

# *Estimation of the Contribution from Solvent Use to the NMVOC Emissions in Germany*

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A. Niedojadło, K. H. Becker, R. Kurtenbach, P. Wiesen



Department of Physical Chemistry  
Faculty of Mathematics and Natural Sciences  
Bergische Universität Wuppertal

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Chemistry, Transport and Impacts of Atmospheric Pollutants with Focus on Fine Particles

Monastery Andechs

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# *Objectives*

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- ◆ **Determination of the NMVOC composition of the city air in Wuppertal, focusing on the characterisation of oxygenated compounds in air samples**
- ◆ **Investigation of different NMVOC emission sources**
- ◆ **Providing more information about relative importance of road traffic and solvent use to the total NMVOC emissions in Germany**

## *Scope of the work*

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- ◆ Task identification - requirement of more experimental data on NMVOC solvent emission
- ◆ Analysis of previous studies - emission inventories and field measurements
- ◆ Decision on the range of investigations - compounds to investigate, measurements to perform
- ◆ Selection, development and optimisation of NMVOC sampling and analysis method
- ◆ Performance of measurement campaigns for data collection
- ◆ Processing of the data
- ◆ Implementation of receptor modelling for emission apportionment analysis
- ◆ Analysis of measurements and modelling results
- ◆ Conclusions and final outcomes

# *NMVOC emissions - state of art*<sub>1</sub>

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- ◆ Non-methane volatile organic compounds (NMVOCs) are emitted to the atmosphere from:
  - natural sources; about 1300 Tg per year (Gunther *et al.*, 1995; Fall, 1999)
  - anthropogenic sources; about 150 Tg per year (Piccot *et al.*, 1992; Middleton, 1995)
  
- ◆ Human activity is responsible for about 10% of the total NMVOC emission on a global scale, but for about 50% in Europe and more than 70% in Germany
  
- ◆ In general the NMVOCs are emitted from:
  - combustion processes,
  - production, treatment, storage and distribution of fossil fuels,
  - application of volatile organic solvents and solvent containing products,
  - industrial production processes and biological processes(Friedrich and Obermeier, 1999)
  
- ◆ Typical total NMVOC concentrations range in heavy polluted urban areas from 500 to 1500  $\mu\text{g}/\text{m}^3$ , in suburban areas from 100 to 250  $\mu\text{g}/\text{m}^3$  and from 30 to 200  $\mu\text{g}/\text{m}^3$  in forest, rural and remote areas (Ciccioli *et al.*, 1999)

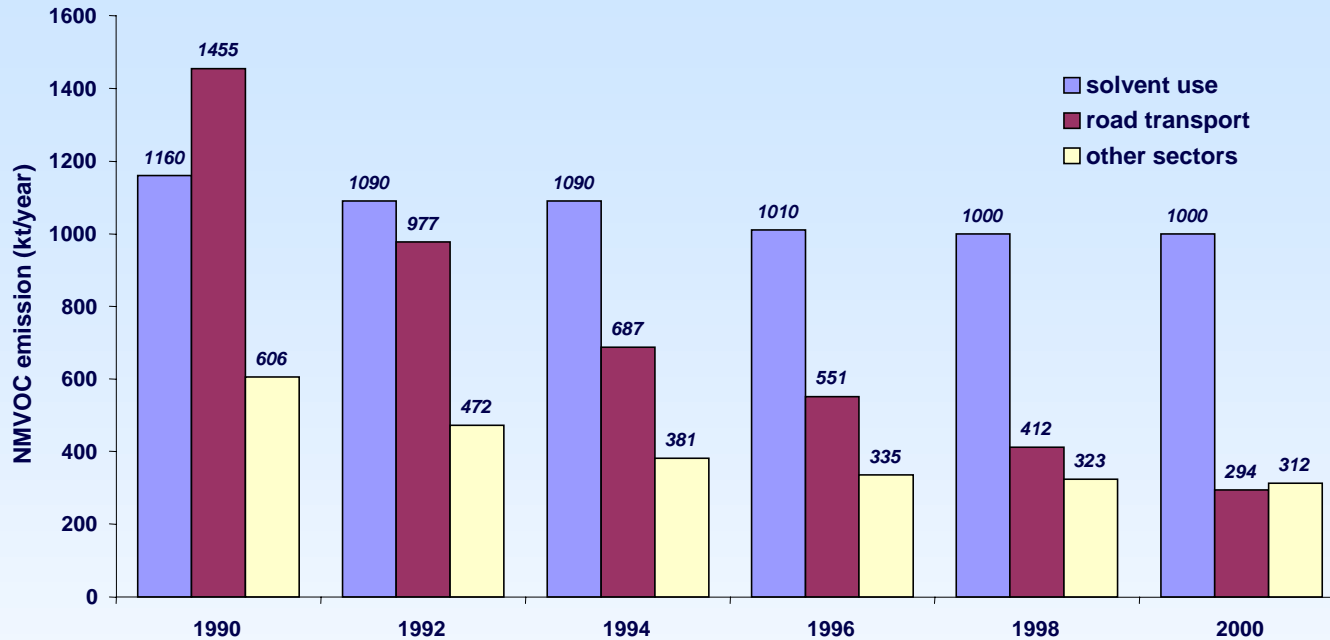
# *NMVOC emissions - state of art* <sub>2</sub>

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- ◆ With respect to the European scale, **road traffic** and **solvent use** are by far the most important sources of anthropogenic NMVOC emissions
  
- ◆ Road traffic emissions are quite reasonably well established due to many:
  - dynamometer tests,
  - tunnel studies,
  - roadside measurements,
  - model calculations
  
- ◆ The about 50% estimated reduction in NMVOC emission from road transport in Europe over the last 15 years (EEA, 2004; Stemmler *et al.*, 2005) is mainly due to the regulation on exhaust gas composition, the introduction of catalysts on new cars and an increased use of diesel vehicles
  
- ◆ Solvent emissions reported in the inventories are estimated
  - only on the basis of calculations using the production and consumption of solvents
  - calculations are based on statistical data on the inland production of solvent containing goods and their import and export
  - emission factors are calculated by considering applications, control techniques and dispersion to other compartments (water and soil)

# Motivation <sub>1</sub>

## ➤ Discrepancy between NMVOC emission inventories and measurement data ◀




*German Environmental Agency (UBA, 2002; UBA, 2003):*

- ◆ The relative importance of NMVOC emission from solvent use has increased in comparison to traffic sources over time
- ◆ Since 1992 more than 50% of anthropogenic emissions in Germany have been attributed to sources related to solvent use

# Motivation 2

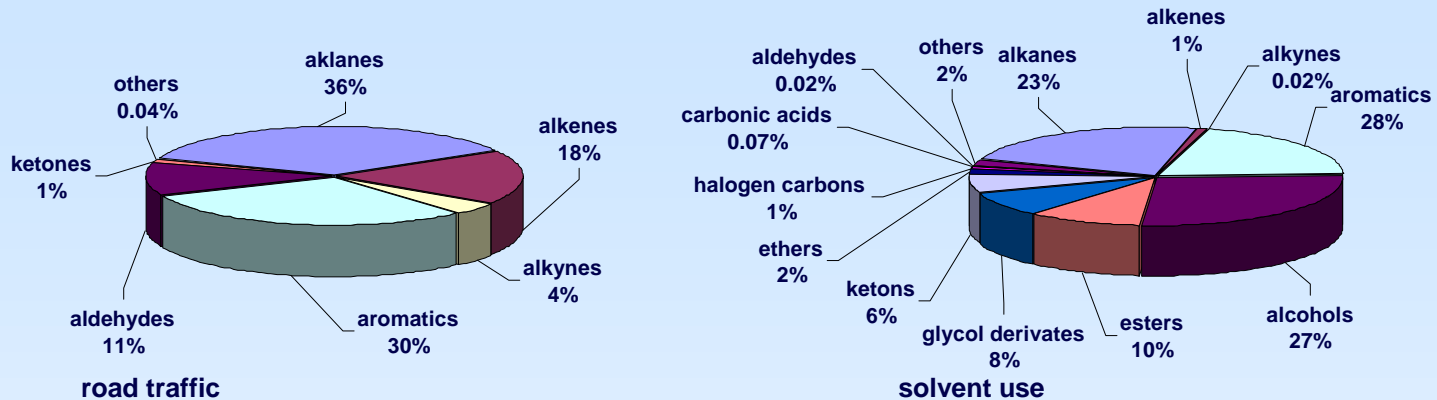
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- ◆ Data of ambient concentration measurements from different German cities (Berlin, Augsburg, Wuppertal) always show that road traffic is still the dominant source of shorter (C<sub>2</sub>-C<sub>10</sub>) hydrocarbons (Thijssse *et al.*, 1999; Mannschreck, 2000; Gomes, 2002; Kurtenbach *et al.*, 2002; Slemr *et al.*, 2002; Winkler *et al.*, 2002)
- ◆ Experimental observations disagree with the German emission inventory in which solvent use is the major source of NMVOC with a contribution of more than 60% to the total NMVOC emissions (UBA, 2003; Theloke *et al.*, 2001)
- ◆ Disagreements may suggest that:
  - the officially accepted emission data from solvent use are currently overestimated
  - many components have not been covered by the ambient measurements



In order to clarify the contribution of solvent use and road traffic to total NMVOC emissions in Germany, the investigation on NMVOCs including oxygenated species in the city air of Wuppertal has been undertaken

# Investigated compounds



NMVOC split (wt%) for road traffic and solvent use in Germany (Friedrich, 2003)

◆ A large number NMVOCs emitted by different anthropogenic sources, in particular from traffic exhaust and solvent use, have been investigated

- hydrocarbons C<sub>2</sub>-C<sub>10</sub> (alkanes, alkenes, alkynes and aromatic hydrocarbons)
- oxygenated compounds:
 

