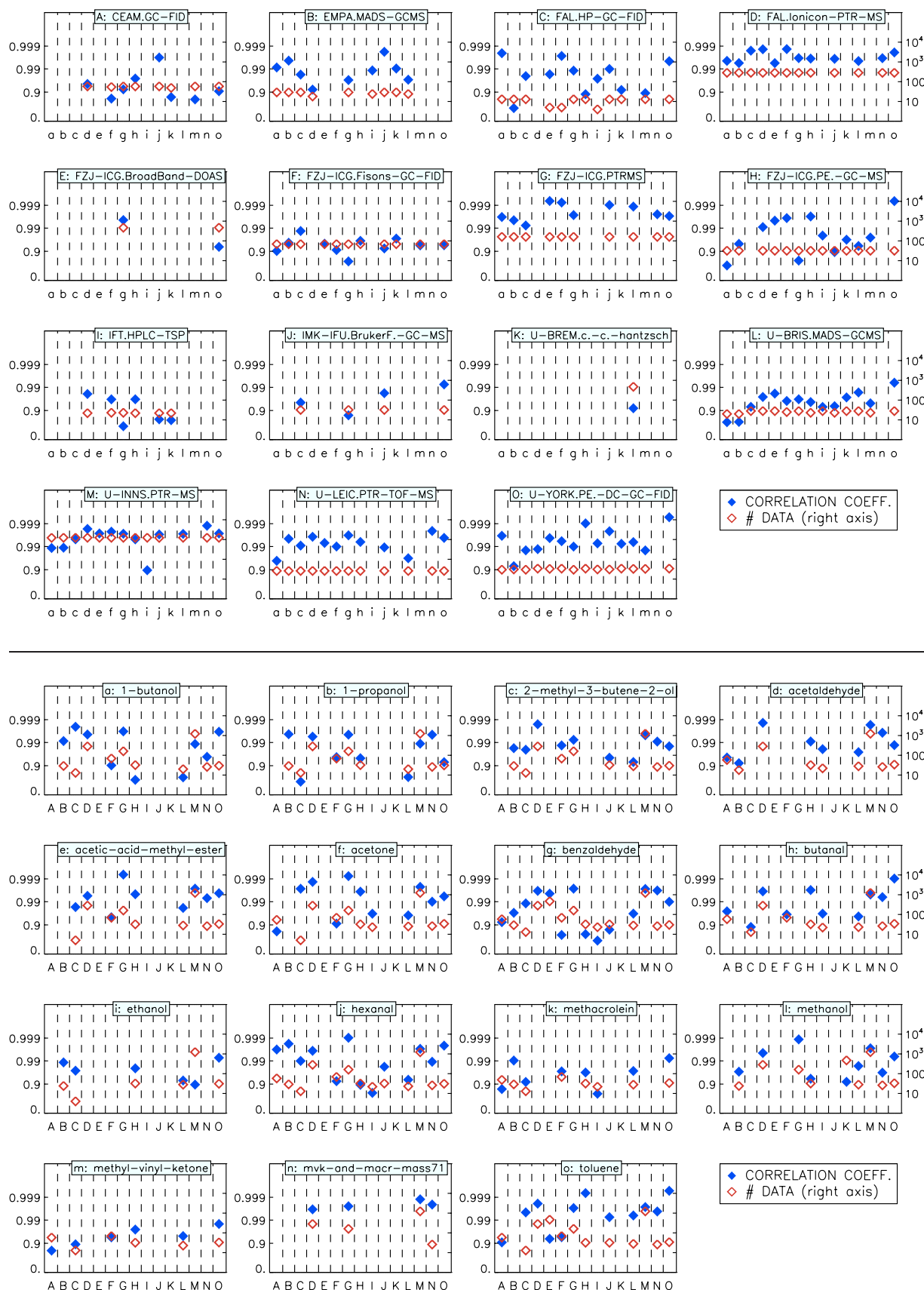


Figure 5. Correlation coefficient (left axis, blue symbols) and number of data points (right axis, red symbols, log axis) for each experimental data set (total = 141). Displayed versus (top) compound (a–o in Table 1) and (bottom) instrument (A–O in Table 2).

