



The contribution of traffic and solvent use to the total NMVOC emission in a German city derived from measurements and CMB modelling

Anita Niedojadlo*, Karl Heinz Becker, Ralf Kurtenbach, Peter Wiesen

Laboratory of Physical Chemistry, Fachbereich C, Bergische Universität, Gaußstr. 20, D-42097 Wuppertal, Germany

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Abstract

In order to quantify the contribution of solvent use and road traffic to the total non-methane volatile organic compound (NMVOC) emissions in Germany, the composition of air in the city of Wuppertal was investigated during three campaigns at different locations. The measurements covered NMVOCs in the range of C₃–C₁₀ hydrocarbons and C₁–C₆ oxygenated compounds. An assessment of the contribution from different emission sources to the observed NMVOC concentrations was attempted with the chemical mass balance (CMB) modelling technique. Emission profiles for traffic were obtained from measurements performed in a traffic tunnel, at a downtown street intersection and during drives through the city and on motorways. Solvent emission profiles were investigated in the vicinity of different factories and workshops using solvents in Wuppertal. Apportionment analyses were performed for several receptor points located down-wind from the city centre, in residential, dense traffic and industrial areas.

The results of the present work show that traffic emission rather than solvent use determines the ambient NMVOC composition. The maximum contribution of solvent use to the NMVOC emission estimated on the basis of experimentally obtained results amounts to about 23% in the whole area of Wuppertal. It can be concluded that the contribution of solvent use to the NMVOC concentrations also in other German cities falls in the range of few to about 20%, assuming that Wuppertal can be considered as a typical German urban area with certain proportions of domestic, traffic and various industrial activities. These results are in strong disagreement with the German Emission Inventory, which states, that in the reference year 2003 about 51% of the total NMVOC emissions originate from solvent use and only 14% from traffic.

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1. Introduction

The number of processes from which anthropogenic non-methane volatile organic compounds

(NMVOCs) are emitted is very large, covering not only many branches of industry, but also transport, agriculture and domestic sources. The total NMVOC emission and the proportions between particular source categories obviously differ from country to country. In Europe, road traffic and solvent use are by far the most important emission sources of anthropogenic NMVOCs (EEA,

*Corresponding author. Tel.: +49 202 439 2513;
fax: +49 202 439 2757.

E-mail address: niedan@uni-wuppertal.de (A. Niedojadlo).

2005), which in particular can clearly be recognised for Germany. According to the German Federal Environmental Agency emission inventory a significant reduction of more than 50% in NMVOC emissions occurred, namely from 3534 kt in 1990 to about 1460 kt in 2003. From the inventory it also follows that the relative importance of NMVOC emissions from solvent use has significantly increased in comparison to traffic sources over time. Since 1992 emissions from sources related to solvents outnumber the emission from traffic, with an increasing disproportion (UBA, 2005).

On the contrary to the emission inventory, data of ambient concentration measurements from different German cities always show that road traffic is still the dominant source of shorter chain (C_2 – C_{10}) hydrocarbons (Thijssse et al., 1999; Mannschreck, 2000; Kurtenbach et al., 2002; Slemr et al., 2002; Winkler et al., 2002). These reported disagreements may suggest that the officially accepted emission data from solvent use are either currently over-estimated or many components have not been covered by the ambient measurements.

In the case of solvent use, the estimation of the emission strength is much more difficult than for road traffic. NMVOCs attributed to solvent use originate from many different sources, processes and activities and their emission is very dispersed and mostly uncontrolled. Moreover, the emissions from solvent use contain oxygenated species, which are more difficult to analyse (McInnes, 1996; Theloke et al., 2001; Ullmann's Encyclopedia, 2001). Hence, relatively few measurements quantifying emissions due to solvent use are available and those, which are available, are normally limited to the aliphatic and aromatic hydrocarbons and the simple aldehydes and ketones (Thijssse et al., 1999; Vega et al., 2000; Choi and Ehrman, 2004).

Consequently, the solvent emissions reported in the inventories are estimated only on the basis of calculations using the production and consumption of solvents. Such estimations include surrogate indicators such as quantification of solvent use or solvent containing products, amount of manufactured goods, areas covered with solvent-based coatings or even emissions calculated per capita in the case of domestic solvent use (Censullo et al., 1996; Wickert et al., 1999; Brandt et al. 2000; Censullo et al., 2000; Jenkin et al., 2000; Klimont et al., 2000; Placet et al., 2000; Passant, 2002; EPA, 2004). In Germany, the model of the Federal Environmental Agency for calculating the emissions

was further developed by Theloke (Theloke, 2005; Theloke et al., 2000, 2001; Friedrich et al., 2002). The calculations are based on statistical data on the inland production of solvent containing goods and their import and export. The emission factors are derived by considering applications, control techniques and dispersion to other compartments.

In order to clarify the contribution of solvent use to the total NMVOC emissions, an investigation of the composition of the city air of Wuppertal has been undertaken in the present study. In this work atmospheric concentrations of a large variety of NMVOCs emitted by different anthropogenic sources including aliphatic and aromatic hydrocarbons and oxygenated species such as alcohols, esters and ketones have been analysed.

The aim of the study was to detect and quantify the contribution from solvent use in comparison to the emission from traffic in the urban air of Wuppertal. A successive task was to create typical, real world NMVOC source profiles of road traffic and solvent use and through the implementation of a chemical mass balance (CMB) source apportionment technique to calculate the contributions from these two source types to the measured total ambient NMVOC concentration.

2. Measurement procedure

The NMVOC concentrations in ambient air were measured by means of GC/FID analysis with cryofocussing as enrichment system and adsorption tubes as sampling device (Woolfenden and McClenny, 1999). The measurements covered volatile hydrocarbons in the range of C_3 – C_{10} and C_1 – C_6 oxygenated compounds. Preparatory tests approved the performance of the method applied in the present work. Glass tubes with 6 mm o.d., wall thickness of 1 mm and 114 mm length, supplied by Supelco were used. They were filled with solid adsorbents up to the bed length of 40 mm. As adsorption material a combination of Carbotrap and Carbosieve SIII was used. Quality assurance and performance criteria for the adsorption sampling in ambient air by means of selected adsorption tubes were tested by specification of such parameters as tube backgrounds, breakthrough volume, safe sampling volume, analytical precision, sample recovery and their storage stability. C_2 hydrocarbons were excluded from further analysis according to very low breakthrough volume.

The sampling was carried out by a fixed flow of 100 ml min^{-1} . The sampling time varied according

to the expected NMVOC concentrations in the sample gas. The total sampled volume ranged from 1000 to 7000 ml. Sorbent tubes were placed as the first element in the sampling train reducing the possibility of contamination from further elements. A membrane pump with operating flows up to 5000 ml min⁻¹ was applied. The sampling rate mass flow was regulated by Bronkhorst HI-TEC controllers. Storage times for sampled tubes before analysis differed from a day up to one month.

The thermal desorption process was performed in the Supelco Thermal Desorption Unit Model 890. Analytes were desorbed from the tube in backflush mode, with the gas flow in reverse direction of the air flow during sampling. The desorption was performed in a helium flow of 40 ml min⁻¹ over 5 min. The desorption temperature was 350 °C for hydrocarbons and 300 °C for oxygenated compounds, respectively.

After thermal desorption the analyte was re-concentrated. Cryo-focusing was applied by using as enrichment technique the Preconcentrator 7100 from Entech Instruments, an automatic sampler, cryo-focuser and injector. As a cooling medium liquid nitrogen was used.

To improve the chromatographic separation, hydrocarbons and oxygenated species were analysed separately by applying two different gas chromatographs. Hydrocarbons were analysed by a GC-FID instrument (Hewlett Packard GC 6890) equipped with a non-polar capillary column (HP-1, 90 m), whereas for oxygenated species a GC-FID instrument (Hewlett Packard GC 5840A) with polar capillary column (DB-WAX, 60 m) was applied.

Calibration was performed using a certified gas mixture containing 30 C₂–C₉ hydrocarbons from the UK National Physical Laboratory and a gas mixture containing 17 C₁–C₆ oxygenated compounds, whose concentrations were determined by FTIR spectroscopy. The detection limits ranged from 0.002 to 0.077 µg m⁻³ depending on the component in a sample volume of 6000 ml. The precision that describes a measure of agreement among the results from repeated measurements using different sampling tubes followed by thermal desorption, preconcentration and GC/FID analysis was on average 17%.