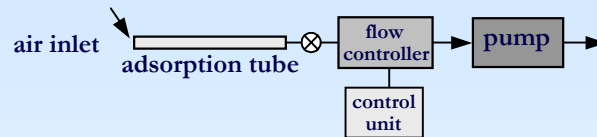
<u>alcohols:</u> methanol ethanol 1-propanol 2-propanol 1-butanol 2-butanol	<u>esters:</u> methyl acetate ethyl acetate propyl acetate isopropyl acetate butyl acetate isobutyl acetate	<u>ketones:</u> acetone 2-butanone 4-methyl-2-pentanone 2-hexanone cyclohexanone
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methyl *tert*-butyl ether

# Measurement procedure

Determination of hydrocarbons and oxygenated compounds was performed by the following procedure (Woolfender and McClenny, 1999) :

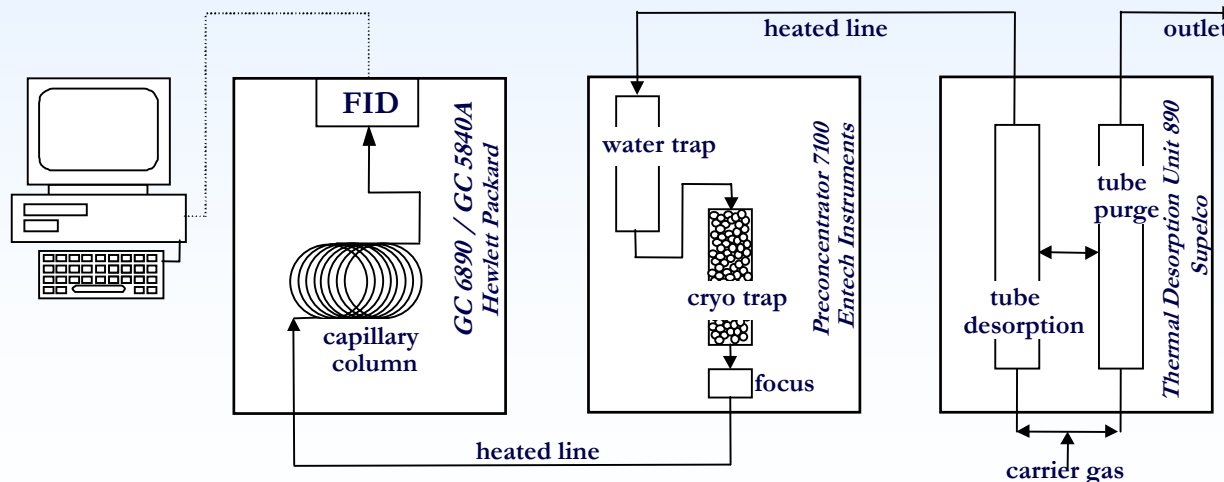
 ambient air collection by active sampling on glass tubes packed with adsorption materials



 thermal tube desorption

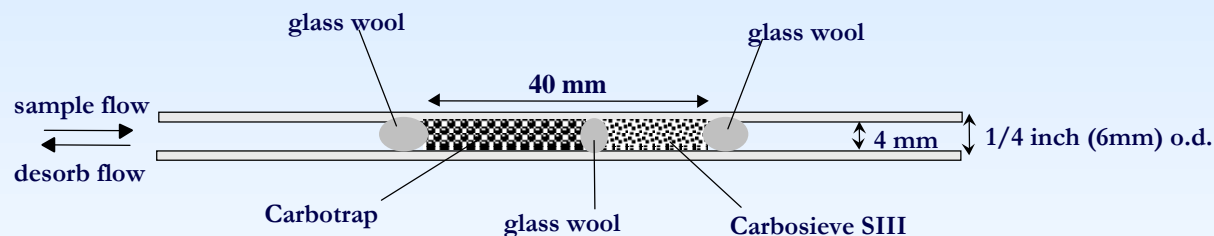
 sample pre-concentration with cryo-trap

 gas chromatography-flame ionisation detection analysis



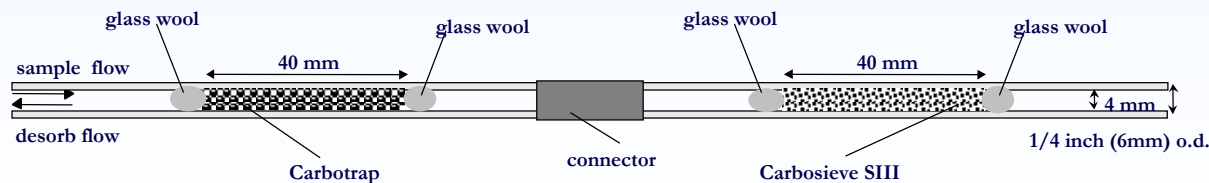
# Separation of HC and OC analysis

- ◆ Analysis of hydrocarbons and oxygenated compounds were performed separately, by means of different capillary columns
- ◆ The partition of analytical procedure followed from application of different adsorption tubes, through separated sampling, desorption, preconcentration to application of different GC systems



## Hydrocarbons (HC)

Multi-bed tubes packed with 125 mg Carbotrap graphitized carbon and 150 mg Carbosieve SIII carbon molecular sieve separated by glass wool



## Oxygenated compounds (OC)

Combination of two adsorbent tubes with different characteristics: tube with 190 mg Carbotrap and tube with 350 mg Carbosieve SIII

# Steps in sample analysis

## Hydrocarbons (HC)

### desorption

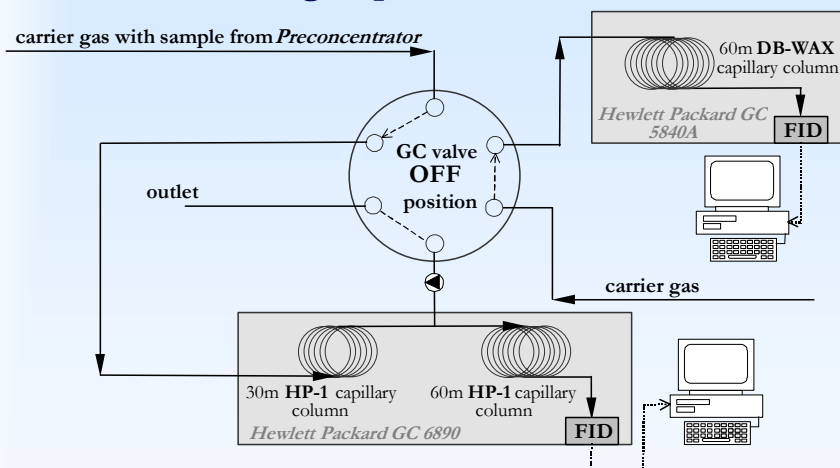
5 min, 350°C

### preconcentration

water trap: -20°C

cryo-trap: -180°C

focussing trap: off



### column

dimethylpolysiloxane, 90m

### GC run

start temp: -50°C, 10 min

ramp: 5°C/min

end temp: 200°C, 20 min

total run: 80 min

## Oxygenated compounds (OC)

### desorption

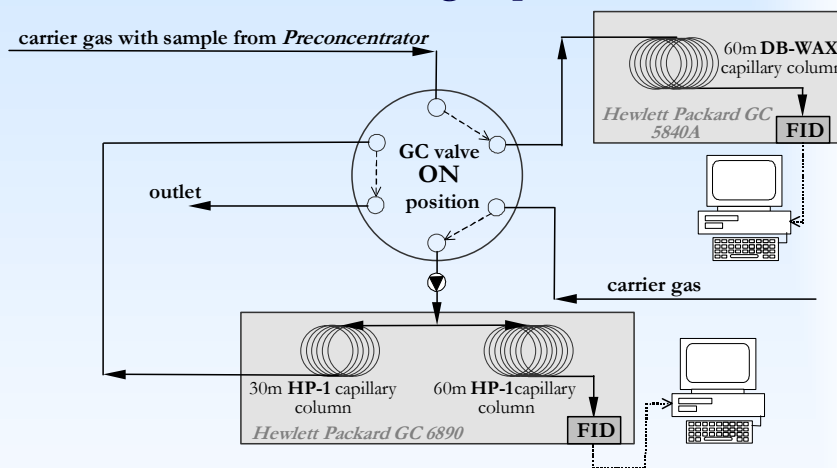
5 min, 300°C

### preconcentration

water trap: off

cryo-trap: -180°C

focussing trap: -80°C



### column

polyethylene glycol, 60m

### GC run

start temp: 30°C, 30 min

ramp: 5°C/min

end temp: 200°C, 6 min

total run: 70 min

# *Parameters of the analytical method*

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◆ Selected analytical method were tested by specification of the following parameters:

- tube backgrounds,
- sampling breakthrough volume ( $C_2$  hydrocarbons excluded from further analysis due to very low breakthrough volume),
- save sampling volume (8 l was accepted as save sampling volume),
- analytical precision of duplicate tube pairs,
- sample recovery,
- storage stability of absorption tubes (stable up to two months),
- precision of GC analysis,
- detection limit,
- calibration response factors,
- agreement with other analytical system

◆ Preparatory tests and measurements results showed that selected method is suited for measurements of hydrocarbons and oxygenated species under ambient concentrations

# Measurements, Wuppertal



◆ Measurements were performed at various sampling sites representing different city areas and different emission sources

◆ Data were collected during 3 measurement campaigns:

1. 17.09.01 - 19.09.01

2. 21.08.02 - 05.09.02

3. 10.10.03 - 17.10.03

◆ Measurements were carried out with a car equipped with:

📄 sampling system for hydrocarbons

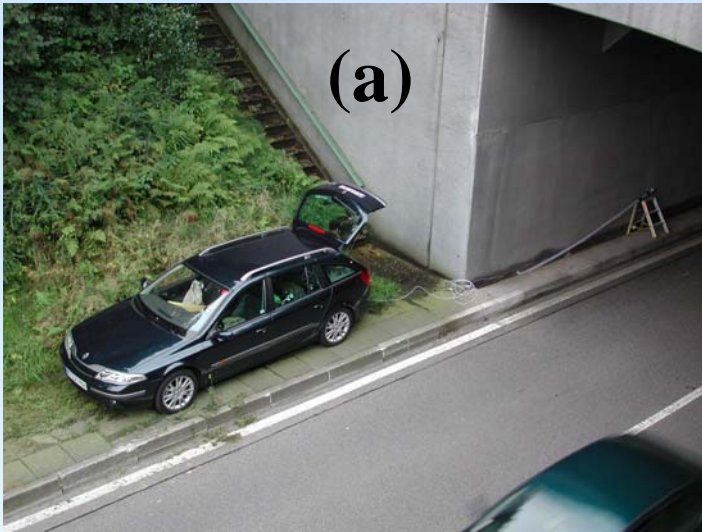
📄 the automatic analysers for measurements of