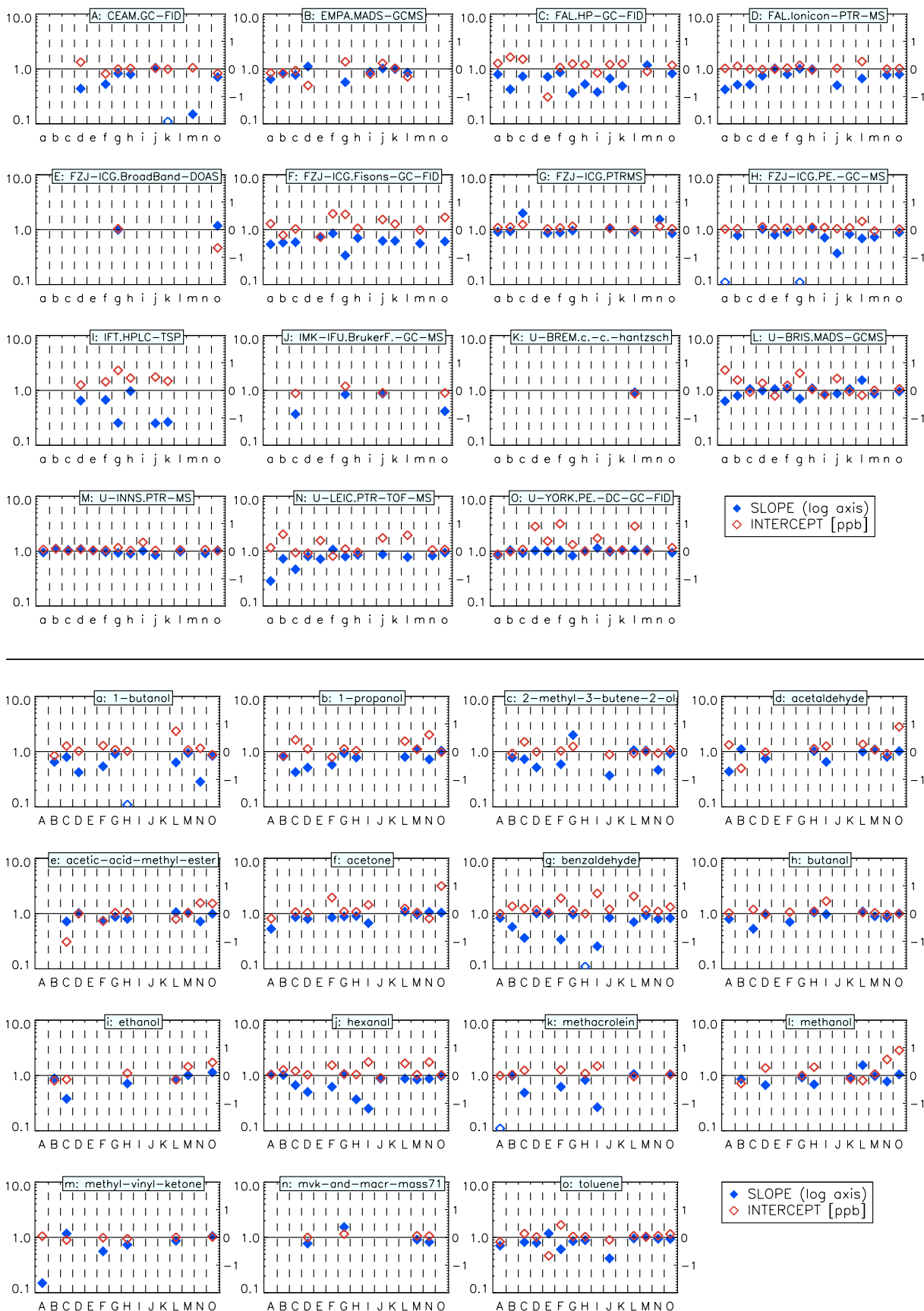


Figure 6. Slope (left log axis, blue symbols) and intercept (right linear axis, red symbols) for each experimental data set (total = 141). Displayed versus (top) compound (a–o in Table 2) and (bottom) instrument (A–O in Table 2).

