

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

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INTRODUCTION

This poster presents the first large scale in-situ intercomparison of oxygenated volatile organic compound (OVOC) measurements. The intercomparison was performed blind with sixteen analytical instruments challenged with measuring atmospherically relevant OVOC species and was conducted at the large (300 m³) simulation chamber, SAPHIR, in Jülich, Germany. The instruments, representing a wide variety of techniques, were challenged with different mixing ratios of OVOCs plus toluene (14 species, C₁ to C₇) in the approximate range 10-0.6 ppbV. Data is presented for days two, three, and four of the experiment. During day two, instruments were challenged with measuring OVOCs in the chamber but no humidity or ozone was added. On day three, instruments measured OVOC mixing ratios at relative humidities of approximately 50% and on day four, instruments measured OVOC mixing ratios at relative humidities of 50% and ozone concentrations of approximately 60 ppbv. 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. Most instruments and species compared to within factor of two with the calculated values. However, a number of instruments compared much better than this. A full statistical treatment of the data has been completed; the performance of each individual instrument was evaluated with respect to reference values in terms of time series and correlation plots for each compound for days two, three, and four.

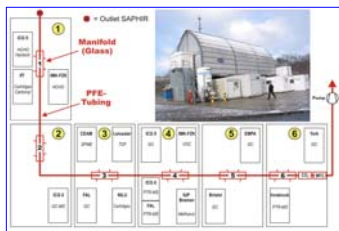


Figure 1: Setup of the instruments at the chamber. All instruments were connected via PFA tubing and each portable laboratory had a glass manifold from which sample could be drawn.

Table 1. Compounds that were compared in the study and their relevance

Compound	ID	relevance	Compound	ID	relevance
1-butanol	a	O, U	ethanol	i	U, B
1-propanol	b	O, U	hexanal	k	Bi
2-methyl-3-butene-2-ol	c	Bi	methacrolein	l	O, Bi
acetaldehyde	d	R, A, O	methanol	m	U, Bi, B
acetic-acid-methyl-ester	e	R, U, B, O	methyl-vinyl-ketone	n	O, Bi
acetone	f	R, U, B, O	mvk+macr	o	O, Bi
benzaldehyde	g	O	toluene	p	U, A
butanal	h	R, A, O			

R-Radical Cycling; A-Aerosol Formation/Modification; U-Urban Tracer; B-Biomass Burning Tracer; O-Oxidation/Processing Indicator; Bi-Biogenic Emission Tracer; Oc-Ocean Emission

Table 2. Experimental procedure followed for Days 2,3, and 4

Date	Day Segment	Relative Humidity (Approximate)	O ₃ Mixing Ratio (Approximate)	OVOC
01-25-05	2	0	0	added
	A			
	B			
01-26-05	3	50%	0	added
	A			
	B			
01-27-05	4	50%	60	added
	A			
	B			

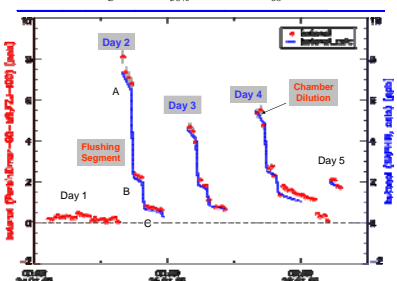


Figure 2: Example (for butanal) showing the calculated values for each day along with experimental data points. The diamonds show the experimental data. The beginning of segment A represents the initial calculated mixing ratio in the chamber. The slope of the line in segment A corresponds to the dilution rate of the chamber (approximately 3% but was calculated exactly). 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.

Table 3. Institute identifications, institute and standard used.

ID	Institute	Instrument identifier	Standard Used
A	CEAM	GC-FID	In-house
B	EMPA	MADS-GCMS	Commercial, certified
C	FAL	HP-GC-FID	Commercial, certified
D	FAL	Ionicon-PTR-MS	Calculated, commercial certified
E	FZJ-ICG	Broad Band-DOAS	Line strength
F	FZJ-ICG	Fisons-GC-FID	Commercial, certified
G	FZJ-ICG	PTRMS	Diffusion source
H	FZJ-ICG	PerkinElmer-GC-MS	Commercial, certified
I	IFT	HPLC-TSP	In-house
K	IMK-IFU	BrukerFranzen-GC-MS	Commercial, certified
L	U-BREM	Catalytic-converter-Hantszsch	In-house diffusion source
M	U-BRIS	MADS-GCMS	Messer-Griesheim methanol in N2
N	U-INNS	PTR-MS	Commercial, certified
O	U-LEIC	PTR-TOF-MS	Commercial, certified
P	U-YORK	PerkinElmer-DC-GC-FID	Commercial, certified

Results: The data were analyzed in statistical detail. The results of these analyses are shown in the graphs that follow.