- CO (AL 5002)
- CO<sub>2</sub> (Carbonido 1000)
- NO/NO<sub>2</sub> (LMA 3D)
- SF<sub>6</sub> (GC-ECD)

📄 meteo-station (Conrad Elec.) for meteorological parameters



# Sampling sites <sub>1</sub>



## to characterise road traffic emission

### Kiesberg Tunnel (a)

- ◆ sampling point was located inside the tunnel, ca. 10 m from the outlet of the tube in direction of Wuppertal Elberfeld; “warm” driving condition

### Road intersection (b)

- ◆ sampling point was located on the big intersection in the city centre of Wuppertal; “stop and go” driving conditions

### City drive

- ◆ samples were collected during driving through the streets of Wuppertal city centre

### Free-way drive


- ◆ samples were collected during driving on the free-ways (A46, A3)



# Sampling sites 2

(e)


## to characterise solvent emission

 samples were collected at points located close to the different solvent factories and workshops:

- a. DuPont Performance Coatings GmbH,
- b. PPG Industries Lacke GmbH,
- c. Bayer AG,
- d. Dr. Alfred Conrads Lackfabrik Nachf. KG,
- e. Karosseriebau Gorn GmbH

(a)

## to characterise ambient concentrations

 samples representing ambient concentrations were collected at different points located in Wuppertal:

- ◆ down- wind from the city centre,
- ◆ at residential areas,
- ◆ at industrial areas

(b)

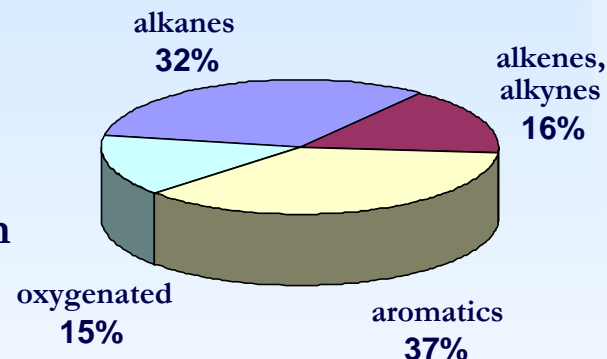
# Measurement results

## ◆ Mixing ratios

- total NMVOC mixing ratios calculated as a sum of 23 measured alkanes, 28 alkenes and alkynes, 14 aromatic hydrocarbons, 18 oxygenated compounds and 19 unidentified species varied during the measurements from 6.58 to 159.61 ppbV, with the average value of 27.90 ppbV

## ◆ Composition of NMVOC-mix

- highest contribution comes from the aromatic hydrocarbons and the second highest from the alkanes - agreement with the results from other urban studies

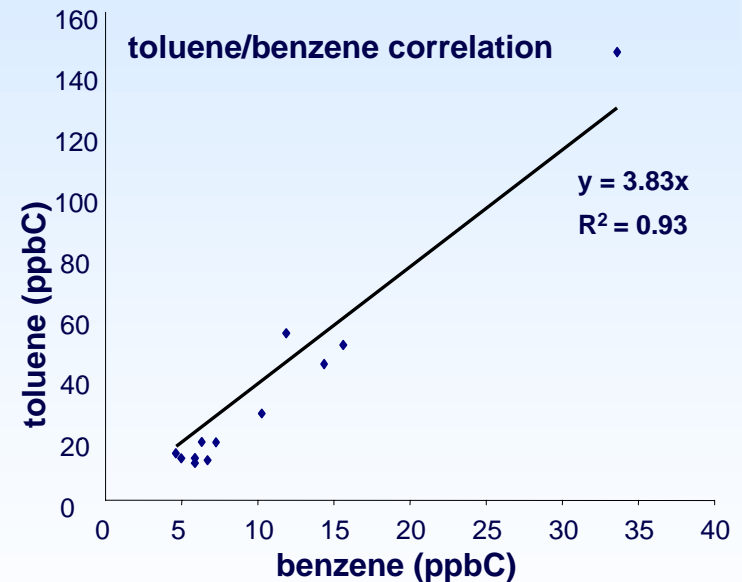


## ◆ NMVOC/NO<sub>x</sub> ratios

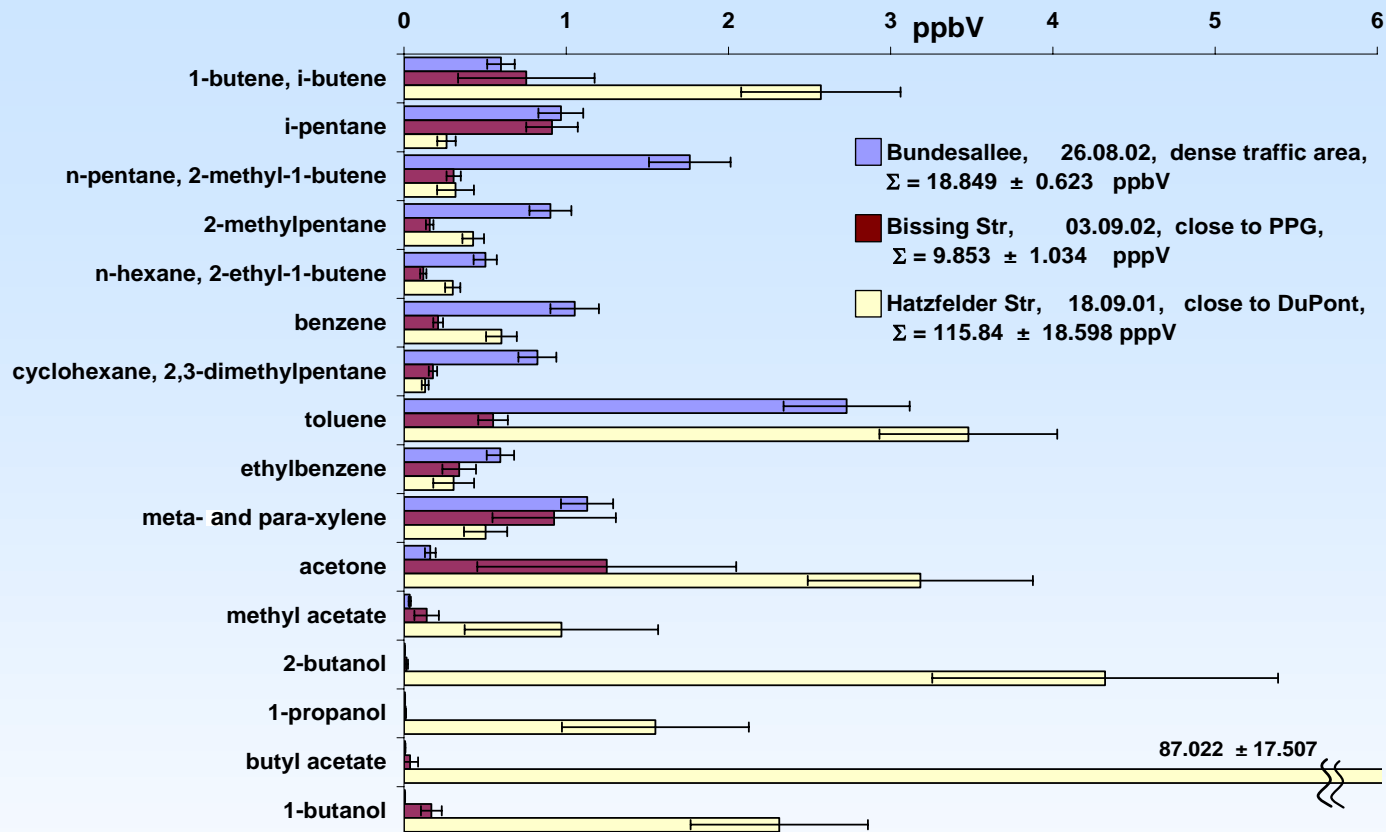
- traffic sites:  $(0.56 \pm 0.06)$  ppbC/ppbV - agreement with the results from previous study performed in Kiesberg Tunnel (Kurtenbach *et al.*, 2002) where ratios from 0.64 up to 1.92 ppbC/ppbV were calculated
- various locations in the city: from 1.76 up to 7.93 ppbC/ppbV with average of  $(3.74 \pm 2.15)$  ppbC/ppbV - values comparable with previous results from Wuppertal and other German cities

# Mixing ratios relative to benzene

- ◆ Average toluene/benzene ratio for traffic sites -  $(3.83 \pm 0.22)$  ppbC/ppbC
  - significantly higher than previously measured ratios in typical traffic areas of 1.50 up to 2.50 ppbC/ppbC (Conner *et al.*, 1995; Derwent *et al.*, 1995; Brocco *et al.*, 1997; Staehelin *et al.*, 1998; Schmitz *et al.*, 2000; Kurtenbach *et al.*, 2002)
- new measured value can be explained by an over proportional decrease of benzene emission compared with other aromatic compounds
- new European regulations on the benzene content in gasoline implemented in year 2000 (Directive 98/70/EC)
- reduction of benzene content in gasoline from 5 to 1% (V/V)
- corresponding downward trend in the concentrations of aromatic compounds are recently reported (Kristensson *et al.*, 2004; Reimann *et al.*, 2004; Stemmler *et al.*, 2005)



# Mixing ratios under influence of different emission sources



- traffic (Bundesallee): toluene, xylenes, benzene and other aliphatic hydrocarbons, except for acetone, no oxygenated VOCs
- close to the PPG varnish factory (Bissing Str.): xylenes, toluene and acetone, also some others oxygenated compounds like 1-butanol, methyl acetate and butyl acetate
- close to the DuPont coatings factory (Hatzfelder Str.): butyl acetate with high mixing ratio of more than 87 ppbV, also other oxygenated compounds and toluene