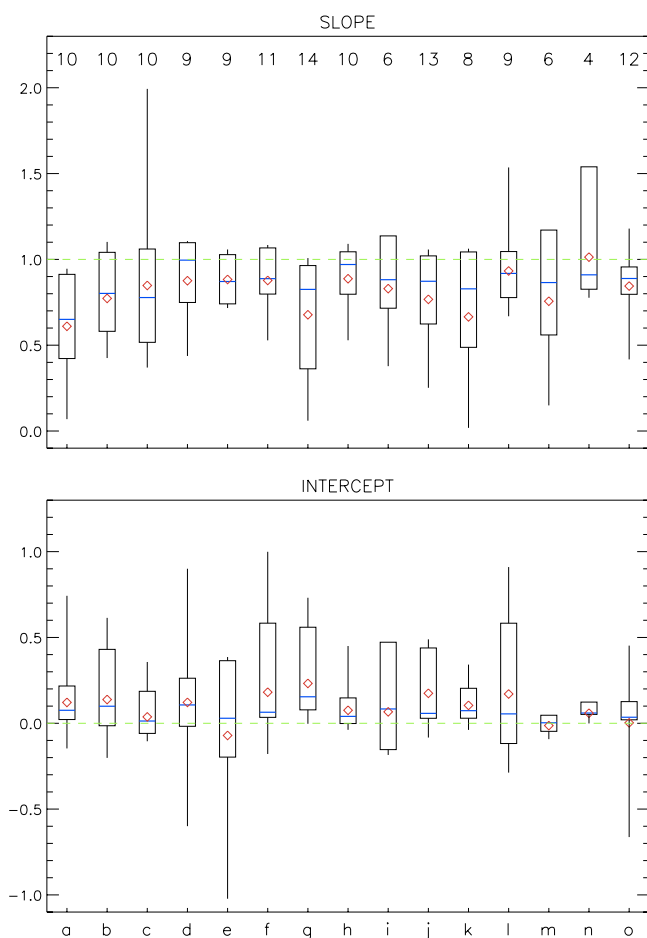


Figure 7. Box and whisker plot of the mean results for the (top) slopes and (bottom) intercepts for each compound (averaged over all groups) denoted by letters a–o which are identified in Table 1. The box whisker symbol denotes 0.05, 0.25, 0.5, 0.75, and 0.95 percentiles; the red diamond symbol indicates the mean. The numeric value in Figure 7 (top) indicates the number of instruments that measured each individual compound.

derivatizing agent has also been reported in the literature [Reisen *et al.*, 2003].

[70] Correlation for all species measured, including those that presented a low bias, were high as shown in Figure 5. No significant y intercepts were observed indicating no background signal problems. No major effects on the results were revealed with the introduction of water or ozone. As previously stated, the system for active sampling was especially designed for participation in the Intercomparison; there is reasonable confidence that these results could be improved by further optimization of the analytical system and calibration procedures.

3.2.2. Swiss Federal Laboratories for Materials Testing and Research (EMPA) MADS-GC-MS

[71] This instrument measured nine compounds during the intercomparison. Examination of Figure 6 and Table S1 shows that the measurements for compounds other than 1-butanol and benzaldehyde, had slopes that ranged from 0.81 (methanol) to 1.10 (hexanal). 1-butanol and benzaldehyde were species for which the deviation of the measured

slope from the calculated values was the largest with slopes of 0.65 and 0.67 respectively. Correlations for all species measured, including 1-butanol and benzaldehyde were high as shown in Figure 5. Despite the good correlation coefficient, it appears that acetaldehyde presented some measurement problems. For day 2, the y intercept was high (2.9 ppbv) and for days 3 and 4 the y intercepts are negative, possibly indicating a problem with blank subtraction. On day 2, there were problems measuring methanol during the dry conditions. However, it is well known that methanol is often not efficiently transferred through tubing under very dry conditions; this is not a problem for most ambient measurements as atmospheric conditions are rarely as dry as the day 2 conditions (Figure 2). Overall the data are solid. Possible explanations for the 1-butanol and benzaldehyde results include (1) the compounds are being lost before they get to the detector or (2) there is a calibration error. In any case, a number of groups had trouble measuring 1-butanol and benzaldehyde and this is discussed in more detail in section 4 on individual compounds.

3.2.3. Swiss Federal Research Station for Agroecology and Agriculture (FAL) HP-GC-FID

[72] Twelve compounds were reported. This instrument was not fully tested before arriving at Jülich and the investigators were aware that the quality of the measurements was not up to the standard operating procedure level. The results were reported here with that caveat. This technique is capable of providing high-quality data and the intercomparison was used as a test and stepping stone toward that end. A maximum of 13 data points for each compound were reported for the entire 3 day experimental period so the data are quite limited and conclusions based on this small number are not as statistically robust as with other instruments. A low bias, relative to calculated values, was observed for most compounds. This was due, in part, to a flow controller calibration error discovered post mission which resulted in a low bias error of 20%. Close inspection of the results displayed in Figure 6 and Table S1 in the auxiliary material, shows that a number of species including 1-propanol, benzaldehyde, butanal, ethanol, and methacrolein were reported very low compared to reference values (slopes ≤ 0.53). The low bias in these data could be due to inefficient transfer or trapping of the species or a problem with the calibration. There is a good deal of scatter (low r) for 1-propanol ($r = 0.58$) but for the remainder of the compounds, correlations with the calculated values were reasonable ($r > 0.88$), which demonstrated the potential of the instrument for ambient OVOC measurements.

3.2.4. Swiss Federal Research Station for Agroecology and Agriculture (FAL) Ionicon PTR-MS

[73] Twelve compounds were also reported with this instrument. A low bias was observed for a number of compounds, most specifically with methanol, 1-butanol, 1-propanol, 2-methyl-3-butene-2-ol (all alcohols), and hexanal (Figure 6). These compounds plus butanal, acetic acid methyl ester and benzaldehyde were calibrated via theoretical considerations (see discussion under section 2) with a stated accuracy on the order of 50%. The accuracy of the calibrated compounds (determined with gas-phase standards) which include acetaldehyde, acetone, methacrolein and methyl vinyl ketone (mass 71) and toluene, are given in Table 2. Similar to the FAL HP-GC FID results described

above, a systematic deviation was found in the Mass Flow controller of the zero airflow used for calibration after the data were submitted. The readings were too low by 20%. As a consequence, the slopes of the measured versus adjusted concentrations would have to be increased by the same amount. If this is done, all slopes for these calibrated compounds approach unity.

[74] The correlations of the experimental results with the calculated results are excellent for all compounds (Figure 5). This technique is solid and only requires the resolution of some calibration issues.