3. Measurement sites

NMVOC measurements were carried out during three campaigns performed in September 2001,

August/September 2002 and October 2003. A car equipped with a NMVOC sampling system and additional automatic analysers for carbon monoxide, carbon dioxide, nitrogen oxides and meteorological parameters was used. Samples were collected at different areas of Wuppertal and near known sources of NMVOCs (Fig. 1).

To obtain representative NMVOC emission profiles for road traffic, measurements were performed in areas characteristic for traffic conditions, e.g. a traffic tunnel, a downtown street intersection, streets within the city centre and motorways.

As traffic tunnel, the Kiesberg Tunnel located in the city of Wuppertal connecting the motorway A46 between Düsseldorf and Wuppertal with the centre of Wuppertal-Elberfeld was chosen. The tunnel has a length of 1.1 km and consists of two independent tubes in east–west direction. During the measurements the samples were collected inside the tunnel, roughly 10 m from the outlet of the tube in direction to Wuppertal-Elberfeld. Due to the short distance to the motorway A46 it could be assumed that the cars passing the tunnel were operated under “warm” driving conditions. It was also assumed that the air at the measurement point was well mixed over the whole tunnel length by the turbulence caused by the traffic flow. For the investigation of the traffic emission under “stop and go” driving conditions a street intersection located in the centre of Wuppertal-Elberfeld was chosen. Samples were collected at the Bundesallee (German National Road B7), directly at the intersection, in between two street lanes. To characterise the traffic emissions, samples were also collected during drives in the city centre of Wuppertal and on motorways.

In order to create the NMVOC emission profiles for solvent use, measurements were performed in the neighbourhood of various paint and coating factories using solvents and workshops in Wuppertal, namely DuPont Performance Coatings GmbH, PPG Industries Lacke GmbH, Bayer AG, Dr. Alfred Conrads Lackfabrik Nachf. KG and Karosseriebau Gorn GmbH. Further down in the text a term solvent factories will be used for those selected factories.

DuPont Performance Coatings is the biggest producer of car coating products worldwide and the fourth biggest varnish factory. The branch in Wuppertal is specialised in the production of automotive coating systems, products for vehicle repair, coatings for plastic surfaces, coatings for

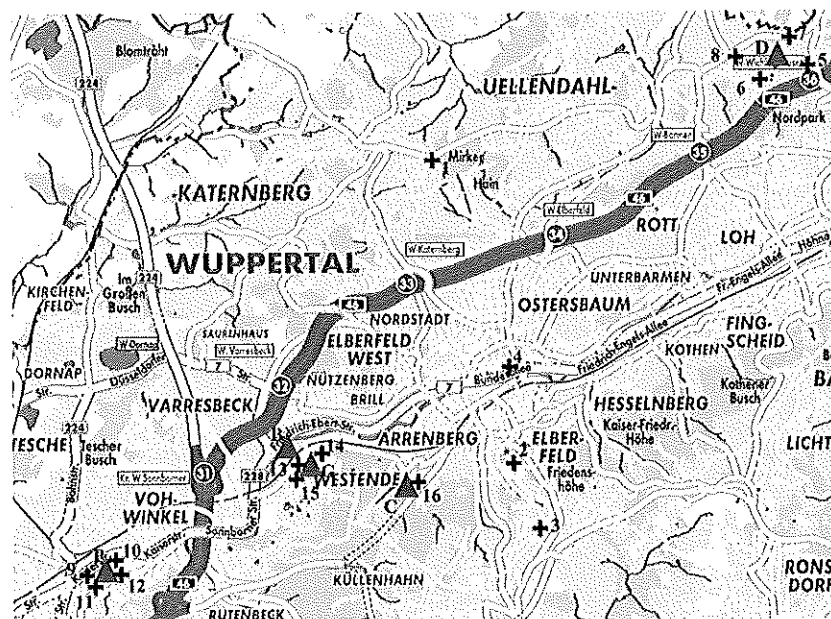


Fig. 1. Location of the receptor points (+) and sites of the investigated solvent factories and workshops (▲). D: DuPont Performance Coating GmbH, P: PPG Industries Lacke GmbH, B: Bayer AG, C: Dr. Alfred Conrads Lackfabrik Nachf. KG, G: Karosserbau Gorn GmbH. 1: GIRAR, 2: UNI, 3: JOTAL—receptor points 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.

metal surfaces, electrodeposition coatings, digital inks, protective coatings and special adhesives. The DuPont plant is located in Wuppertal-Barmen and is the most important emitter of NMVOCs in Wuppertal with an estimated annual emission (year 2000) of about 206 Mg (LUA, 2004). PPG Industries Lacke is the next biggest producer of paints and coatings in Wuppertal. The product range of the factory contains automobile and general industrial coatings, automobile repair coatings, coatings for the packaging industry, coil coating and coatings and sealings for the aircraft industry. PPG is located in Wuppertal-Vohwinkel with an annual NMVOC emission (year 2000) of about 6 Mg (LUA, 2004). The Bayer plant with its annual NMVOC emission (about 51 Mg in 2000) belongs also to the most important emitters in Wuppertal (LUA, 2004). The branch in Wuppertal-Elberfeld produces pharmaceuticals, but mainly chemical materials. Dr. Alfred Conrads Lackfabrik is located in the Wuppertal-Elberfeld and belongs to the 20 most important NMVOCs emitters in Wuppertal with an annual emission (year 2000) of about 2 Mg (LUA, 2004). Beside industrial and corrosion protection coatings, also a number of specialities for artists, architects and restorers belong to the product assortment of the Conrads enterprise. The

workshop Gorn located in Wuppertal-Elberfeld was also investigated with respect to NMVOC emissions. The plant is mainly engaged in car repair coating.

Due to the fact that the emissions from solvent factories are spread over a larger area different to a single point source, the direct determination of the emission strength was not possible. Because of this, the emission profiles of particular factories were measured down-wind of the source and in the background. Additionally, for a better identification of the contaminated plume coming from the investigated source, tracer experiments were performed. Sulphur hexafluoride as tracer gas was emitted up-wind from the source and measured down-wind.

The ambient NMVOC concentrations were measured at different points located in Wuppertal. The sampling sites represented residential, industrial, mixed settings and areas down-wind from the city centre. The locations of the receptor points and of the investigated solvent factories are shown in Fig. 1.

4. Measurement results

The mixing ratios measured during the campaigns are summarised in Table 1 showing the maximum,

minimum and average values. It is evident that among alkanes 2-methylpentane and *i*-pentane, among alkenes and alkynes *i*-butene and 1-butene, among aromatic hydrocarbons toluene followed by *meta*- and *para*-xylene and among oxygenated compounds *n*-butyl acetate and acetone showed the largest mixing ratios.

Because the measurements were carried out at different sites being influenced by different NMVOC sources also different patterns of the measured NMVOC-mix were observed. As an example, the comparison of mixing ratios of some

of the most abundant compounds in different areas is presented in Fig. 2. For the sampling point relevant for traffic (Bundesallee) toluene has the highest mixing ratio. The values of other important compounds such as xylenes, benzene and other aliphatic hydrocarbons fall in the same mixing ratio range, whereas, except for acetone, no oxygenated NMVOCs are important here. For the samples collected close to the PPG varnish factory (Bissing Street) the most important compounds are xylenes, toluene and acetone. On the contrary to traffic, also some other oxygenated compounds such as

Table 1
Overview of NMVOC mixing ratios (ppbV)^a measured during the study carried out in Wuppertal