# Chemical Mass Balance Modelling

- ◆ The CMB model uses an effective variance least squares solution to a set of linear equations, which expressed each measured concentration  $c_i$  of species  $i$  as a linear sum of products of source profile abundances  $x_{ij}$  and contributions  $s_j$  of source  $j$  (Watson *et al.*, 1998; 2001)
- ◆ The mass concentration  $c_i$  at the receptor point is expressed by the following mass balance equation:

$$c_i = \sum_{j=1}^k x_{ij} s_j + e_i, \quad i = 1, \dots, p$$

with:

- $c_i$ : ambient mass concentration of species  $i$  at the receptor point in  $\mu\text{g}/\text{m}^3$ ,
- $x_{ij}$ : fraction of species  $i$  in the emission from source  $j$ ,
- $s_j$ : mass contribution of source  $j$  to the receptor point in  $\mu\text{g}/\text{m}^3$ , given by  $s_j = \sum c_{ij}$  (sum over  $i$ ) and understood as sum of partial mass concentrations  $c_{ij}$  of all species in the NMVOC emission from source  $j$ ,
- $e_i$ : measurement error of concentration  $c_i$  at the receptor point for species  $i$  in  $\mu\text{g}/\text{m}^3$ ,
- $k$ : number of pollution sources,
- $p$ : number of chemical species

# *Model assumptions*

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- **Fundamental principle** - mass conservation can be assumed - composition of source emissions are constant over the ambient and source sampling period
  - no chemical transformation, no deposition
- all sources which may significantly contribute to the receptor have been identified and their emissions characterised (minor contributors may be omitted)
- number of source categories is less than or equal to the number of chemical species (the larger the difference, the better)
- source profiles are linearly independent (degree of independence depends on the variability of the source profile, CMB requires species with different abundances in different source types)
  - measurement errors are random, uncorrelated and normally distributed
- assumptions are fairly restrictive and difficult to be fulfilled in practice, however, the CMB model tolerates some deviations, which increase the final uncertainties of the source contribution estimations

# *Input data for CMB model*

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- ↖ NMVOC emission source profiles, so-called source fingerprints, which are the sets  $\{x_{ij}\}$  of the fractional amounts  $x_{ij}$  of the chemical species  $i$  in the NMVOC emissions from source  $j$ ,
- ↖ the total NMVOC mass  $\Sigma c_i$  (sum over  $i$ ) at a receptor point and the concentrations  $c_i$  of the individual compounds for which the contributions from all emission sources have to be considered
- ↖ realistic uncertainties for source and receptor values which are used to weigh the relative importance of input data to model solutions and to estimate uncertainty of the source contributions

## *It has been assumed*

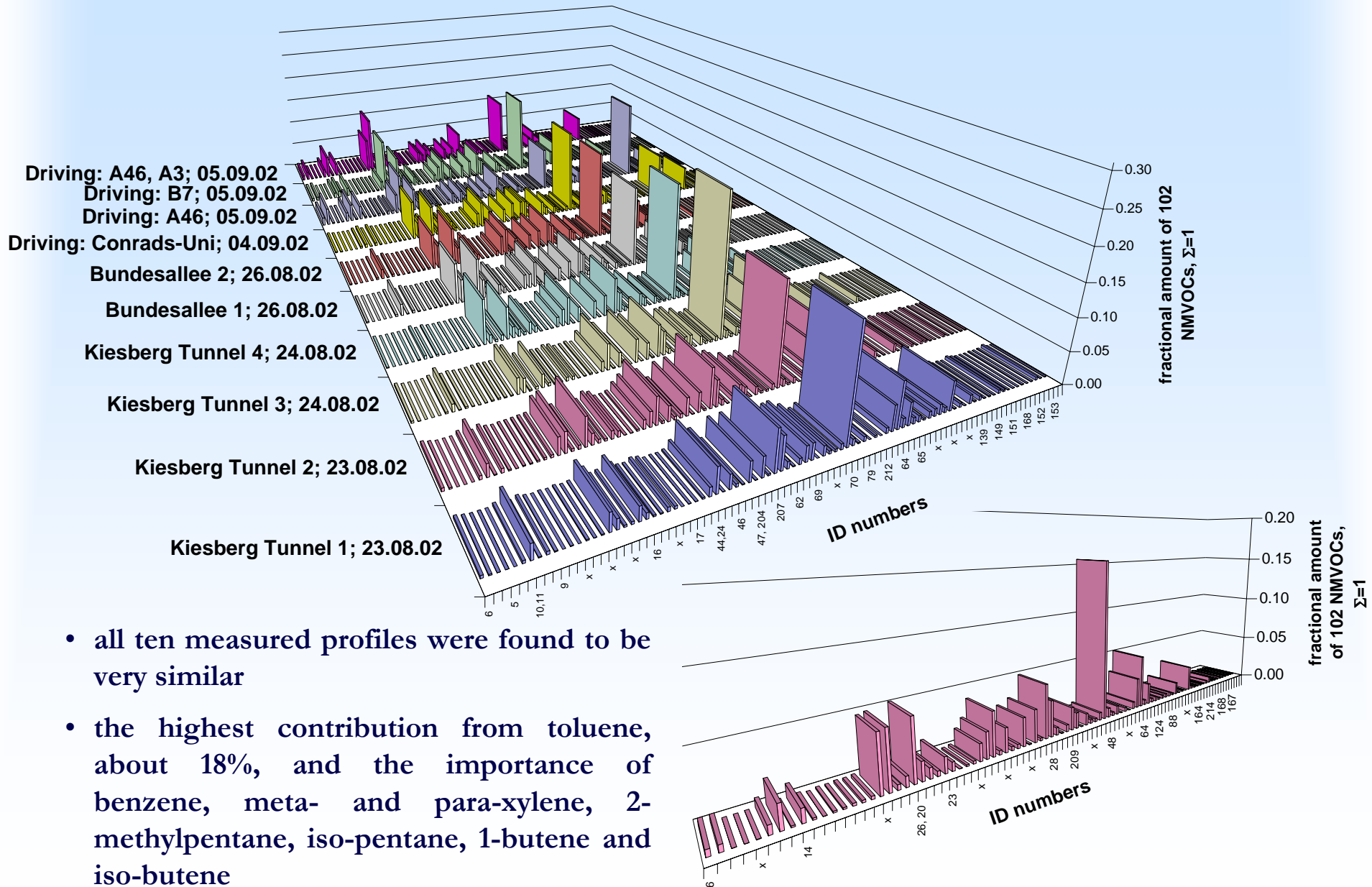
- concentration profiles measured at sites dominated by traffic emissions like traffic tunnels, free-ways, street intersections etc. are determined only by traffic emission and provide the traffic emission profile
- concentration profile measured near a particular solvent factory, but down-wind from this emission source is exclusively originating from solvent emissions and provide (after corrections for the background concentration) a solvent use emission profile at least for the emission type of the particular factory

# *Input data*

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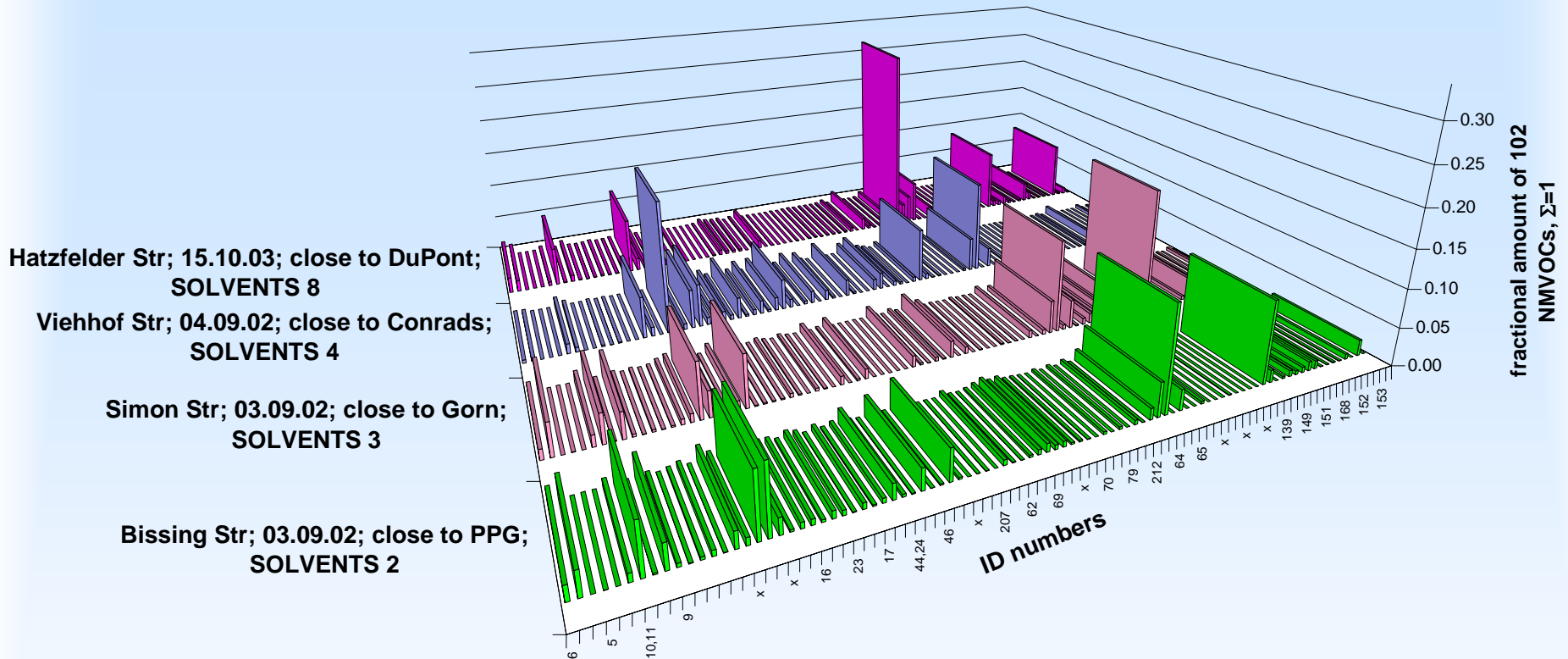
- ◆ all profiles contained the contributions of **102** NMVOC species
- ◆ from about 190 NMVOCs peaks detected in GC-FID signals, the following compounds were selected for further investigation and CMB analysis:
  - 65 hydrocarbons in the range of C<sub>3</sub>-C<sub>10</sub> from the hydrocarbon groups: alkanes, alkenes, alkynes and aromatics,
  - 18 oxygenated compounds in the range of C<sub>1</sub>-C<sub>6</sub> including alcohols, ketones and esters and also methyl *tert*-butyl ether (MTBE),
  - 19 hydrocarbon compounds with known carbon number but unidentified structure; these species were selected on basis of their abundance and variation (compounds with average concentration above 0.3 µg/m<sup>3</sup> and significant variation) and because of their high significance to the source profiles diversification