3.2.5. Forschungszentrum Jülich: Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) Broadband DOAS

[75] This instrument measured two compounds, benzaldehyde and toluene. The DOAS technique is more sensitive for the detection of benzaldehyde and the results compared to calculated values for this compound look very good (see Table S1 in the auxiliary material and Figures 5 and 6). This is a very important finding because it provides a validation for the methodology used to obtain the calculated results because the DOAS results are not dependent on an external calibration. For toluene, the results are in agreement with the calculated values based on the stated precision of the measurement technique for this compound.

3.2.6. Forschungszentrum Jülich: Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) Fisons-GC-FID

[76] The results for this instrument show a low bias compared to the calculated values for each of the eleven measured compounds (Figure 6), with benzaldehyde demonstrating the lowest bias (slope = 0.34). The correlation, r , (Figure 5) is fair for most compounds with benzaldehyde, again, showing the poorest result indicating perhaps an analytical problem with the measurement of this compound. There is high variability in the y intercepts, which may point to a problem with instrument blanks. On day 4, ozone appears to have caused an increase in the toluene background signal.

[77] The systematically low results are difficult to explain. It is possible that the standard used for calibration is in error. However, because all values are low, this is unlikely since all of the compounds in the standard cylinder would have to be systematically biased in the same direction. A more likely possibility is that a systematic bias is present in the analytical or calibration system. One candidate would be bias associated with the dilution of the standard mixture.

3.2.7. Forschungszentrum Jülich: Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) PTRMS

[78] For most compounds, the experimental results (Figures 5 and 6) agree quite well with calculated results. Two measurements show a high bias, 2-methyl-3-buten-2-ol (slope = 1.99) and the combined methyl vinyl ketone and methacrolein measurement (slope = 1.54). It is likely that the observed bias is due to errors in the diffusion source calibration system for these compounds. The correlation was outstanding for each compound measured and was among the best of all instruments that were compared. No significant y intercepts were observed indicating no background signal problems. The results for all three experimental days were generally consistent; no major effects on

the results were revealed with the introduction of water or ozone. Overall, instrument performance was very good.

3.2.8. Forschungszentrum Jülich: Institute for Chemistry and Dynamics of the Geosphere (FZJ-ICG) PerkinElmer-GC-MS

[79] Thirteen compounds were measured with this instrument. Overall, a low bias was observed relative to calculated values. Three compounds had a particularly low bias: 1-butanol (slope = 0.07), benzaldehyde (slope = 0.06) and hexanal (slope = 0.37) (Figure 6 and auxiliary material). The bias in the hexanal results was due primarily to day 4 results for this compound which were lower than days 2 and 3. Relatively poor correlations were observed with 1-butanol and benzaldehyde but the remaining compounds showed very good correlations (Figure 5). For acetone and acetaldehyde, there is a noticeable y intercept value for day 4 which perhaps indicated artifact formation of these compounds in the analytical system possibly associated with the presence of ozone. There are clear analytical issues for the analysis of the lowest vapor pressure compounds (see discussion below).

3.2.9. Institut für Troposphärenforschung (IFT) HPLC-TSP

[80] Six OVOC (carbonyl) compounds were measured with this instrument. It is well known that at relative humidities less than 5% the hydrazone yield for the DNPH-formaldehyde reaction is severely reduced [Gilpin *et al.*, 1997]. Reduced yields have also been documented by the IFT group for other carbonyls. Thus, the day 2 experiments are not expected to yield valid results. Indeed, reported levels for hexanal, benzaldehyde, and methacrolein were significantly lower than calculated results, but surprisingly, acetone and acetaldehyde were not strongly affected. The best agreement with calculated results was for day 3, when humidity was added but no ozone was present. Correlations coefficients were good for days 3 and 4. Larger discrepancies existed for a number of the other species with benzaldehyde, hexanal, and methacrolein showing the poorest agreement with slopes of less than 0.5 for day 4. Although reasons for these discrepancies are not clear, calibration standards, collection efficiency and collection efficiency variability are candidates for further investigation. It has been recommended in the literature [Gilpin *et al.*, 1997; Apel *et al.*, 1998] that certified gas phase standards be used to calibrate cartridge sampling systems. The results may have been markedly better had this been done as the only remaining identified parameter that could cause difficulty under the scenario of using gas-phase standards would be variability in the collection efficiency. All species showed increased y intercepts on day 4 possibly indicating the generation of background counts as a result of the presence of ozone. Butanal agreed well with the calculated measurements for all days (slope = 0.97, r = 0.97).

3.2.10. Institute for Meteorology and Climate Research (IMK-IFU) BrukerFranzen-GC-MS

[81] This instrument measured four compounds during the intercomparison. Measurements of benzaldehyde and hexanal compared well with the calculated values. This is reflected in the r values, 0.84 and 0.98 respectively, and the slopes, 0.85 and 0.87 respectively (Table S1 in the auxiliary material and Figures 5 and 6). However, significant negative y intercept values were observed for these species on day 4,

possibly indicating that the blank (or zero) value was overestimated. 2-methyl-3-butene-2-ol and toluene correlated well with calculated values ($r = 0.95$ and 0.99 respectively) but the slopes were low compared to calculated values, 0.37 and 0.42 , respectively. There are a number of possible reasons for this but the calibration for these compounds is a leading candidate for further inquiry.