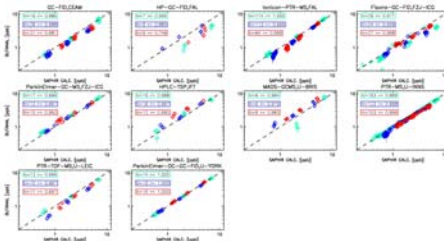


Figure 3: Example of data processed for butanal. The calculated data are plotted on the x-axis and the individual instrument provided data is plotted on the y-axis. Each panel represents the results from an individual instrument. Day 2 is given in red, day 3 is given in green and day 4 is given in blue. Instrumental data points are represented by open diamonds. The 1:1 fit is given by the dashed line and the correlation coefficient, r, for each day is given in the legend.

Note the excellent agreement shown by some groups (e.g., U-INNS*, U-York). Other compounds proved more difficult to measure for some groups, e.g., acetaldehyde, but some groups measured all or nearly all compounds well. See following overview graphs.

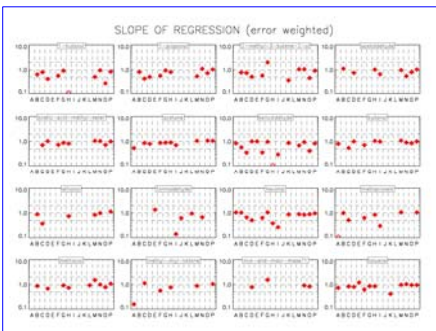


Figure 4: Error-weighted slope of regression for each compound. Data points are given for individual instruments designated by a letter (x-axis) corresponding to Table 1.

* U-INNS PTR-MS measured all compounds but due to a processing error, U-INNS acetone values do not appear on these graphs. U-INNS agreement was excellent for acetone.

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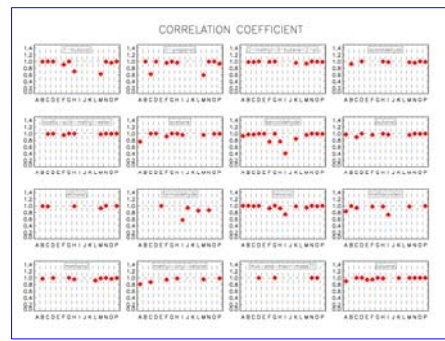


Figure 5: Correlation coefficient for each intercompared compound. Data points are given for individual compounds designated by a letter (x-axis) corresponding to Table 1.

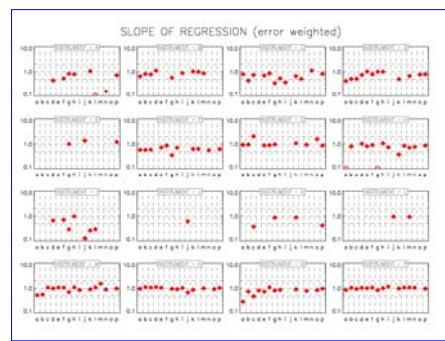


Figure 6: Error-weighted slope of regression for each individual compound as measured by participating instruments. Data points are given for individual instruments designated by a letter (x-axis) corresponding to Table 3.

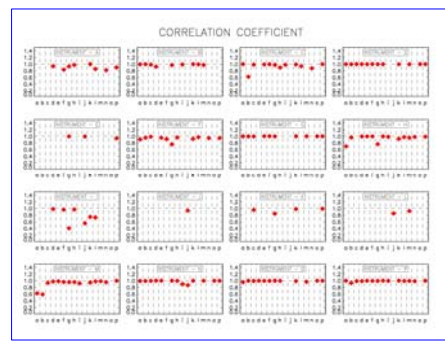


Figure 7: Correlation coefficient for individual compounds from as measured by participating instruments. Data points are given for individual instruments designated by a letter (x-axis) corresponding to Table 3.

Summary:
 Good overall agreement of measured and calculated mixing ratios – some group's measured values were extremely close to calculated values.
 Problems were identified and research groups used the feedback to improve their analysis capabilities.
 SAPHIR was an excellent facility for conducting this experiment. All compounds were effectively intercompared.