# Traffic emission profiles



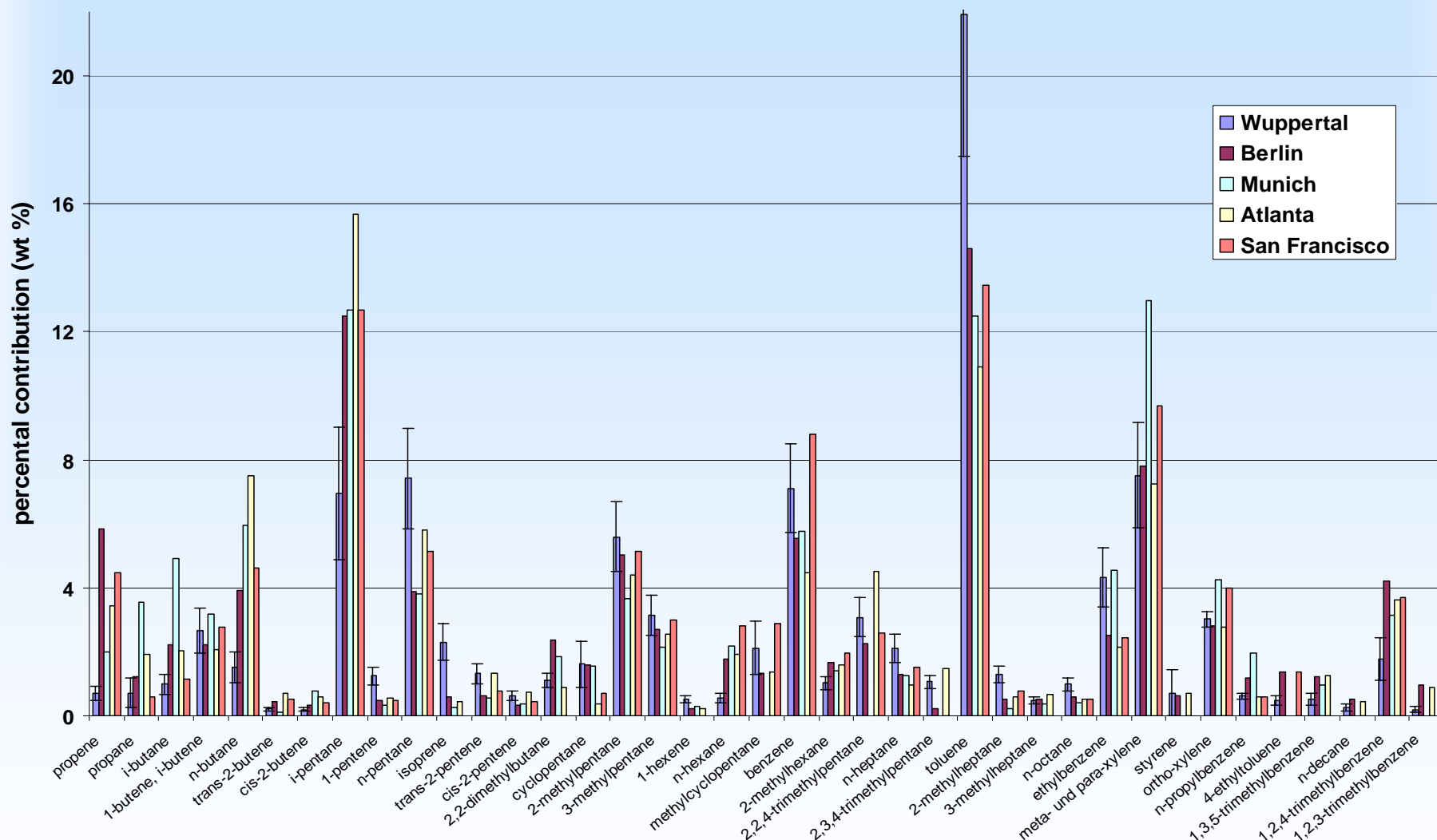
- all ten measured profiles were found to be very similar
- the highest contribution from toluene, about 18%, and the importance of benzene, meta- and para-xylene, 2-methylpentane, iso-pentane, 1-butene and iso-butene

# Solvent use emission profiles



- solvent fingerprints exhibit much higher contributions from oxygenated compounds
- butyl acetate, ethanol and acetone contribute significantly to the total mass
- from the hydrocarbons the xylenes and also toluene are important markers for the emission of solvents
- solvent profiles obtained at the different receptor points differ significantly from each other - four different solvent use emission profiles were applied in the CMB analysis

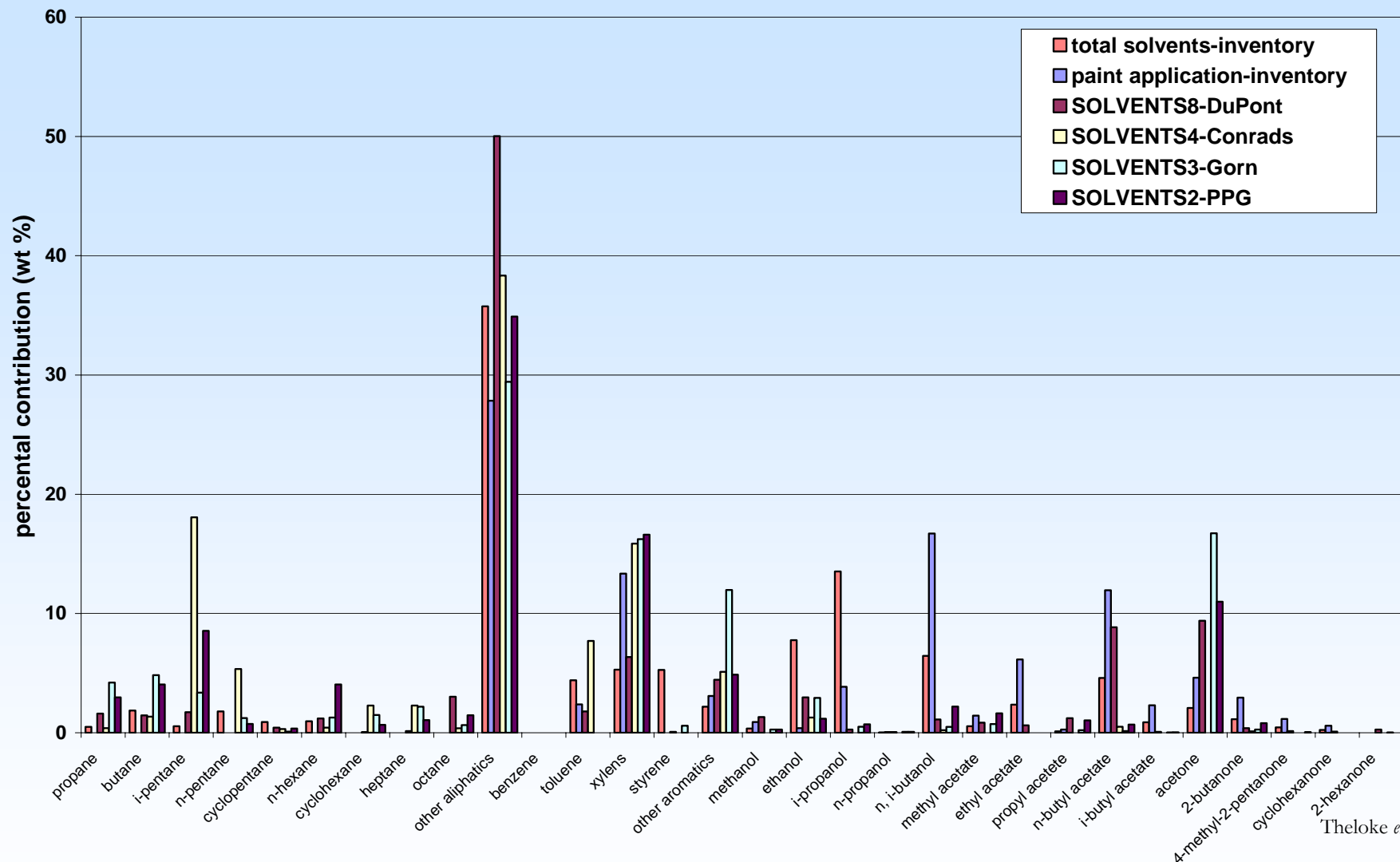
# Traffic emission profile - comparison with other studies



Berlin (Thijssse *et al.*, 1999), Munich (Kern *et al.*, 1998), Atlanta (Conner *et al.*, 1995) and San Francisco (Fujita *et al.*, 1994)

- propene, n-butane, i-pentane, n-hexane and 1,2,4-trimethylbenzene show lower contributions in comparison with the other profiles
- toluene and isoprene are considerably more abundant in Wuppertal

# Solvent use emission profiles - comparison with inventory data



Theloke *et al.*, 2000

- higher contributions of the hydrocarbons propane, i-pentane, cyclohexane, heptane, octane and the oxygenated hydrocarbon acetone and lower of other oxygenated species like ethanol, i-propanol, n-, i-butanol, ethyl acetate and i-butyl acetate
- contributions of the sum of all other not specified aliphatic and aromatic hydrocarbons agree reasonably well
- DuPont fingerprint shows the best compatibility with the calculated emission profile for paint applications