3.2.11. University of Bremen (U-BREM) Catalytic Converter–Hantzsch

[82] This instrument measured methanol and formaldehyde (reported as a separate study). A strong correlation was found with the calculated values ($r = 0.92$) and the slope was reflective of good overall agreement (0.93). This indicates that the methanol was efficiently converted to formaldehyde with this system and subsequently quantitatively detected. There is a significant negative y intercept value on day 4, which may be indicative of a blank that is overestimated, resulting in the subtraction of too large a value from the signal. For day 2, which was carried out in dry air and which had the highest chamber methanol values of the 3 days, the results were low compared to calculated values (Figure S1). It is well known that, in the absence of water, methanol can stick to surfaces. This may be the case at these high concentrations. However, this is not a large concern because, except on high-altitude aircraft, these conditions would not be present in the ambient atmosphere. Another possibility is that the limit of efficient conversion of methanol to formaldehyde is being approached at these concentrations although laboratory studies by the investigators have shown that maximum conversion efficiency should be achieved up to approximately 20 ppbv.

3.2.12. University of Bristol (U-BRIS) MADS-GCMS

[83] This instrument measured all 14 compounds. With the exception of 1-butanol and 1-propanol, good correlations (Figure 5) were observed with the calculated values (>0.9). 1-butanol (slope = 0.64), benzaldehyde (slope = 0.70) and methanol (slope = 1.54) showed the highest discrepancies in the observed versus calculated values (Figure 6 and auxiliary material). For the remainder of the compounds, the slopes fell in the range of ($0.8 < \text{slope} < 1.1$). For day 2, a number of species showed a slope different from days 3 and 4. This is likely similar to the case described above; efficient transfer of polar compounds through inlet and analytical systems is difficult under very dry conditions. Acetaldehyde and benzaldehyde have significant y intercepts which are highest during the day 4 experiments. This indicates that the system may have an above zero background for these compounds which may be exacerbated under the influence of ozone. Overall, the system performed solidly during this study.

3.2.13. University of Innsbruck (U-INNS) PTR-MS

[84] This instrument measured all compounds in the chamber but without resolving the isomers methacrolein and methyl vinyl ketone individually. This instrument also recorded the greatest total number of measurements. Excellent correlations were found for all species when compared to calculated values ($r = 0.99$ or better for all compounds except ethanol which was 0.90). Recall from the instrumental discussion that the PTR-MS has to run in the nonstandard mode to measure ethanol. Thus the somewhat reduced performance (compared to the other compounds measured) is not surprising for the analysis of this compound. The

slopes for all compounds reflected very good agreement ranging from 0.84 to 1.10 with calculated values and there was very little error in the slope (Table S1 in the auxiliary material). There were no particular problems in the measurement for any compound in this study; this instrument performed very well. The measurements compared consistently well with calculated values during each of the 3 days with no observed effects from dryness, humidity or ozone. The results from this and other instruments that closely followed the calculated values lends confidence that the calculated values in the chamber are likely quite accurate.

3.2.14. University of Leicester (U-LEIC)

PTR-TOF-MS

[85] This instrument measured 12 species. Excellent correlation with the calculated values was found for all species (>0.96 , Figure 5). Figure 6 and Table S1 (auxiliary material) reveal that 1-butanol (slope = 0.29) and 2-methyl-3-butene-2-ol (0.47) were the species for which the deviations from calculated values were the largest. This has been discussed by the investigators in a previous publication [Wyche *et al.*, 2007]. The authors attributed the deviations to the presence of an unknown loss of these compounds prior to detection. The slopes for all other species fell in the range of 0.72 – 1.07 . 1-propanal, methanol, and hexanal showed significant y intercepts which is indicative of background counts leading to a baseline that is not well characterized for these ions in the spectrometer. 2-methyl-3-butene-2-ol showed an anomalously low slope that remains unexplained (however, see section 4.1 below for a further discussion). Overall performance of the instrument was good and this experiment demonstrated the viability for its use for the measurement of atmospherically relevant VOCs in the future.

3.2.15. University of York (U-YORK)

PerkinElmer-DC-GC-FID

[86] This instrument measured all 14 species. Excellent correlation with all species was observed ($r \geq 0.98$ except for 1-propanol, 0.93). The slopes for all species fall in the range of 0.84 to 1.14 which is very good agreement for this study. There were significant y intercepts for a number of compounds: acetaldehyde (0.9 ppbv), acetone (1.0 ppbv), and methanol (0.9 ppbv) which may be indicative of background counts in the instrument under blank conditions. The investigators note that background zeros are normally assessed as having reached optimal levels on this instrument (and hence subtracted from data) only after at least two weeks of continuous operation, a time period not available for this intercomparison. The remainder of the compounds measured showed very good agreement with the calculated values. Overall the instrument performed well.