Compounds	ID number	Max	Min	Average	St. dev. ^b
Propene	6	1.06	0.06	0.35	0.25
Propane	7	1.53	0.01	0.43	0.46
Propadiene	4	0.09	0.01	0.01	0.02
Propyne	5	0.06	0.01	0.01	0.02
2-Methylpropane	13	0.74	0.02	0.24	0.19
1-Butene/ <i>i</i> -butene	10,11	2.57	0.28	0.86	0.53
1,3-Butadiene	8	0.12	0.01	0.05	0.03
<i>n</i> -Butane	14	1.16	0.03	0.41	0.35
<i>trans</i> -2-Butene	9	0.23	0.02	0.07	0.05
1-Butyne	203	0.05	0.01	0.01	0.01
<i>cis</i> -2-Butene	12	0.19	0.02	0.06	0.05
3-Methyl-1-butene	18	0.32	0.02	0.06	0.06
<i>i</i> -Pentane	25	5.49	0.22	1.20	1.23
1-Pentene	19	1.83	0.03	0.20	0.33
<i>n</i> -Pentane/2-methyl-1-butene	26,20	9.76	0.10	1.13	1.79
2-Methyl-1,3-butadiene	16	1.22	0.03	0.34	0.29
<i>trans</i> -2-Pentene	21	2.13	0.01	0.20	0.40
<i>cis</i> -2-Pentene	22	1.03	0.01	0.13	0.19
2,2-Dimethylbutane	43	1.01	0.01	0.13	0.19
Cyclopentene	17	0.29	0.01	0.04	0.06
Methyl <i>tert</i> -butyl ether	123	1.19	0.01	0.27	0.26
2,3-Dimethylbutane/cyclopentane	44,24	4.65	0.06	0.55	0.86
2-Methylpentane	45	6.70	0.09	0.78	1.21
3-Methylpentane	46	3.80	0.03	0.44	0.68
1-Hexene	37	0.59	0.02	0.08	0.10
<i>n</i> -Hexane/2-ethyl-1-butene	47,204	3.75	0.08	0.53	0.69
2,3-Dimethyl-1,3-butadiene	205	0.26	0.01	0.02	0.05
Methylcyclopentane/1-methyl-1-cyclopentene	41,206	5.24	0.06	0.58	0.95
2,3-Dimethyl-2-butene	207	0.53	0.01	0.05	0.09
Benzene	28	5.60	0.16	0.99	1.08
Cyclohexane/2,3-dimethylpentane/1,3-cyclohexadiene	42,58,208	4.98	0.08	0.68	0.90
2-Methylhexane	62	0.98	0.02	0.12	0.18
Cyclohexene	30	0.11	0.01	0.02	0.02
1-Heptene	209	0.87	0.02	0.12	0.15
2,2,4-Trimethylpentane	69	2.89	0.04	0.32	0.52
<i>n</i> -Heptane	61	1.84	0.05	0.27	0.34
1,4-Cyclohexadiene	210	0.04	0.01	0.01	0.01
2,3,4-Trimethylpentane	70	1.10	0.01	0.12	0.20
Toluene	48	21.00	0.38	3.09	4.00
2-Methylheptane	78	1.13	0.03	0.16	0.21

Table 1 (continued)

Compounds	ID number	Max	Min	Average	St. dev. ^b
3-Methylheptane	79	0.38	0.01	0.05	0.07
4-Methylheptane/1-methyl-1-cyclohexene	80,211	1.37	0.02	0.15	0.26
1-Octene	212	0.37	0.02	0.09	0.09
<i>n</i> -Octane	81	1.06	0.03	0.18	0.22
Ethylbenzene	64	2.17	0.05	0.54	0.50
<i>meta</i> - and <i>para</i> -Xylene	66,67	3.05	0.07	0.95	0.77
Styrene	145	0.34	0.01	0.06	0.08
<i>ortho</i> -Xylene	65	1.05	0.01	0.28	0.26
α -Pinene	124	0.68	0.01	0.09	0.15
<i>n</i> -Propylbenzene	85	0.23	0.01	0.05	0.06
4-Ethyltoluene	91	0.18	0.01	0.04	0.05
1,3,5-Trimethylbenzene	88	0.22	0.01	0.04	0.06
<i>n</i> -Decane	120	0.12	0.01	0.02	0.02
1,2,4-Trimethylbenzene/ <i>tert</i> -butylbenzene	87,213	0.80	0.01	0.13	0.19
1,2,3-Trimethylbenzene	86	0.11	0.01	0.01	0.02
1,2,3,4-Tetramethylbenzene	115	0.01	0.01	0.01	0.01
Acetone	139	17.39	0.07	1.80	3.29
Methyl acetate	164	1.23	0.01	0.16	0.27
Ethyl acetate	165	0.39	0.01	0.05	0.08
Methanol	149	1.00	0.01	0.17	0.26
2-Butanone	159	0.42	0.01	0.05	0.08
<i>i</i> -Propyl acetate	214	0.50	0.01	0.03	0.09
<i>i</i> -Propanol	151	0.84	0.01	0.15	0.19
Ethanol	150	12.47	0.01	0.78	2.36
<i>n</i> -Propyl acetate	166	0.49	0.01	0.06	0.10
<i>i</i> -Butyl acetate	168	0.28	0.01	0.02	0.05
4-Methyl-2-pentanone	160	0.18	0.01	0.01	0.03
<i>i</i> -Butanol	215	6.79	0.01	0.62	1.58
<i>n</i> -Propanol	152	1.55	0.01	0.06	0.29
<i>n</i> -Butyl acetate	167	87.02	0.01	3.14	16.14
2-Hexanone	216	0.10	0.01	0.01	0.03
<i>n</i> -Butanol	153	2.31	0.01	0.13	0.43
Cyclohexanone	161	0.14	0.01	0.02	0.03
Σ NMVOC		159.61	6.58	27.90	32.72

^aVolume mixing ratio.

^bSt. dev.—standard deviation (1σ).

1-butanol, methyl acetate and *n*-butyl acetate show high mixing ratios. In the case of the measurement performed close to the DuPont coatings factory (Hatzfelder Street) *n*-butyl acetate exhibits a very high mixing ratio of more than 87 ppbV. Also others oxygenated compounds and toluene show a large abundance.

Due to the fact that the absolute concentrations measured at different sampling sites cannot directly be compared because of different dilution factors, the commonly used normalisation to benzene is also applied in this work. Benzene is considered as a compound emitted almost exclusively from road traffic since benzene is officially prohibited from using as a solvent component in the European Union (Directive 89/677/EEC, 1989, Wickert et al., 1999).

From the NMVOC profiles (ppbC ppbC⁻¹ (benzene)) the average percentage composition of the hydrocarbon mix for all measurement points in Wuppertal was calculated. The highest contribution comes from aromatic hydrocarbons (37%) and the second highest from alkanes (32%). The contribution of alkenes and alkynes was 16% followed by the oxygenated compounds with 15%.

5. CMB analysis

An assessment of the contribution of emission categories to the observed NMVOC concentrations was made by using the CMB modelling technique, version 8, from the US Environmental Protection Agency (Watson et al., 1998). The CMB model uses an effective variance least squares solution to a set

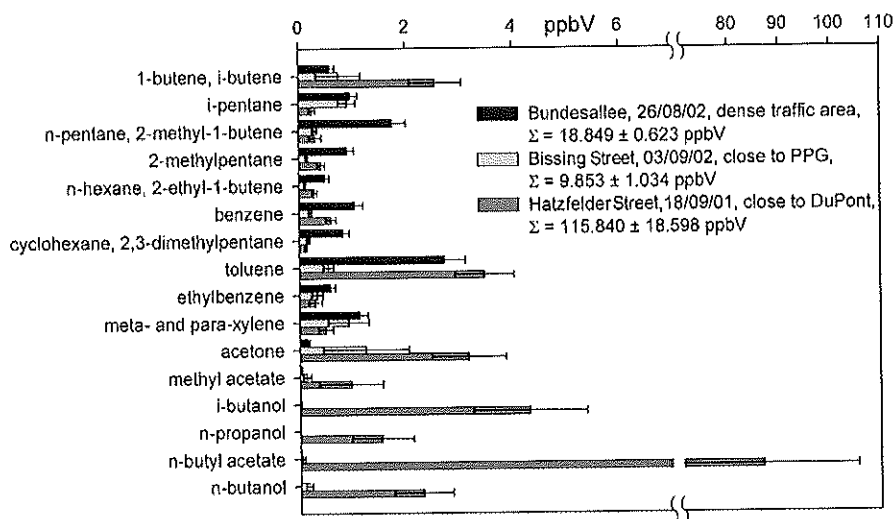


Fig. 2. Mixing ratios (ppbV) of some abundant compounds at sites under the influence of different emission sources.

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; Watson et al., 2001).

The fundamental principle of the receptor models is that mass conservation can be assumed and the composition of source emissions remains constant over the receptor and source sampling period. Therefore, the ratios between components emitted by a single source are identical to the ratios between the resulting concentrations at the receptor points. This is based on the assumption that the species undergo no chemical transformations and there is no deposition during the transport from the source to the receptor. CMB assumptions are fairly restrictive and difficult to be fulfilled in practice. However, the model tolerates some deviations, which increase the final uncertainties of the source contribution estimations (Watson et al., 1998).

5.1. Input data

As input to the CMB model serves:

- 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 Σc_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 e_i for source and receptor values, which are used to weight the relative importance of input data to model solutions and to estimate uncertainty of the source contributions.

Because the purpose of this study was to provide more information about the contribution of road traffic and solvent use to the total NMVOC emission only these two source categories were included in the CMB analysis.

In the present work concentration profiles were measured at different sites. It has been assumed, that the concentration profiles measured at sites dominated by traffic emissions like traffic tunnels, motorways, street intersections, etc. are determined only by traffic emission and provide the traffic emission profile.

