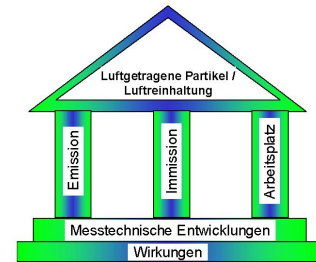




Abteilung:
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Bereich:
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Luftreinhaltung“



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**Identifizierung von Quellgruppen
für die Feinstaubfraktion**

Identification of Source Groups for Fine Dust

Im Auftrag vom:

Ministerium für Umwelt und Naturschutz,
Landwirtschaft und Verbraucherschutz
des Landes Nordrhein-Westfalen (MUNLV)
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1. Summary

1.1. Goals and scope of the project

Measurements of airborne particles and their chemical composition were carried out within a project funded by the North Rhine-Westphalia Ministry of Environment. The measurements took place over a period of approximately one year (28.02.02 to 01.04.03) at one central site and during two intensive campaigns (23.04.02-27.05.02; 22.10.02-16.12.02) at three sites simultaneously. This project was based on expected exceedance of PM₁₀ ambient air limit values (especially daily limit values) and the ongoing discussion related to new regulations of air quality standards. Major goals of the project were:

- *Method comparisons* of filter based measurements with corresponding continuous „on-line“ methodologies
- *Determinations of site characteristic concentrations* for PM₁₀, PM_{2.5}, PM₁, number concentrations and size distributions
- *Site comparisons* based on the parameters measured during the intensive campaigns
- *Analyses of diurnal variations* of continuously measured parameters as basis for further investigations to identify relevant particle sources and processes
- Application of *source apportionment* methods to identify relevant source groups for PM₁₀ mass concentrations.

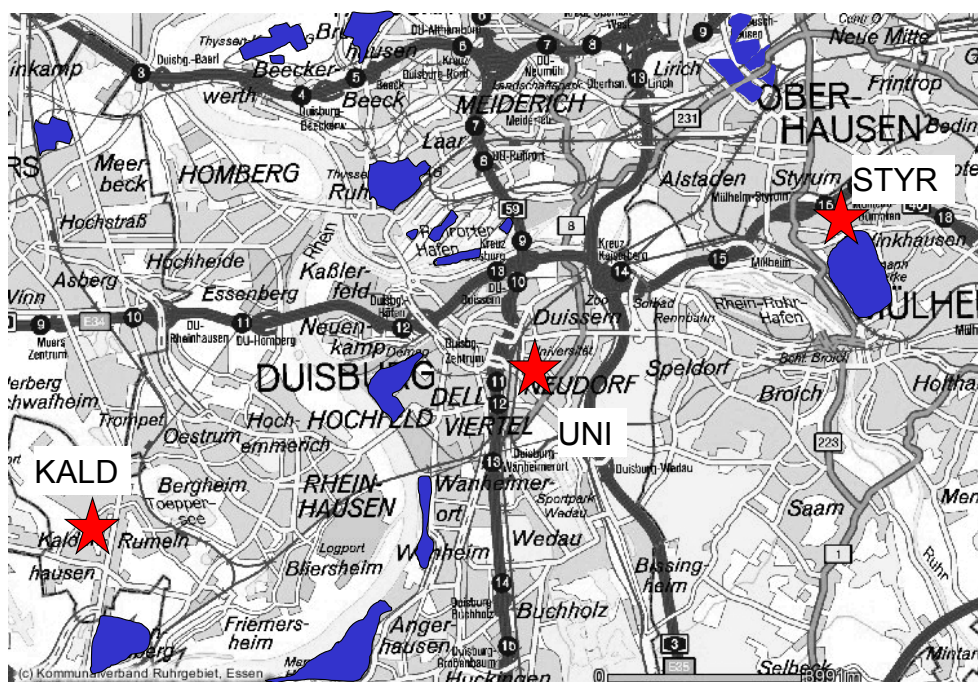


Figure 1: Site location

The locations of the three measurement sites are shown in Figure 1; the sites were arranged roughly along the main wind direction of this region. Table 1 provides an overview of the site characteristics.

Site	Casting	Northing	Type	Remarks
Duisburg-Kaldenhausen (KALD)	2545530	5695104	Urban background	LUQS ^{*)} measurement site, sub-urban area
Duisburg Universität (UNI)	2554501	5699925	Urban background	Measurement site of IUTA e.V.; urban living area influenced by industry and traffic
Mülheim-Styrum (STYR)	2560165	5702458	Urban background	LUQS measurement site, urban living area influenced by industry and traffic

Table 1: Characteristics of measurement sites
 *) LUQS: air quality measurement network of North Rhine Westphalia State Environment Agency (LUA)

An overview on measured parameters is given in Figure 2. Parameters which were only measured at the central site (UNI) are marked with red circles. Additionally, local meteorological data were gathered at the central site. Details on the measurement methods are summarized in Table 2.