4. Discussion

4.1. Individual Compound Analysis

[87] The correlation coefficients for individual compounds are shown in Figure 5 (bottom). The error weighted slope of regression for each individual compound as measured by individual instruments is shown in Figure 6 (bottom); each individual compound is shown as a separate panel with individual instrument measurements identified by a letter (Table 2) on the x axis. These plots are intended to provide a snapshot of the analyses on a compound by

compound basis and to discern if there are trends that distinguish particular compounds. Figure 7 shows a box and whisker plot of the mean results for the slopes and intercepts for each compound (averaged over all groups). The box whisker symbol denotes 0.05, 0.25, 0.5, 0.75, 0.95 percentiles, the red diamond symbol indicates the mean. Except for the combined PTR-MS measurements for methyl vinyl ketone and methacrolein, the average slope for all compounds is less than one. There are a number of possible reasons for this: (1) the sample injection volume was not accurately transferred from the injection port to the chamber; (2) there were losses at the walls of the chamber; (3) there were losses in the transfer manifold; (4) losses occurred between the sample manifold and the detector of instruments; (5) gases used to calibrate instruments were in error and were, on average, higher than the reference values given; or (6) errors occurred in the dilution of calibration gases that lead to, on average, higher than actual concentrations used for the reference calibration. Because of possible reasons 1–3 above, the calculated chamber values may be considered to represent an upper limit of the true values although as discussed below we believe that any OVOC losses, up to the point of the investigators' inlets, are small.

[88] Falling under a slope of 0.80 for the combined, averaged, measurements were a number of compounds: 1-butanol, 1-propanol, benzaldehyde, hexanal, methacrolein, and methyl vinyl ketone. Table 1 shows the vapor pressure for all compounds in this study. It is interesting to note that four of the six compounds with slopes less than 0.8, were the lowest four in vapor pressure. Methacrolein and methyl vinyl ketone were the exceptions. In each case, however, there are instruments that measure values that are equivalent within experimental error to the calculated values (see Figure 6). The reasons for the discrepancies are not entirely clear but we can get some clues by looking at different techniques and approaches. The DOAS measures benzaldehyde and requires no external calibration source; agreement with the calibrated values is very good for this compound which indicates that the calculated chamber values are accurate to within stated errors. It is possible that there could be a loss of some compounds as the chamber air is drawn through the manifold (Figure 1) prior to reaching the instruments. This appears unlikely for benzaldehyde because measurements from U-York (O) and U-INNS (M) which are at the end of the manifold train show good agreement with each other and with the calculated values for this compound (see Table S1 in the auxiliary material and Figure 6). Similarly, good agreement is observed for these instruments and 1-butanol. Since these are the two compounds with the lowest vapor pressures, it seems likely that there are no major issues with the chamber or the manifold. Therefore, we assume that the differences are due to problems experienced with individual instruments in getting the sample air from their respective inlets to their detectors, i.e., an instrument-intrinsic issue.

[89] Individual methyl vinyl ketone and methacrolein measurements were performed only with the GC techniques except for methacrolein which was also measured by the IFT HPLC-TSP technique. Although there were individual instrument measurement issues for these compounds, it is clear from the good results (Figure 6) from other instru-

ments that there are no problems with the calculated values; measurement problems may be attributed to one of the analytical steps, e.g., calibration, transfer through analysis system, or chromatography.

[90] 2-methyl-3-butene-2-ol (MBO) was measured by ten different groups with varying results as seen from the large spread in Figure 7. Some of the problems with quantification we have attributed to probable calibration issues, i.e., instruments D (FAL-PTR-MS), G (FZJ-ICG PTR-MS), and J (IMK-IFU-GC-MS). It has been noted in the literature [Harley *et al.*, 1998] that quantitative analysis of MBO with GC techniques presents a number of challenges. The primary problem is that MBO may be converted to isoprene through dehydration; this is most pronounced under dry conditions. The results obtained in this experiment are surprising in that investigators did not report to the referee any evidence for conversion of MBO to isoprene under any of the conditions experienced in this study. It is possible that some investigators reported the sum of MBO and isoprene as MBO, since there was no isoprene in this experiment. This would not be an option in ambient air because of the simultaneous fluxes of MBO and isoprene present in a forest environment. It is possible that conversion of MBO to isoprene contributed to the low values reported by instrument N (PTR-TOF-MS).

[91] By the metrics employed here, acetaldehyde, acetone, and methanol were measured reasonably well by most groups and the correlation coefficients were generally good. However, background levels that were not sufficiently subtracted were present in some instruments (Figure 6); this problem has the potential to manifest itself as being much more serious at ambient levels approaching 1 ppbv or less, a condition experienced often in clean background air. The PTR-MS instruments did not show this same problem; the error in the slope, $\sigma(b)$ was noticeably lower for the three PTR-MS measurements compared to the GC-based instruments with the exception of instrument A (CEAM GC-FID). This difference is partially but not fully attributable to higher sampling rates leading to increased sampling statistics for the PTR-MS.