The same assumption was made for the concentration profiles measured down-wind near a particular solvent factory. In this case it has been assumed that the concentration profile is exclusively originating from solvent emissions and provide a solvent use emission profile at least for the emission type of the particular factory. In reality even close to solvent factories an influence of traffic emissions on the measured c_i has to be expected. Only those concentration profiles for particular solvent sources, which significantly differed

from concentration profiles obtained from measurements in traffic areas had been taken as profiles of solvent emission after corrections for the background concentrations measured up-wind from the sources.

All measured profiles contained the concentrations of 102 NMVOC species, namely:

- 65 hydrocarbons in the range of C_3 – C_{10} from the hydrocarbon groups: alkanes, alkenes, alkynes and aromatics,
- 18 oxygenated compounds in the range of C_1 – C_6 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 $0.3 \mu\text{g m}^{-3}$ and significant variation) and because of their high significance to the source profiles diversification.

The convention has been used in this work that the sum over the relative mass distribution of the measured compounds i in the fingerprint of source j is normalised, $\sum x_{ij} = 1$.

5.2. Traffic profiles

The measurements of the source profiles from traffic emission were carried out in a traffic tunnel (Kiesberg Tunnel), at a downtown street intersection and during driving in the city centre of Wuppertal and on the motorways around Wuppertal. All profiles from measurements at sites dominated by traffic emission have been compared for establishing similarities. Fig. 3 presents the concentration distributions of the analysed compounds for all sites dominated by traffic emission.

All 10 measured profiles dominated by traffic were found to be very similar; they all show the highest contribution from toluene, about 18%, and the importance of benzene, *meta*- and *para*-xylene, 2-methylpentane, *i*-pentane, 1-butene and *i*-butene.

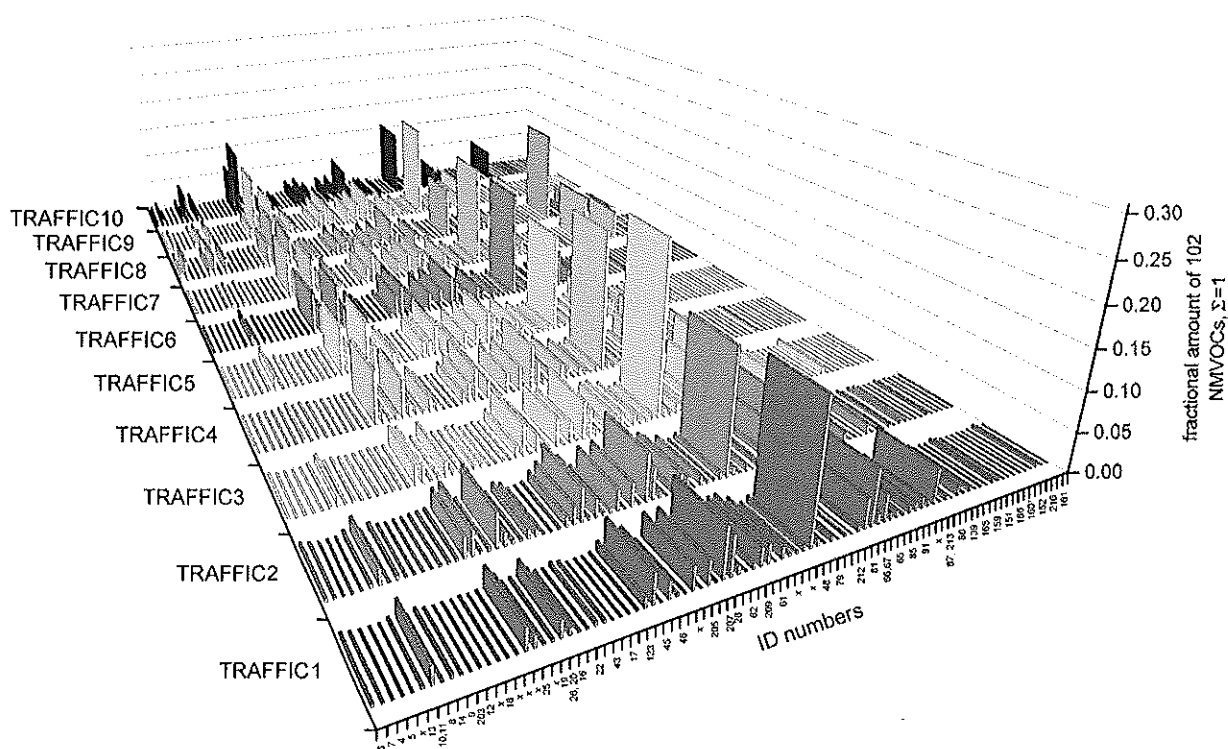


Fig. 3. Emission profiles as relative mass distribution of 102 compounds at different sites dominated by traffic emission. TRAFFIC1: Kiesberg Tunnel 1, 23/08/02, TRAFFIC2: Kiesberg Tunnel 2, 23/08/02, TRAFFIC3: Kiesberg Tunnel 3, 24/08/02, TRAFFIC4: Kiesberg Tunnel 4, 24/08/02, TRAFFIC5: Bundesallee 1, 26/08/02, TRAFFIC6: Bundesallee 2, 26/08/02, TRAFFIC7: Drive on Wuppertal streets, 04/09/02, TRAFFIC8: Drive on motorway A46, 04/09/02, TRAFFIC9: Drive on street B7, 05/09/02, TRAFFIC10: Drive on motorway A46/A3, 05/09/02, ID numbers: compounds identification numbers, see Table 1.

According to the good agreement between these profiles, they have been averaged to obtain only one traffic emission profile. This profile represents all characteristic traffic conditions and was used in the CMB analysis. The averaged traffic fingerprint is shown in Fig. 4.

The traffic profile measured in Wuppertal was compared with profiles measured in the Tegel Tunnel, Berlin (Thijssse et al., 1999), close to a busy road in Munich (Kern et al., 1998), in a tunnel-like underpass in Atlanta (Conner et al., 1995) and in the Caldecott Tunnel, San Francisco Bay area (Fujita et al., 1994). These studies are most suitable for a comparison because a large number of identical NMVOCs have been measured in the different studies. The results of the comparison are presented in Fig. 5. The figure shows, that the average profile obtained for Wuppertal agrees well with the other profiles, only a few larger deviations can be observed. Compounds like propene, *n*-butane, *i*-pentane, *n*-hexane and 1,2,4-trimethylbenzene show lower contributions in comparison with the other profiles, whereas toluene and isoprene are considerably more abundant in Wuppertal. These disagreements can be due to differences in the traffic fleet for the particular profiles. In addition, the discrepancy in fuel composition between Europe and the US and the years of the particular measurements might cause some deviations.

5.3. Solvent use profiles

To obtain relevant solvent emission profiles, measurements were performed around various

solvents factories and workshops in Wuppertal. The emission profiles for solvent use were finally obtained by subtracting the background concentration profiles normalised to benzene from the profiles measured down-wind from the factories. The solvent use fingerprints are presented in Fig. 6.

The presented solvent fingerprints exhibit much higher contributions from oxygenated compounds than in the case of traffic. For example, the measurements performed close to the DuPont factory (measurements on 15/10/2003) show a relative mass contribution of *n*-butyl acetate of about 10%. Also 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. However, the solvent profiles obtained at the different receptor points differ significantly from each other, which does not allow averaging them to one solvent emission profile as in the case of the traffic profile. Accordingly, four different solvent use emission profiles were applied in the CMB analysis.

Solvent use emission profiles measured in Wuppertal were compared with solvent profiles derived from data of emission calculations for the solvent sector in Germany. The authors are only aware of the inventory from 1994 (Theloke et al., 2000) in which the detailed emission information of individual hydrocarbons is presented. The comparison was limited to those compounds covered by the measurements in Wuppertal, namely C₃–C₁₀ hydrocarbons, alcohols, esters and ketones. The emissions reported in the inventory are specified only to several

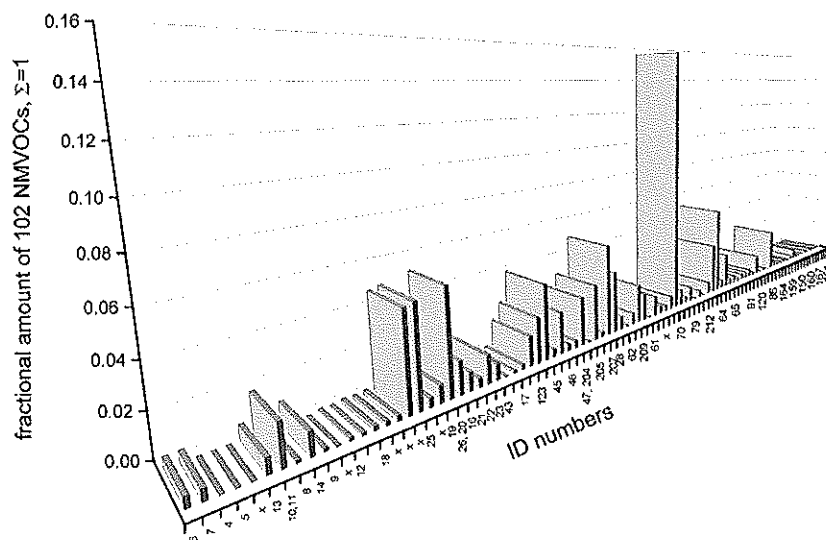


Fig. 4. Average emission profile of road traffic. ID numbers: compounds identification numbers, see Table 1.