# Ambient air concentrations - receptor points



Location of the receptor points (+) and sites of the investigated solvent factories and workshops (▲):

D: DuPont Performance Coating GmbH, P: PPG Industries Lacke GmbH, B: Bayer AG, C: Dr. Alfred Conrads Lackfabrik Nachf. KG, G: Karosseirbau Gorn GmbH

1: GIRAR, 2: UNI, 3: JOTAL – receptor points located down-wind from the city centre

4: BUNDA, 5: MARKIS – receptor point located at dense traffic areas

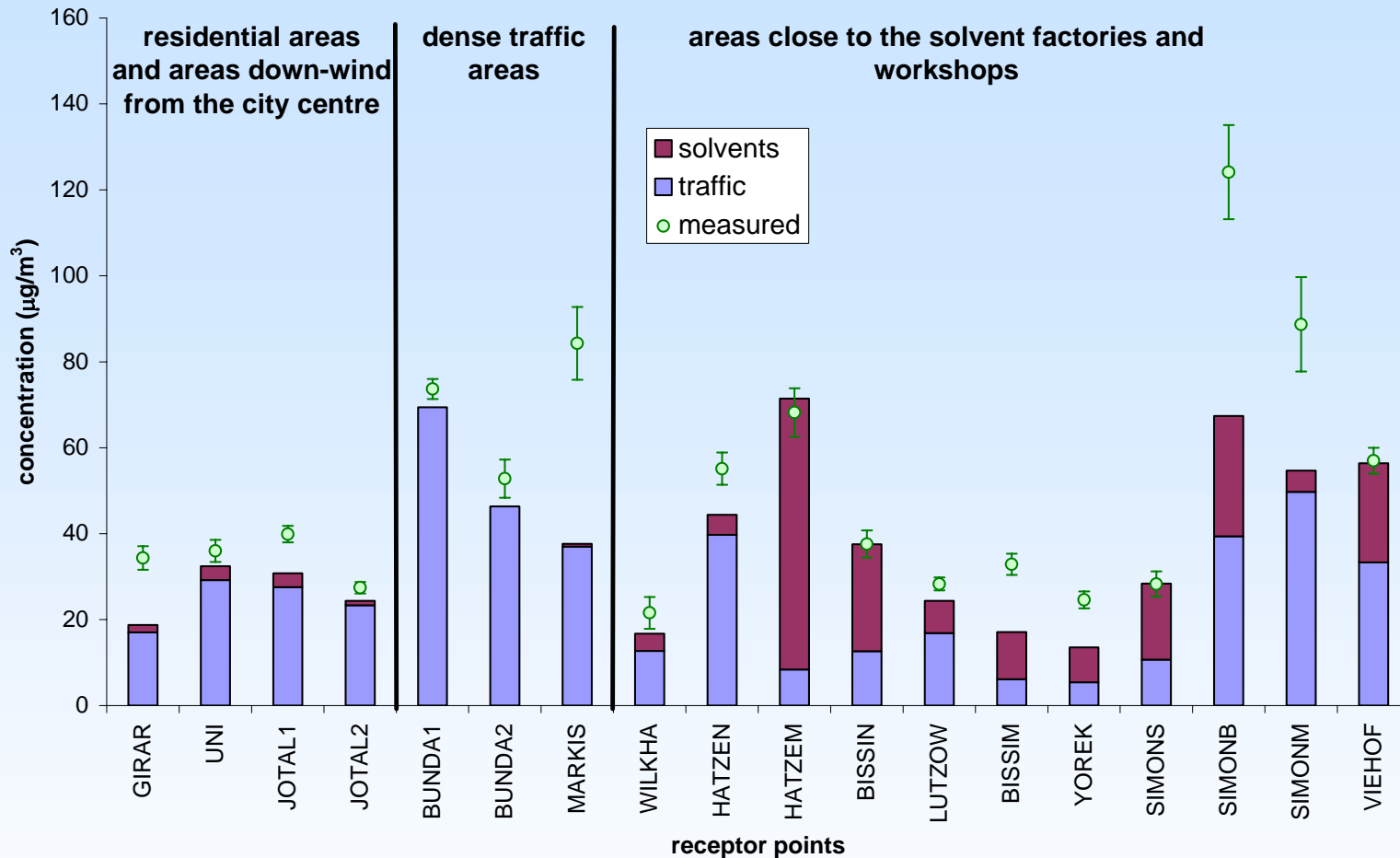
6: WILKHA, 7: HATZEN, 8: HATZEM, 9: BISSIN, 10: LUTZOW, 11: BISSIM, 12: YOREK, 13: SIMONS, 14: SIMONB, 15: SIMONM, 16: VIEHOF – receptor points located at areas close to solvent factories and workshops

# Outcomes of the CMB analysis

receptor points (CMB IDs)	source fingerprints (CMB IDs)	TRAFFIC1	SOLVENTS2	SOLVENTS3	SOLVENTS4	SOLVENTS8
		average traffic emission profile	solvent emission profile for PPG factory	solvent emission profile for Gorn workshop	solvent emission profile for Conrads factory	solvent emission profile for DuPont factory
GIRAR	source contributions	positive	negative	negative	negative	positive
UNI	source contributions	positive	negative	positive	negative	negative
JOTAL1	source contributions	positive	positive	negative	positive	negative
JOTAL2	source contributions	positive	negative	negative	positive	negative
BUNDA1	source contributions	positive	negative	negative	negative	negative
BUNDA2	source contributions	positive	negative	negative	negative	negative
MARKIS	source contributions	positive	negative	negative	negative	positive
WILKHA	source contributions	positive	negative	positive	negative	negative
HATZEN	source contributions	positive	negative	positive	negative	negative
HATZEM	source contributions	positive	negative	negative	negative	positive
BISSIN	source contributions	positive	positive	negative	negative	negative
LUTZOW	source contributions	positive	positive	negative	negative	negative
BISSIM	source contributions	positive	positive	negative	negative	negative
YOREK	source contributions	positive	positive	negative	negative	negative
SIMONS	source contributions	positive	negative	positive	negative	negative
SIMONB	source contributions	positive	negative	negative	negative	positive
SIMONM	source contributions	positive	negative	negative	negative	positive
VIEHOF	source contributions	positive	negative	negative	positive	negative

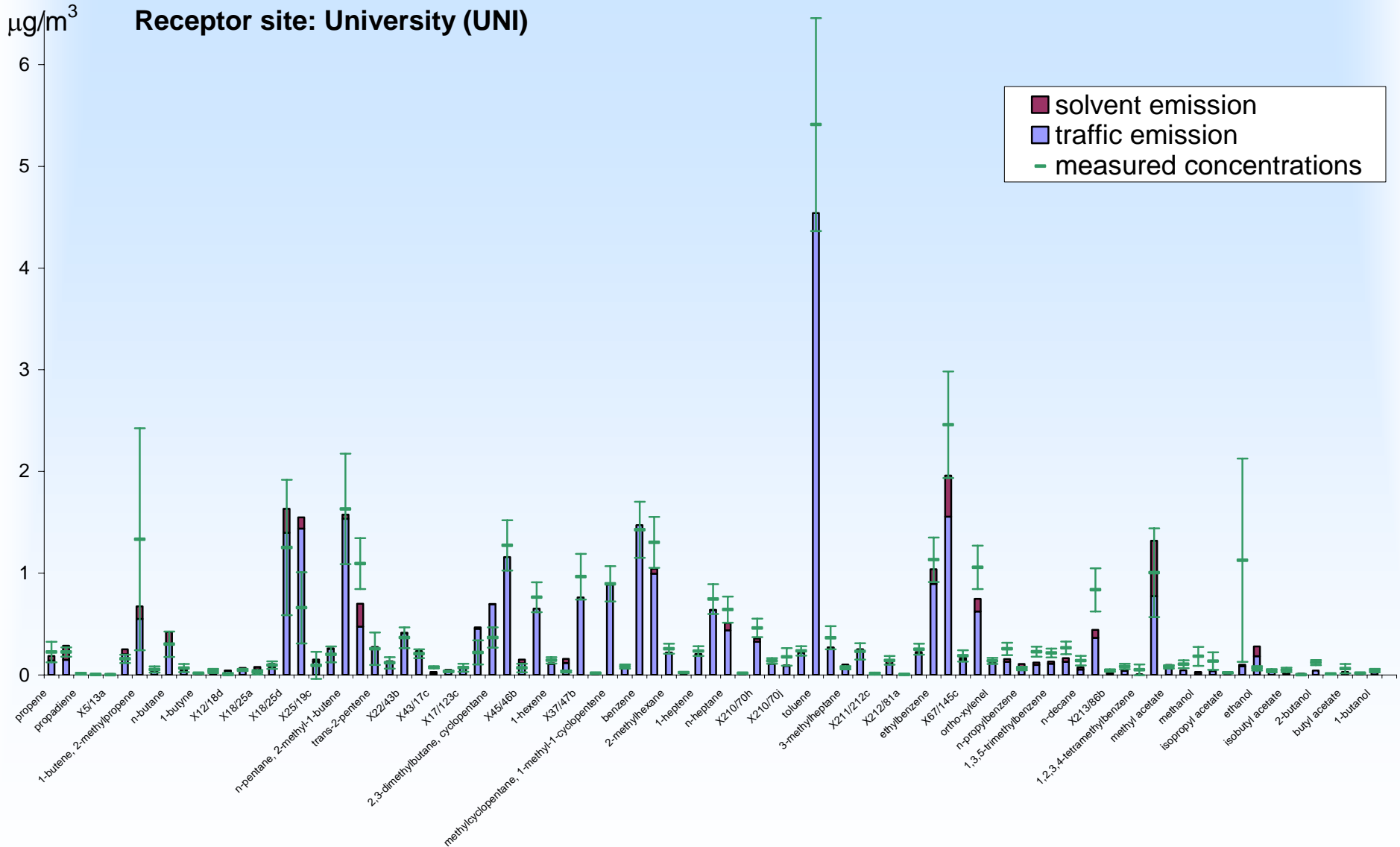
- CMB analysis has been executed with 102 NMVOCs
- all measured receptor profiles were analysed using *one* average fingerprint for traffic and *four* selected different fingerprints for solvent use emissions
- some of the solvent fingerprints did not fit to the concentration profiles of a particular receptor point; negative contributions were obtained
- in a second step the CMB analysis was executed only with those profiles which gave positive contributions