4.2. Effect of Humidity and Ozone

[92] Day 2 was carried out with no humidity or ozone, day 3 with added humidity, and day 4 with added humidity and ozone. Thus, day 4 more realistically mimicked ambient atmospheric conditions. In general, the performance of most instruments was fairly consistent throughout the 3 day experiment. As mentioned in section 3, day 2 presented some additional problems with regard to the transfer of OVOC species through analytical systems and into the detector. This is consistent with the notion that water helps to passivate inlet tubing, thereby promoting efficient transfer of polar compounds. These conditions also present problems with hydrazone formation in derivatization techniques. Day 3 (humidity added) yielded few surprises but showed, again, that for some analytical systems water is a necessary requirement for quantitative measurements. The implications for this are not grave under most experimental conditions that would be experienced by the groups that participated in this study; except for aircraft measurements at high altitude there will almost always be sufficient water in the air to effectively passivate inlet tubing. The results for

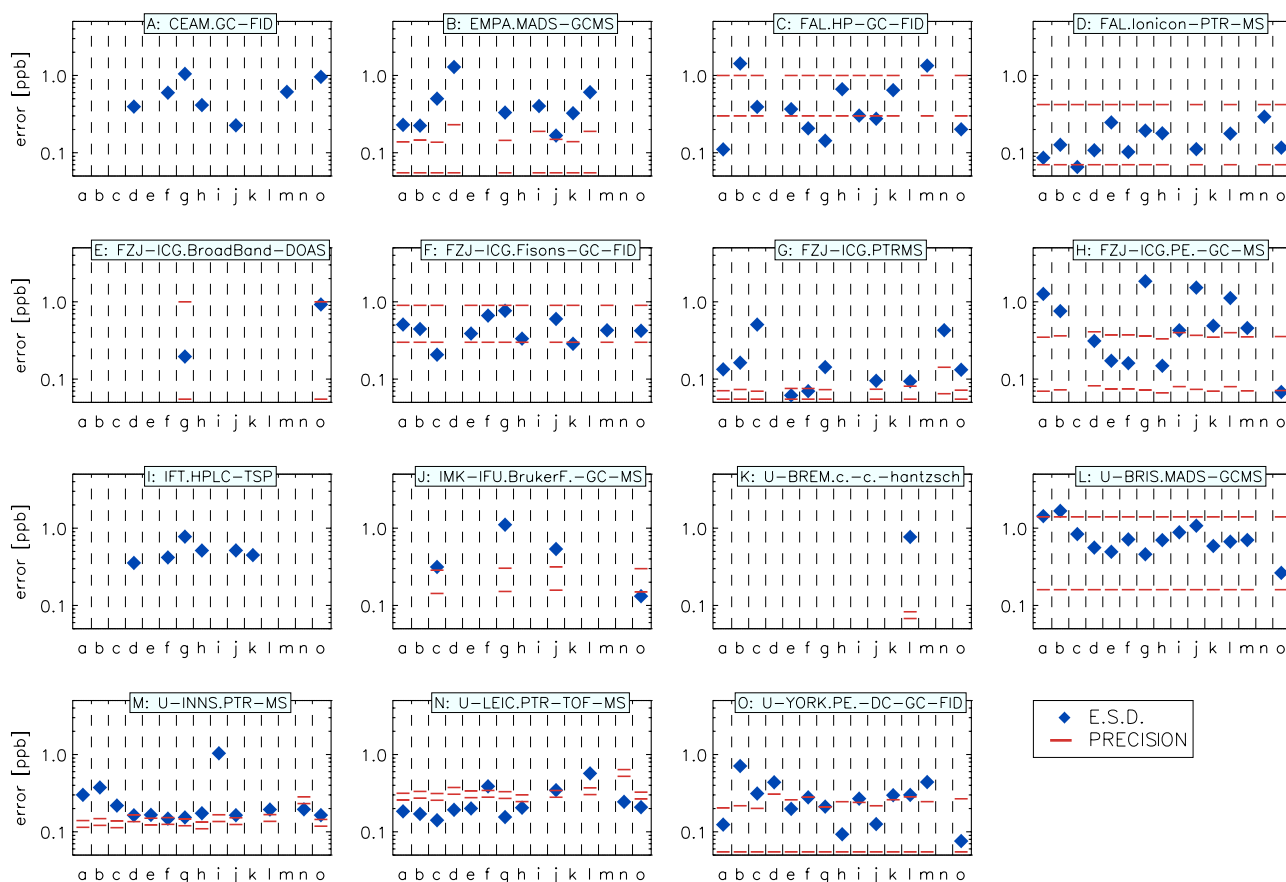


Figure 8. Statistical measurement error: Blue symbols represent estimated standard deviation (e.s.d.) as calculated from $\sigma = 1 - \sqrt{(1 - r^2) * \text{var}(X)}$. The red bar indicates the range of precision a priori specified by the respective PI (see Table 2 for details).