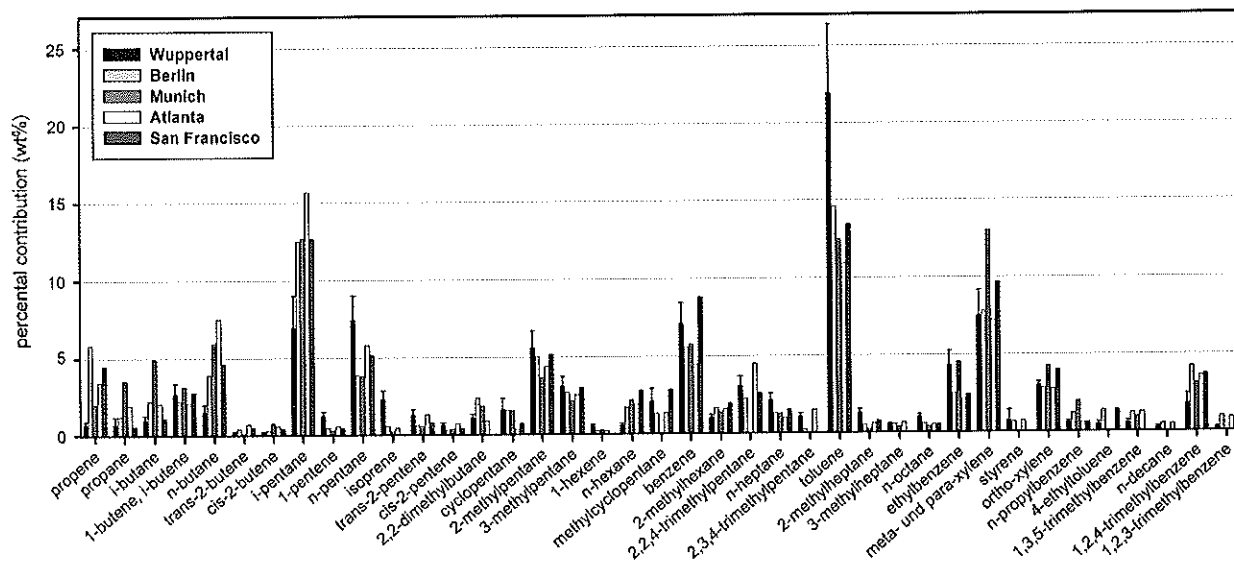


Fig. 5. Comparison of the road traffic emission profile from Wuppertal with the results from other studies.

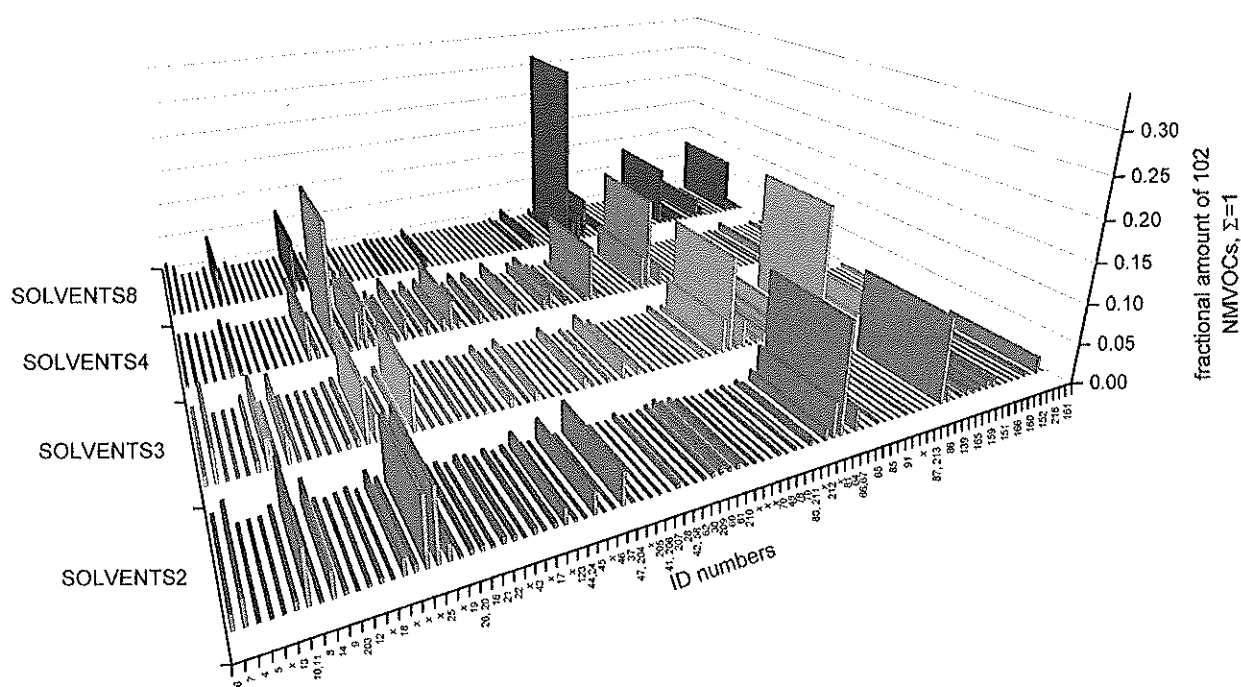


Fig. 6. Emission profiles as relative mass distribution of 102 compounds for sites points strongly influenced by emission sources of solvent use. SOLVENTS2: Bissing Street, 03/09/02, close to PPG, SOLVENTS3: Simon Street, 03/09/02, close to Gorn, SOLVENTS4: Viehof Street, 04/09/02, close to Conrads, SOLVENTS8: Hatzfelder Street, 15/10/03, close to DuPont, ID numbers: compounds identification numbers, see Table 1.

individual compounds, whereas the more significant part of the emission is represented as a total of petroleum distillates defined as “Spezialbenzin”, “Testbenzin” and “Solvent Naphta”. These market

names epitomise the hydrocarbon mixtures with rough content specifications. The ratios between particular components in these mixtures can be different for different producers making the detailed

compound specification impossible. Accordingly, only a limited number of individual compounds could be directly compared and all others were grouped under aliphatic and aromatic hydrocarbons.

All solvent emission profiles measured in Wuppertal represent sources, which are relevant to the production and application of paints and varnishes. According to the emission inventories (Theloke et al., 2000; Theloke, 2005) emissions from paint application and paint manufacturing have the same emission profiles, both sectors emit the same compounds in the same proportions. Hence, the four profiles obtained from the city measurements were compared with the calculated emission profile from total solvent use and with the calculated profile from paint applications. The results of the comparison are presented in Fig. 7.

Comparing with the total solvent emission (Fig. 7), profiles of Wuppertal solvent factories show higher contributions of the hydrocarbons propane, *i*-pentane, cyclohexane, heptane, octane and the oxygenated hydrocarbon acetone, whereas the contributions of other oxygenated species like ethanol, *i*-propanol, *n*-, *i*-butanol, ethyl acetate and *i*-butyl acetate are significantly lower. The contributions of the sum of all other not specified aliphatic and aromatic hydrocarbons agree well. For the calculated paint application emission profile, significant differences are observed with respect to profiles measured in Wuppertal for all specified

individual aliphatic hydrocarbons. According to the emission inventory, these compounds do not contribute to the emission from paint applications, but they can clearly be recognised in the profiles measured in Wuppertal. Contrary, some of the measured oxygenated species show lower contributions than the calculated equivalents. In general, among all solvent profiles measured in Wuppertal the DuPont fingerprint shows the best compatibility with the calculated emission profile for paint applications.