# CMB results

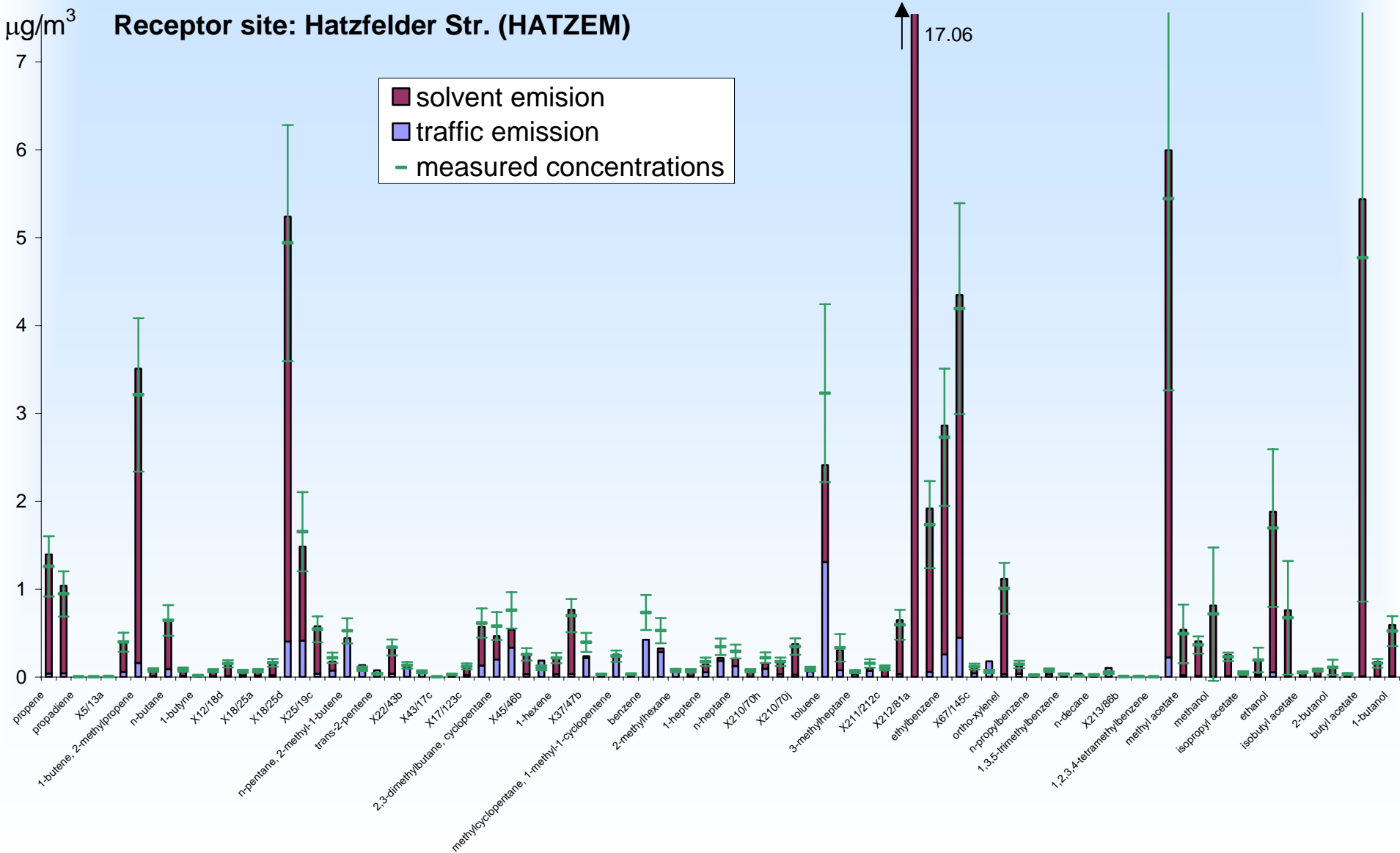


- the contribution of source categories vary in location
- the concentrations reproduced by the CMB model do not completely cover the measured concentrations
- on average ( $77.0 \pm 19.5$ ) % of the measured total NMVOC concentration were accounted by the CMB analysis

# Source contributions- receptor site UNI

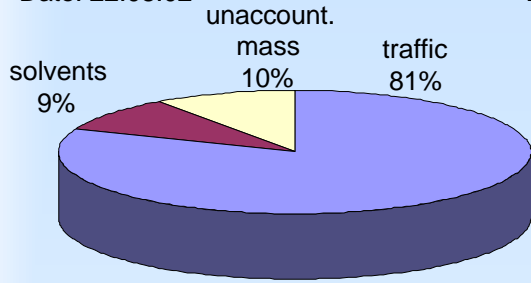


# Source contributions - receptor site HATZEM

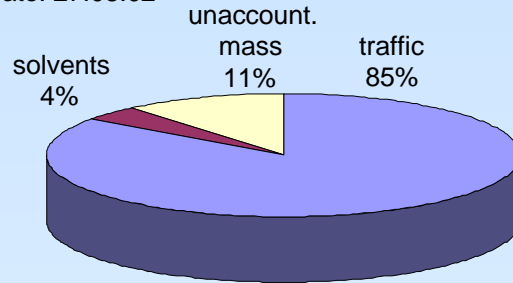


# Source contributions

Receptor site: **University(UNI)**  
Date: 22.08.02

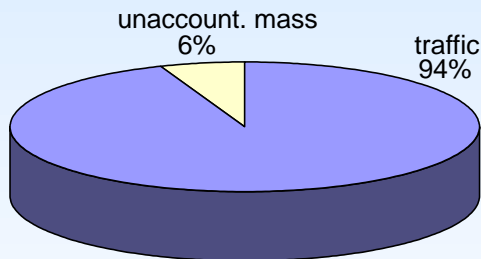


Receptor site: **Im Johannistal(JOTAL2)**  
Date: 27.08.02



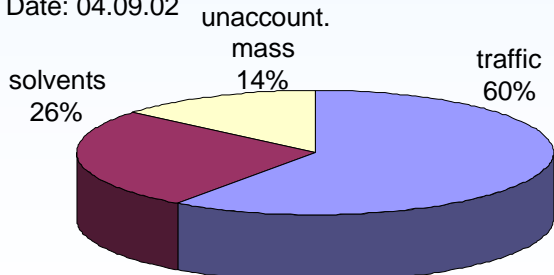
- for the receptor points located down-wind from the city centre the relative contributions of traffic and solvents to the total concentration at the sites were about **91** and **9%**, respectively

Receptor site: **Bundesallee(BUNDA1)**  
Date: 26.08.02

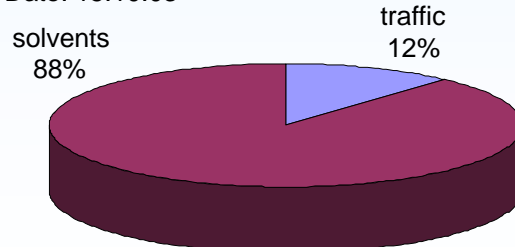


- for receptor points located in dense traffic areas more than **99%** of the apportioned concentrations come from traffic emission

Receptor site: **Lützow Str.(LUTZOW)**  
Date: 04.09.02



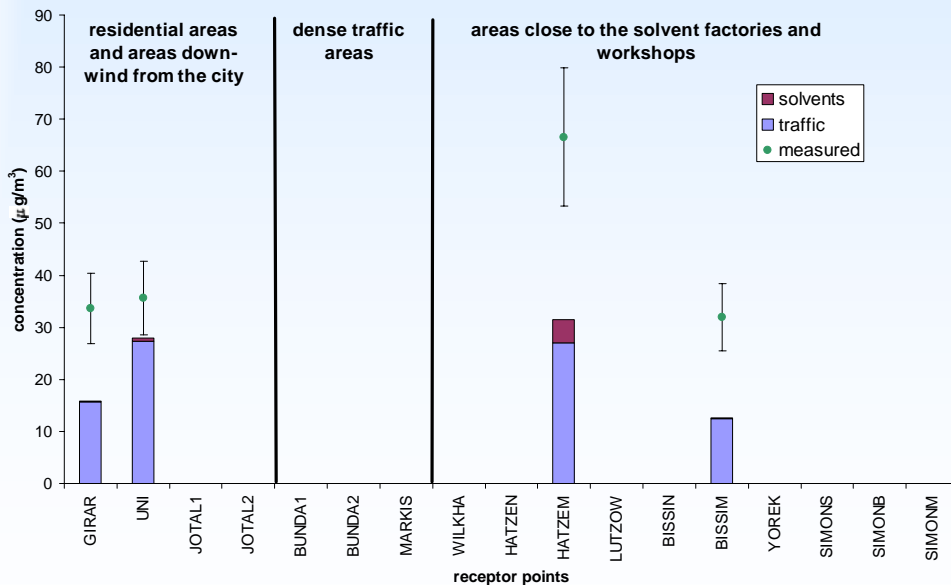
Receptor site: **Hatzfelder Str.(HATZEM)**  
Date: 15.10.03



- for receptor points located in close neighbourhood of solvent factories and workshops the relative contributions of traffic and solvents to the total concentrations were about **55** and **45%**, respectively

# Additional CMB analysis

- analysis for receptor points located in Wuppertal performed with solvent use emission profiles taken from the emission calculations of Theloke *et al.* (2000)
- besides the traffic profile obtained from the measurements performed in Wuppertal three calculated solvent profiles were applied; the profile representing the total solvent use emission, the profile for paint application and the profile for domestic solvent use
- all profiles were limited to 30 variables according to limitations of the compound speciation of the emission inventory