day 4 (humidity plus ozone) hinted that increased background levels of some OVOCs were present in some systems under these conditions which was manifested as a y intercept significantly higher than zero. Acetaldehyde, acetone, and ethanol showed the greatest effect with averaged changes (over all instruments) in the y intercepts from day 3 to day 4 equal to 0.23 ppbv, 0.29 ppbv and 0.22 ppbv respectively. In general, for these specific compounds, the GC-based instruments appeared to be more affected by the presence of ozone than the PTR-MS instruments; the only GC instruments that used an ozone scrubber were instruments F (Fisons-GC-FID) and H (PerkinElmer-GC-FID). These instruments use the method of NO titration scrubbing which is not widely used in the community. It is not possible to draw conclusions on the effectiveness of the ozone scrubber because of general variability observed in the data. More data are necessary at different ozone levels to substantiate and quantify this effect. However, it is clear that investigators using GC-based techniques need to be aware of the potential ozone has to degrade the quality of the instrument's response and test accordingly before deployment of instruments in the field.

4.3. Stated Accuracies and Precision

[93] The participant-provided stated accuracies and precisions (Table 2) are overly optimistic for many of the

instruments and too pessimistic for others, as seen from statistical measurement error results shown in Figure 8.

5. Conclusions

[94] A large-scale in situ blind intercomparison of oxygenated volatile organic compound (OVOC) measurements was conducted at the large (270 m³) simulation chamber, SAPHIR, at the Forschungszentrum research center in Jülich, Germany. A motivating factor for this study was that very few side-by-side comparisons of OVOC measurements have been done and yet measurements are reported in the literature on a regular basis. The SAPHIR chamber proved to be a very suitable facility for this experiment. A variety of measurement techniques were involved in the study ranging from HPLC to DOAS to PTR-MS. Error-weighted regression plots were generated for all of the compounds measured by each instrument. For nearly all instruments, correlations with the calculated values were good. When the calculated data (x axis) were plotted against the reported data (y axis), the slopes and correlation coefficients showed that a number of instruments compared extremely well with the calculated values for all or nearly all compounds. For others, discrepancies were identified, often along with probable or possible causes.

[95] These included problems with calibrations and zeros. However, even when the slopes and correlation coefficients

looked very good, an examination of the y intercept values revealed that, for some instruments, background values were present for specific OVOCs, i.e., nonzero values reported from instruments when SAPHIR calculated values were zero. For specific compounds this problem was present in some, but not all, of the GC techniques and in the HPLC cartridge technique; at the levels studied here offsets were not present in the PTR-MS instruments using quadrupole mass spectrometry. Nonzero offsets present potentially serious problems for ambient air measurements. For some compounds, such as benzaldehyde, many instruments detected substantial offsets. Ambient concentrations of benzaldehyde are fairly small and usually below the offsets encountered during the intercomparison. The implications for this are that ambient measurement quality for this compound (and others with substantial offsets) would be seriously compromised.

[96] Overall, instrument M (U-INNS-PTR-MS) showed the best performance. We venture that the reasons for this include: a high-quality instrument, experience in atmospheric measurements by the investigator, and experience with the instrument including strict attention to analytical procedures such as zeroing the instrument and calibration. All instruments showed the potential for making good measurements of OVOCs but this potential cannot be realized for hard-to-measure compounds under varying atmospheric conditions unless investigators are committed to fully characterizing their instruments and developing analytical methods that are tested and assessed to the fullest extent possible.

[97] It is clear that for ambient measurements, improvements are necessary for most analytical techniques, from zeroing, separation, and detection to calibration. A simple fix for some of the poor results in this experiment would be the use of high-quality calibration gases which are readily available. The DNPH cartridge measurement community continues to resist using gas-phase standards when it is clear that using them would be in their best interest.

[98] Some compounds, such as 1-butanol and benzaldehyde, were generally more difficult to measure than others, with low vapor pressure identified as a probable contributing factor. This experiment was a first attempt to obtain data on the performance of European instrumentation that have been or will be used in the field for OVOC measurements. This intercomparison tested instruments in an environment that is considerably less challenging than the ambient atmosphere and yet some significant problems were identified. Two of the intents of this exercise were to provide useful feedback to investigators on possible problems so that the quality of measurements could be improved and to serve as a test bed for developing instruments; some novel instruments including the solid phase microextraction (SPME) GC-FID (for carbonyl measurements), catalytic converter–Hantzsch (for methanol measurements), and PTR-TOF-MS (general OVOC measurements) were recently developed and participated in this intercomparison; the ACCENT program and the SAPHIR facility provided the means to test these instruments at an important stage in their development.

[99] There will be a need in the future for further intercomparisons not only for the instruments commonly deployed in Europe but in the rest of the world as well. Future intercomparisons under simulated and ambient

atmospheres will be necessary to gauge the state of the art for ambient OVOC measurements from investigators who have significant experience under a wide range of ambient conditions.

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