The differences between solvent profiles measured in Wuppertal and profiles calculated from the inventory can be due to various factors. Higher contributions of some individual aliphatic hydrocarbons in the profiles measured in Wuppertal can be due to the influence of some non-solvent sources on the measured profiles. However, they can also originate from the emission of unspecified hydrocarbon mixtures defined as “Spezialbenzin” and “Testbenzin” whose contribution is presented in inventory profiles as the sum of aliphatic and aromatic hydrocarbons.

Lower contributions of oxygenated compounds in the measured profiles may indicate that the emission of these compounds is overestimated in the emission inventory or the processes and applications responsible for the emission of these particular compounds were of less importance for the emission sources of Wuppertal, however, the latter argument

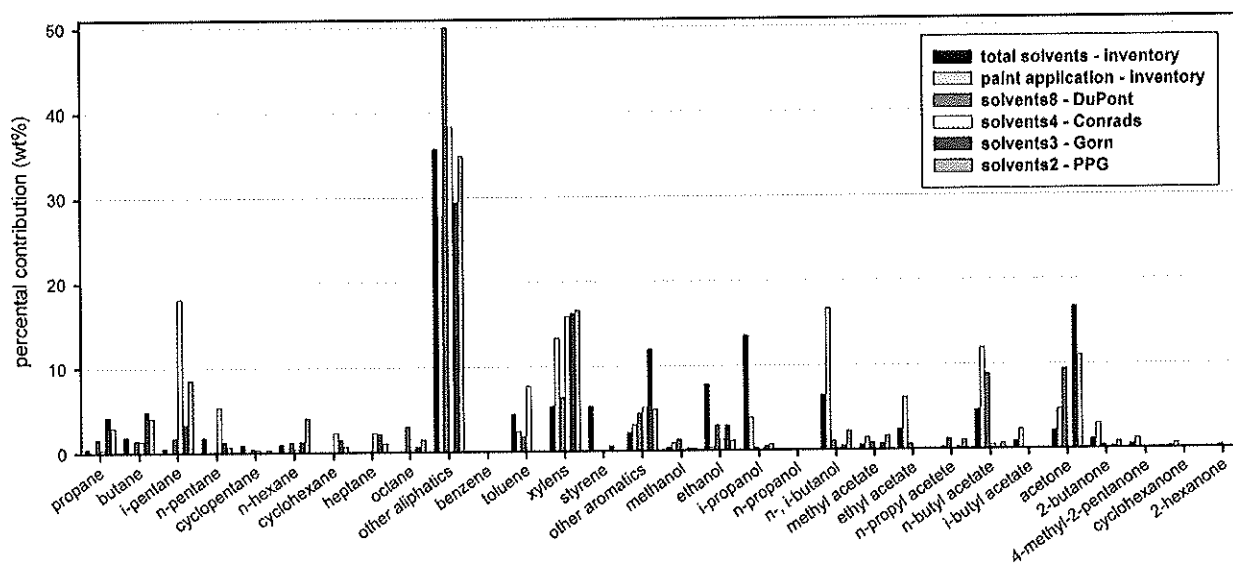


Fig. 7. Comparison of solvent use emission profiles measured in Wuppertal with the results of speciated emission calculations for Germany (Theloke et al., 2000).

seems to be unlikely. The profile based on the data of the emission inventory assumes that a certain fraction from the solvent application is always emitted into the atmosphere, which also may create a larger uncertainty in the speciation of the data from the inventory. Furthermore the activity data, solvent contents and emission factors used for the calculations of solvent emissions have an uncertainty in the range of 30–50% (Theloke, 2005). Accordingly, the computed emission data have the same uncertainty and for the single species the uncertainty is even higher.

Nevertheless, it seems to be reasonable to assume that the profiles obtained from the measurements performed in Wuppertal near several very different solvent factories and workshops represent quite well the solvent emission sector, which is related to production and application of paints and varnishes, which according to the emission inventories is responsible for about 52% of the total solvent emissions in Germany (Theloke, 2005).

5.4. Receptors

CMB analyses with the emission profiles from traffic and solvent use have been applied to the NMVOCs concentrations measured at the different receptor points in Wuppertal. The characteristics of particular receptor points, with specification of different receptor areas, are shown in Table 2.

The CMB analysis assumes that the source profiles are constant over the ambient and source sampling period, which excludes the degradation of individual compounds during the transport time from source to receptor. Based on the prevailing wind speeds during the experiments the transport time from the sources to the receptors did not exceed 40 min. Within that period the degradation of the investigated compounds by reactions with OH radicals typically does not exceed 15%, more reactive hydrocarbons like isoprene will undergo a degradation at the most of about 30%. For example, assuming a concentration of OH radicals of $1.6 \times 10^6 \text{ cm}^{-3}$ the degradation of isoprene during 40 min transport time is 32%. In addition, the reaction of ozone with isoprene will contribute around 4% to the decay of the compound (concentration of O_3 $1.23 \times 10^{12} \text{ cm}^{-3}$; 50 ppbV). Furthermore, the loss of other compounds, which are much more relevant for the study, is significantly lower. Degradation of toluene, *meta*-xylene and *n*-butyl acetate during 40 min transport time is 2%, 8% and 1%, respectively. Since the average

uncertainty of measurements of the individual compounds is about 20%, the degradation of species transported from sources to receptor points can be neglected.

6. Results of the CMB analysis

The CMB analysis has been executed with 102 NMVOC species. All measured receptor profiles were analysed using one average fingerprint for traffic and four selected different fingerprints for solvent use emissions. However, for some of the solvent fingerprints negative contributions were obtained, which can occur when the source contribution is close to zero. In a second step the CMB analysis was executed only with those profiles, which gave positive contributions. Table 3 presents the results of these CMB analyses. Shown are: (i) which emission profiles were applied in particular cases, (ii) contributions of traffic and solvent use emissions to the total NMVOC concentrations as result of the CMB analysis, (iii) the total NMVOC mass concentration calculated by the model and the measured values at the receptor points. Additionally, the error limits, performance parameters as R^2 , reduced χ^2 and percent mass accounted by the model (% mass) are given.

The results for particular receptor points are shown in Fig. 8. Plotted are the measured total NMVOC concentrations (presented as points with error limits) and the results from the CMB model for the concentrations caused by traffic and solvent use emissions (as bars), which add to the total NMVOC concentrations and can be compared with the experimental data.

Fig. 8 shows that the contributions of source categories vary in location. According to expectations, for the receptor points located in the city centre and in areas with high traffic densities, the contribution from traffic emission is dominating. On average, for receptor points located in dense traffic areas more than 99% of the apportioned concentrations result from traffic emission.

In the case of receptor points located outside of the city centre and in residential areas the contribution of traffic emission was similar as in the city centre. On average, the relative contributions of traffic and solvents to the total concentration at these sites were about 91% and 9%, respectively. The contribution diagrams of selected receptor points located down-wind from the city centre (points UNI and JOTAL2) are presented in Fig. 9.

Table 2
Receptor points for CMB analyses

Receptor points	CMB ID	Characteristic	Sampling time		Wind sector	Σ NMVOC	
						($\mu\text{g m}^{-3}$)	\pm
<i>Residential areas, down-wind from the city centre</i>							
Girardet Street	GIRAR	Down-wind from the city centre of Wuppertal	19/09/01	11:10–12:10	SE–E	34.35	2.73
Uni	UNI	Down-wind from the city centre of Wuppertal	22/08/02	15:06–16:06	N–NW	35.10	2.59
Im Johannistal	JOTAL1	Residential area outside from the city centre	27/08/02	15:55–17:05	W–NNW	39.87	1.90
Im Johannistal	JOTAL2	Residential area outside from the city centre	27/08/02	17:12–18:24	W–NNW	27.44	1.34
<i>Dense traffic areas</i>							
Bundesallee	BUNDA1	City centre of Wuppertal, dense traffic intersection	26/08/02	15:35–16:35	N–NE	73.63	2.33
Bundesallee	BUNDA2	City centre of Wuppertal, dense traffic intersection	26/08/02	16:40–17:40	N–NE	52.81	4.45
Märkische Street	MARKIS	Close to freeway A46	15/10/03	13:08–14:08	S–SE	84.29	8.47
<i>Areas close to solvent factories and workshops</i>							
Wilkhaus Street	WILKHA	Industrial area, close to DuPont solvent factory	29/08/02	13:06–14:10	NW	21.56	3.69
Hatzfelder Street	HATZEN	Industrial area, close to DuPont solvent factory	29/08/02	14:55–15:55	W–NW	55.12	3.74
Hatzfelder Street	HATZEM	Industrial area, close to DuPont solvent factory	15/10/03	12:55–14:00	S–SE	68.19	5.64
Bissing Street	BISSIN	Industrial area, close to PPG solvent factory	03/09/02	12:52–13:52	E	37.59	3.16
Lützwow Street	LUTZOW	Industrial area, close to PPG solvent factory	04/09/02	14:29–15:30	SW	28.28	1.51
Bissing Street	BISSIM	Industrial area, close to PPG solvent factory, down-wind from the object	13/10/03	13:06–14:06	E–SE	32.87	2.47
Yorck Street	YOREK	Industrial area, close to PPG solvent factory, up-wind from the object	13/10/03	13:06–14:06	E–SE	24.61	1.96
Simon Street	SIMONS	Industrial area, close to Gorn solvent workshop	03/09/02	10:35–11:40	N	28.25	2.97
Simon Street	SIMONB	Industrial area, close to Gorn solvent workshop	17/10/03	09:45–10:45	NE	124.13	10.40
Simon Street	SIMONM	Industrial area, close to Gorn solvent workshop	17/10/03	09:45–10:55	NE	88.71	10.97
Viehhof Street	VIEHOF	Industrial area, close to Conrads solvent factory	04/09/02	16:17–17:17	SW	57.00	3.01