- no satisfying results
- calculated solvent profiles based on the data from the emission inventory could not be recognised in the measured concentrations at the receptor points
- only for some receptor points the minor contributions from the calculated solvent profiles were found
- the fact that the calculated solvent profiles do not fit to the measured NMVOC concentrations very likely indicates some major disagreements between the calculated and effective solvent use emissions

# *CMB results from Wuppertal in comparison with other studies*

- compared studies differ in terms of the chemical compounds used in the calculation and the applied source profiles
- all studies came to the similar conclusion, that the emissions from road traffic together with evaporative losses of fuel still dominate the NMVOC composition in urban air

emission sources	Wuppertal <sup>a</sup>			Berlin <sup>b</sup>			Augsburg <sup>c</sup>
	dense traffic areas <sup>1</sup>	residential areas and areas down-wind from the city centre <sup>1</sup>	industrial areas <sup>1,2</sup>	street sides	residential areas	rural back-ground	areas down-wind from the city centre
traffic exhaust	99%	91%	55%	89%	83%	60%	19%
fuel evaporation	-	-	-	6%	7%	7%	29%
natural gas	-	-	-	5%	10%	33%	-
household	-	-	-	-	-	-	22%
solvent use	1%	9%	45%	-	-	-	5%
trade and industry	-	-	-	-	-	-	24%

<sup>a</sup> this study; <sup>b</sup> Thijsse and van Oss, 1977; <sup>c</sup> Mannschreck, 2000

<sup>1</sup> average from the results for various receptor points; <sup>2</sup> areas close to the solvent factories

- many others NMVOC apportionment analyses, mostly from United States, reported at least qualitatively similar results (Watson *et al.*, 2001 and references therein)
- vehicle exhaust and gasoline evaporation contribute with 50% or more to the ambient NMVOC concentrations for most of these studies
- the relative contributions from motor vehicle emissions were significantly larger from CMB modelling than the numbers given in the national emissions inventories
- the contributions from coating and solvent applications derived from CMB analysis were much lower than the proportions attributed to these sources in the national emission inventories

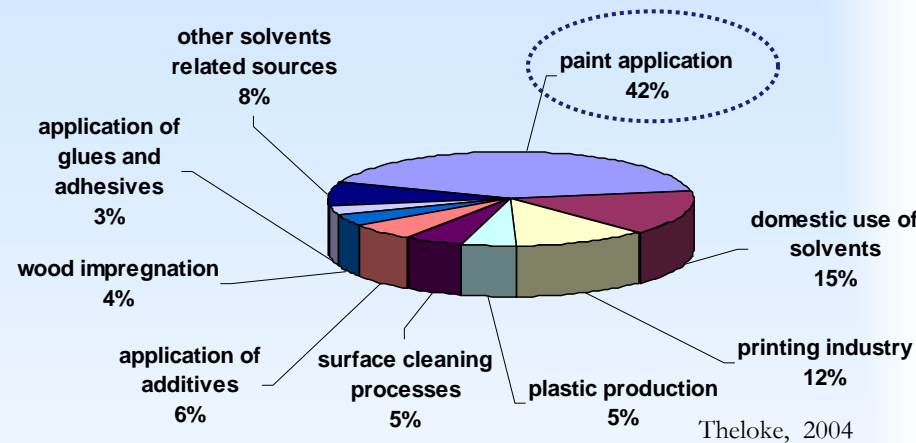
# Upper limit of solvent use contribution

- solvent profiles applied in the CMB analysis do not cover the whole solvent use emission
- they represent the most important emission sector of production and application of paints and varnishes
- this sector is responsible for about 40% of total solvent emission

**9%** maximum contribution of solvent emission, understood as emission of the paint application sector, apportioned by the CMB analysis to the receptor points down-wind from the city centre of Wuppertal

**14%** maximum contribution of remaining solvent sectors to the NMVOC concentrations in Wuppertal, calculated using the CMB results and the ratio between the paint application sector and the total solvent use emission of 0.4

**23%** maximum contribution of solvent use to the total NMVOC emission in the whole urban area of Wuppertal



lower limit of the solvent use contribution - the lowest apportionment by CMB solvent contribution at the receptor points located down-wind from the city centre - about **4%**

# *Final conclusions*

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- ◆ The results of the CMB analysis showed that road traffic rather than solvent use mainly contributes to the ambient NMVOC concentrations
- ◆ Contribution of traffic emission was dominant at all investigated sites located down-wind from the city centre, with a relative contribution on average of about 90%. At dense traffic areas the traffic emission was responsible for almost 100% of the NMVOC concentrations. A significant influence of solvent emissions could only be observed in the close vicinity of solvent factories, where the impact of the investigated solvent sources amounted on average to about 45% of the measured NMVOC concentrations.
- ◆ Obtained estimations of maximum **20%** of solvent use contribution can be taken for the whole of Germany as Wuppertal can be considered as a German city with a typical share of traffic, industry and domestic activities
- ◆ The results strongly disagree with the German Emission Inventory which states, that at present (reference year 2000) about 62% of the total NMVOC emissions originate from solvent use and only 18% from road traffic (UBA, 2001; Theloke *et al.*, 2001)
- ◆ This disagreement is supported by the results of two other experimental studies previously carried out in Berlin(1996) and Augsburg (1998)
- ◆ More measurements and calculations are necessary in order to improve the emission profiles for solvent use and to include additional emission sources into the CMB apportion analysis
- ◆ It is hoped that the outcome of the present work will also initiate further experimental studies aimed at improving the NMVOC emission inventories in Europe





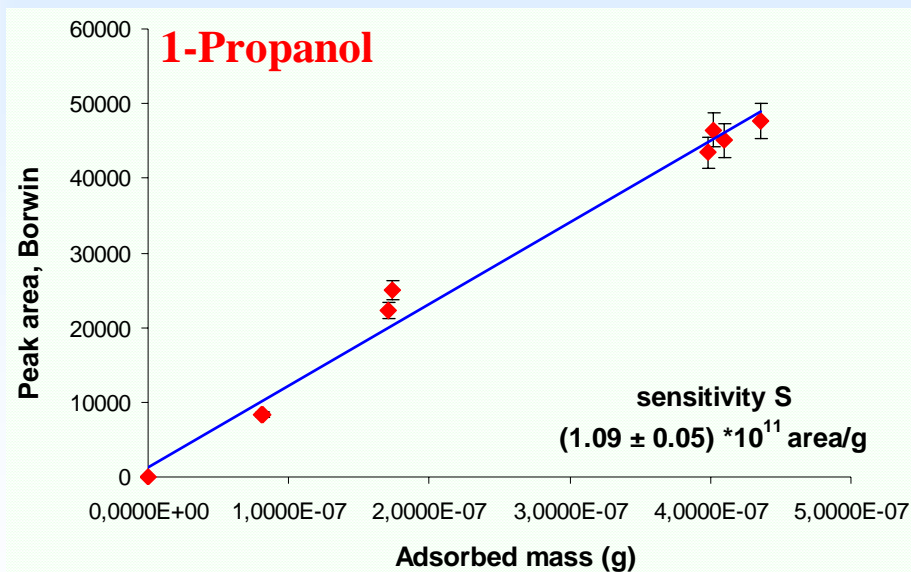
# Calibration

## 1. Hydrocarbons

NPL (*National Physics Laboratory*) standard gas mixture with 30 C<sub>2</sub>-C<sub>10</sub> compounds

## 2. Oxygenated compounds

pure liquid substances (*Aldrich, Lancaster, Merck*)



- ★ substrate - synthetic air mixtures in a 405 l reaction chamber (298 K and 760 Torr)
- ★ determination of the substrate concentration by FTIR spectroscopy (*Nicolet Magna 550*)
- ★ active sampling onto adsorption tubes
- ★ thermal desorption, GC-FID analysis

# Oxygenated compounds mixing ratios

	<i>methanol</i>	<i>ethanol</i>	<i>i-</i> <i>butanol</i>	<i>ethyl</i> <i>acetate</i>	<i>propyl</i> <i>acetate</i>	<i>butyl</i> <i>acetate</i>	<i>acetone</i>	<i>2-</i> <i>butanone</i>
Wuppertal 2001-2003 <sup>a</sup>	0.17	0.78	0.13	0.05	0.06	3.14	1.79	0.05
Milan, Italy <sup>b</sup>	-	-	0.20	-	-	-	-	-
Grenoble, France <sup>c</sup>	-	2.20	-	-	-	-	-	-
Creteil, France <sup>c</sup>	-	2.96	-	-	-	-	-	-
Porto Alegre, Brazil <sup>d</sup>	-	10.30	-	-	-	-	5.30	0.71
Rio de Janeiro, Brazil <sup>e</sup>	14.00	66.40	-	-	-	-	-	-
Sao Paulo, Brazil <sup>e</sup>	19.60	36.20	-	-	-	-	-	-
Los Angeles, USA <sup>f</sup>	16.70	17.70	-	-	-	-	-	-
Hamilton, Kanada <sup>g</sup>	-	-	0.40	0.03	0.06	0.03	2.28	0.44
Alabama, USA (rural) <sup>h</sup>	11.00	1.20	-	-	-	-	4.20	0.49
Wank, Germany (remote) <sup>i</sup>	2.26	0.24	-	-	-	-	1.71 <sup>1</sup>	0.19
Arctic <sup>j</sup>	-	-	-	-	-	-	1.30	-

<sup>1</sup> acetone and propanal

<sup>a</sup> this study; <sup>b</sup> Ciccioli, 1993; <sup>c</sup> Mond *et al.*, 2003; <sup>d</sup> Grosjean *et al.*, 1998; <sup>e</sup> de Paula Pereira *et al.*, 1999;

<sup>f</sup> Lonneman *et al.*, 1997; <sup>g</sup> Aiello *et al.*, 2000; <sup>h</sup> Goldan *et al.*, <sup>i</sup> Leibrock and Slemr, 1997; <sup>j</sup> Yokouchi *et al.*, 1994

# *Percentage NMVOC emission from road transport and solvent use over Europe in 1994 (CORINAIR)*