Larger influences of solvent use emissions on the total NMVOC concentration were found for the receptor points located in areas with solvent industry (solvent factories and workshops). On average, 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. As an example, the contributions of traffic and solvent use emissions at two receptor

points located close to the solvent factories DuPont (point HATZEM) and PPG (point LUTZOW) are presented in Fig. 9.

The results from the CMB analysis for different receptor points show that 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 (Table 3). It can be concluded that some other

Table 3
Results of the CMB analyses for receptor points measured in Wuppertal

Receptor points (CMB IDs)	Source fingerprints used (CMB IDs)	Source contributions ($\mu\text{g m}^{-3}$)		Total NMVOC ($\mu\text{g m}^{-3}$)		Performance parameters		
		Traffic	Solvent use	CMB	Measured	R^2	χ^2	% mass
<i>Residential areas, down-wind from the city centre</i>								
GIRAR	TRAFFIC, SOLVENTS8	17.02±0.91	1.72±0.39	18.73±0.87	34.35±2.73	0.64	3.01	54.5
UNI	TRAFFIC, SOLVENTS3	29.18±1.65	3.27±0.95	32.45±1.37	35.99±2.59	0.83	1.29	90.2
JOTAL1	TRAFFIC, SOLVENTS2, SOLVENTS4	27.57±1.42	3.24±0.64	30.81±1.26	39.87±1.90	0.79	1.79	77.3
JOTAL2	TRAFFIC, SOLVENTS4	23.32±1.018	1.04±0.33	24.36±0.95	27.44±1.34	0.76	2.39	88.8
<i>Dense traffic areas</i>								
BUNDA1	TRAFFIC	69.42±2.33	0.00±0.00	69.42±2.33	73.67±2.33	0.89	1.22	94.2
BUNDA2	TRAFFIC	46.31±2.22	0.00±0.00	46.31±2.22	52.81±4.45	0.88	0.63	87.7
MARKIS	TRAFFIC, SOLVENTS8	36.97±2.21	0.66±0.25	37.63±2.20	84.29±8.47	0.54	2.80	44.6
<i>Areas close to solvent factories and workshops</i>								
WILKHA	TRAFFIC, SOLVENTS3	12.70±1.24	4.10±0.82	16.69±0.99	21.56±3.69	0.81	0.77	77.4
HATZEN	TRAFFIC, SOLVENTS3	39.72±2.38	4.65±1.51	44.38±2.03	55.12±3.74	0.79	1.41	80.5
HATZEM	TRAFFIC, SOLVENTS8	8.41±0.64	63.01±3.88	71.42±3.80	68.19±5.64	0.91	0.59	104.7
BISSIN	TRAFFIC, SOLVENTS2	12.64±0.84	24.89±1.71	37.54±1.53	37.59±3.16	0.99	0.07	99.9
LUTZOW	TRAFFIC, SOLVENTS2	16.87±0.90	7.49±0.85	24.36±0.92	28.28±1.51	0.84	1.57	86.1
BISSIM	TRAFFIC, SOLVENTS2	6.13±0.65	10.95±1.33	17.08±1.23	32.87±2.47	0.54	2.43	52.0
YOREK	TRAFFIC, SOLVENTS2	5.47±0.49	8.13±0.91	13.54±0.80	24.61±1.96	0.56	3.41	55.0
SIMONS	TRAFFIC, SOLVENTS3	10.66±0.66	17.72±1.11	28.38±1.01	28.25±2.97	1.00	0.04	100.5
SIMONB	TRAFFIC, SOLVENTS8	39.37±2.91	28.01±3.64	67.37±3.65	124.13±10.94	0.68	2.00	54.3
SIMONM	TRAFFIC, SOLVENTS8	49.72±2.93	4.93±1.80	54.64±3.08	88.71±10.96	0.70	1.55	61.6
VIEHOF	TRAFFIC, SOLVENTS4	33.28±1.79	23.10±2.04	56.38±1.90	57.00±3.01	0.96	0.41	98.9

NMVOC source categories like evaporative losses of motor fuel, natural gas leakage, other than traffic fuel combustion, biogenic emissions and other solvent relevant sources (wood conservation, domestic use of solvents, dry cleaning, printing industry) are missing in the CMB analysis.

The present results obtained from the CMB analysis from Wuppertal were compared with two former German studies from Berlin (Thijssse et al., 1999) and Augsburg (Mannschreck, 2000; Slemr

et al., 2002). These studies differ in terms of the chemical compounds used in the calculations and the applied source profiles. In contrast to the present study, no oxygenated compounds were analysed in these studies making a direct comparison quite difficult. In the Berlin study the solvent sector was neglected in the CMB source apportionment analysis as no indication of a contribution of the solvent sector to the total NMVOC emission was found, however, only a part of NMVOCs was

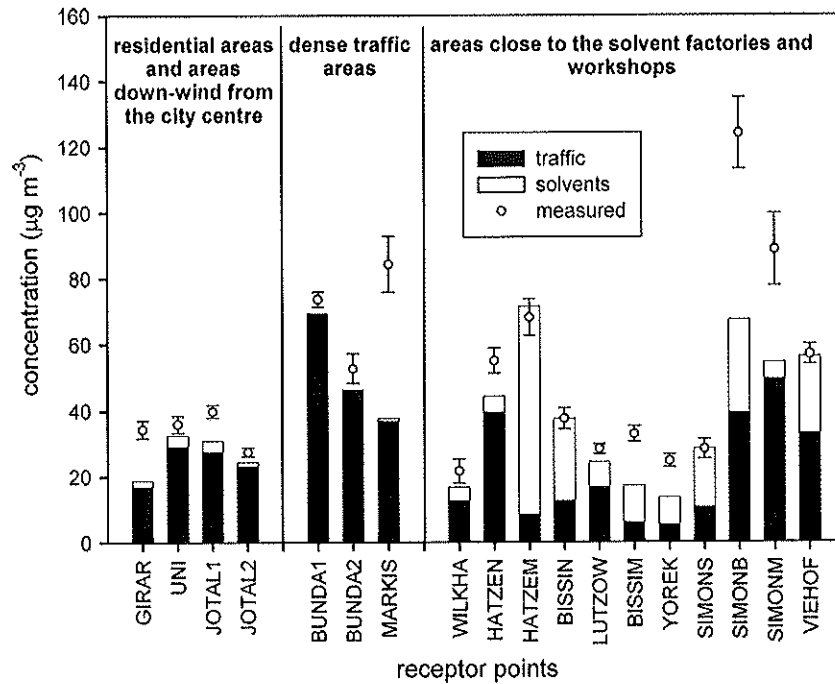


Fig. 8. The measured total concentrations of NMVOC and the concentrations reproduced by the CMB model for traffic and solvent use emissions at different receptor points in Wuppertal.

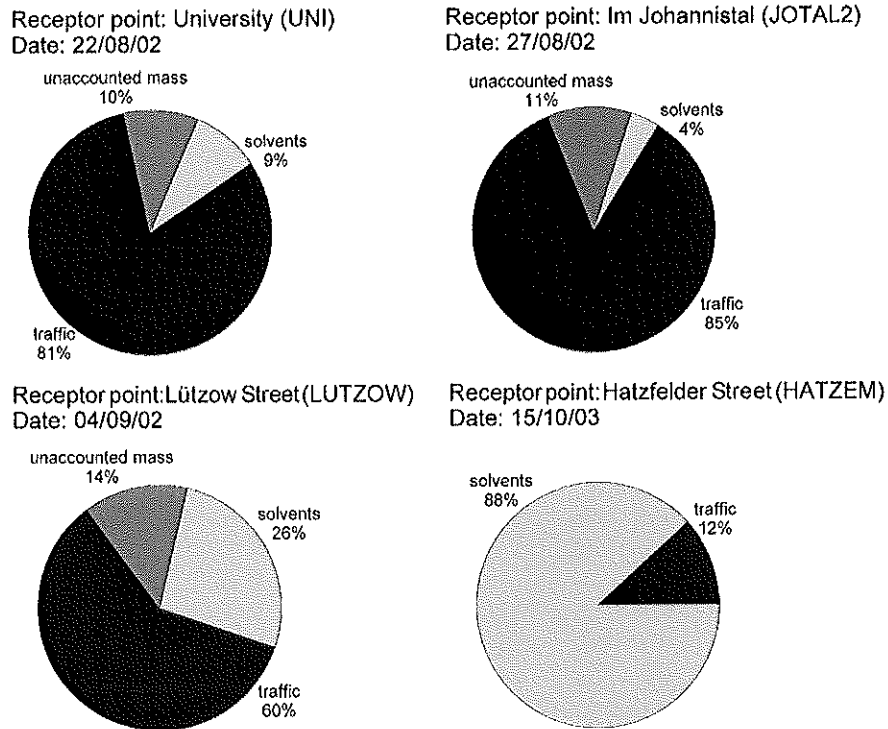


Fig. 9. Contribution of traffic and solvent use emissions to the total NMVOC concentrations measured in residential areas, down-wind from the city centre and close to the solvent factories in Wuppertal.

investigated. Nevertheless, all studies came to the similar conclusion, namely that the emissions from road traffic together with evaporative losses of fuel still dominate the NMVOC composition in urban air (Table 4).

In addition to the mentioned German CMB studies, also many others NMVOC apportionment analyses, mostly from the United States, reported at least qualitatively similar results (Watson et al., 2001 and references therein). The results of these studies varied with the total apportionment fraction, the calculation method, the chemical compounds used in the calculations and the source profiles applied. But even so, they show qualitatively similar source contributions to the NMVOC composition. Vehicle exhaust and gasoline evaporation contribute with 50% or more to the ambient NMVOC concentrations for most of these studies.

The solvent emission profiles obtained from the measurements performed at industrial sites in Wuppertal obviously do not cover the whole solvent use emissions, since some important solvent sectors like domestic solvent use, printing industry, dry cleaning and others were not investigated. In spite of this, it can be assumed that the solvent profiles applied in the CMB analysis represent the most important emission sector, namely production and application of paints and varnishes. According to the emission inventories and information about solvent production and consumption (Theloke

et al., 2000; Dore et al., 2003; EEA, 2005; Theloke, 2005), the paint manufacturing and application sector is responsible for about 40% of the total solvent use emission in Europe as well as in Germany.

A maximum contribution from the solvent use emission, understood as emission from the paint manufacturing and application sector, apportioned by the CMB analysis to the receptor points downwind from the city centre of Wuppertal, yielded about 9%. According to the special topography of Wuppertal, which causes the accumulation of emissions in the city centre, with the downwind direction from the city centre the well-mixed emissions are transported to the receptor points located on the slope of the Wupper valley. It allows to assume that selected receptor points are representatives for the whole city. Using the ratio between the paint application sector and the total solvent use emission of 0.4 the results of the CMB analysis support that the remaining solvent sectors contribute at the most 14% to the NMVOC concentrations in Wuppertal. Such an estimated contribution of other solvent sources can partly explain the unaccounted NMVOC mass obtained from the CMB analysis performed only with traffic and paint applications source profiles. Therefore, it is concluded that the maximum contribution of solvent use to the total NMVOC emission in the whole urban area of Wuppertal is about 23%. The

Table 4

Percentage contributions of different emission sources to the total NMVOC concentrations calculated from the CMB analysis for various German cities

Emission sources	Wuppertal ^a			Berlin ^b			Augsburg ^c
	Dense traffic areas (%) ^d	Residential areas and areas downwind from the city centre (%) ^d	Industrial areas (%) ^{d,c}	Street sides (%)	Residential areas (%)	Rural background (%)	Areas downwind 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

^aThis study.

^bThijssse et al. (1999).

^cMannschreck (2000).

^dAverage from the results for various receptor points.

^eAreas close to the solvent factories.

lower limit of the solvent use contribution has been taken from the lowest apportionment by CMB solvent contribution at the receptor points located down-wind from the city centre, which yielded about 4%.

Wuppertal belongs to the 20 biggest cities in Germany with a population of 360 000 inhabitants (2005) and can be considered as a German city with a typical share of traffic, industry and domestic activities (City Wuppertal, 2006; LUA, 2004). The composition of the NMVOC-mix as well as the NMVOC/NO_x ratios measured in Wuppertal are in agreement with results from other German cities. The share of NMVOC emissions from traffic, industry, small combustion facilities, trade and domestic sources in year 2000 were 43%, 7%, 2%, 31% and 17%, respectively (LUA, 2004). This agrees well with the NMVOC emission share of North-Rhine Westphalia for which traffic, industry, small combustion facilities, trade and domestic sources contribute 40%, 8%, 3%, 34% and 15%, respectively (LUA, 2004).

The characteristic of Wuppertal is a high contribution of activities connected with the solvent sector among the industries. The NMVOC emissions resulting from these activities account for 66% of all the emissions from the Wuppertal industry, whereas in the other cities like Cologne or Dortmund it is only 25% and 10%, respectively. This makes the city of Wuppertal interesting for the investigation of solvent use emissions. It can be assumed that, whereas the contributions from traffic, domestic solvent use and other NMVOC sources in Wuppertal are probably much the same as in other German cities, the solvent industry in Wuppertal plays a significantly higher role compared to other German cities. Therefore, the present study performed in Wuppertal is well suited to estimate upper limits for solvent use emissions.

Accordingly, estimations made for Wuppertal can be extrapolated to the whole country with some confidence. These results are in strong disagreement with the German Emission Inventory, which states, that at present (reference year 2003) about 51% of the total NMVOC emissions originate from solvent use and only 14% from road traffic (UBA, 2005).

It is obvious that national emission inventories calculate NMVOC emission for the whole country and for one reference year and that the ambient air measurements performed in one city cannot exactly prove or disprove the calculated values. However,

the German Emission inventory shows the clear trend of a strong dominance of NMVOC emissions from the solvent sector. Since 1995 more than 50% of the total NMVOC emissions in Germany are attributed to solvents (UBA, 2005). Accordingly, the results from ambient measurements performed in one city should at least roughly reflect the emission inventory and are useful for validation of emission inventory data.

7. Conclusions

The inconsistency of the German Emission Inventory data, which assign about 51% (in year 2003) of the total German NMVOC emissions to the solvent use sector with the real-world situation, is clearly demonstrated by the results of the present work. This finding is supported by two other German experimental studies, which were previously carried out in Berlin and Augsburg. Some shortcomings of the previous studies with respect to an incomplete cover of the oxygenated species were resolved in the present work.

The results from the CMB analysis with the application of source profiles and receptor concentrations obtained from city measurements in Wuppertal showed that road traffic rather than solvent use still dominates the NMVOC emission. The contribution of traffic emission was dominant at all investigated points located down-wind from the city centre, with a relative contribution on average of about 90%. In dense traffic areas the traffic emission is responsible for almost 100% of the NMVOC concentrations. Significant contribution from solvent emissions could only be observed in the close vicinity of solvent factories, where the impact of investigated solvent sources accounted on average for about 45% of the measured NMVOC concentrations.

The maximum contribution of solvent use to the NMVOC emission, estimated on the basis of experimentally obtained results, amounts to about 23% for the whole city area of Wuppertal. According to the characteristic of Wuppertal, particularly of the industry which was described above, the findings from Wuppertal were extrapolated to all German cities. The calculated contribution of emissions from solvent use is considered as an upper limit of the solvent use contribution. Accordingly, it can be concluded that the contribution of solvent use to the NMVOC concentration in German cities falls in the range of a few to about 20%.

The presented results raise some serious doubts as to whether the trends predicted by the European Emission Inventories, in particular in the German Inventory, where the relative contribution from the solvent sector has increased to 51% and is still increasing, whereas the emissions from traffic have significantly decreased and are still decreasing, reflect the reality. All experimentally based findings so far show that traffic emissions still dominate the NMVOC fingerprint in the ambient air of German and possibly European cities.

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