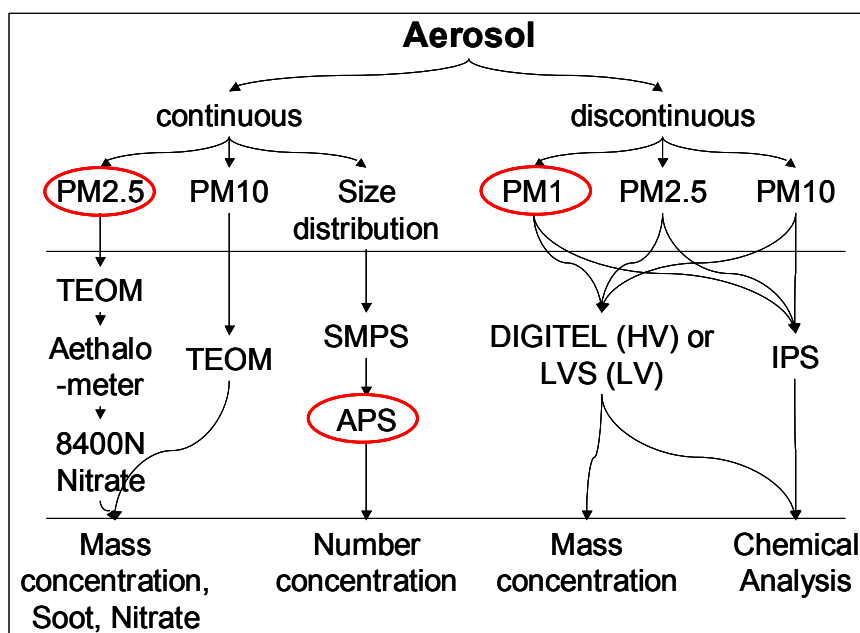


Figure 2: Scheme of methods and analysers used in the project

Analyser/ method	parameter	Principle	Time resolution
TEOM (R&P)	Aerosol mass concentration (PM ₁₀ / PM _{2.5})	Quasi-continuous measurement; deposition on filter bound to a tapered oscillating element	10 min
Aethalometer (GIV)	Mass concentration of soot (ca. PM _{2.5})	Deposition on filter tape, infra-red reflection measurement	10 min
8400N (R&P)	Mass concentration of particle-bound nitrate (PM _{2.5})	Impaction onto metal strip, flash pyrolysis, NO _x -detection	10 min
SMPS (TSI)	Aerosol size distribution (14 nm to 700 nm)	Particle separation due to electrical mobility; condensation nuclei counter	5 min
APS (TSI)	Aerosol size distribution (0,5 µm to 14 µm)	Particle separation due to acceleration, optical detection	10 min
Digitel (Digitel)	Mass concentration, chem. composition (PM ₁ , PM _{2.5} , PM ₁₀)	High-Vol filtration (30 m ³ /h)	24 h
LVS (Derenda)	Mass concentration, chem. composition (PM _{2.5})	Low-Vol filtration (2,3 m ³ /h)	24 h
IPS	chem. composition (~PM ₁ , PM(2.5-1), PM(10-2.5))	Impaction on quartz-carriers (3-stage impactor), TXRF analysis	24 h

Table 2: Details of used measurement equipment and methodologies

1.2. Method comparisons

PM₁₀ mass concentrations determined by the TEOM (1400AB, 40°C) were about 70% (arithmetic mean) of the mass concentration values obtained with the manual filtration method. The filter/TEOM ratio increased to 0,99 (arithmetic mean) after adding the concentrations of semi volatile compounds (ammonium, nitrate, chloride) that had been analysed from the filter samples. Regression analysis showed a slope of 0.97 and intercept of 0.5 µg/m³. Hence, the differences between TEOM and filtration based mass concentrations are due to losses of semi volatile compounds occurring within the TEOM-system.

More detailed analysis on the volatilisation of nitrate based on data obtained from chemical analysis of the filter and the on-line nitrate monitor (8400N, R&P) revealed significant losses of nitrate from the quartz fibre filter at mean daily temperatures above 20°C. Nitrate volatilisation from airborne particles became significant in the temperature range of 25°C to 30°C.

1.3. Characteristic concentration data

Characteristic concentration data for PM mass concentrations at the three measuring sites are presented in Table 3. Average PM₁₀ mass concentrations cover the range from 32 µg/m³ to 35 µg/m³. These values compare well with concentration levels determined for the Duisburg area by the State Environmental Agency (LUA NRW, 2003+2004).

Period:	Total			Comparable days					
	28.02.02-01.04.03			23.04.-27.05/22.10.16.12.2002 ^{*)}					
Site	UNI			UNI		STYR		KALD	
Fraction	PM ₁₀	PM _{2.5}	PM ₁	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
days	184	180	111	78	76	78	77	78	61
Mean [$\mu\text{g}/\text{m}^3$]	32.9	25.4	24.8	35.3	27.8	34.5	24.6	32.9	29.4
Median [$\mu\text{g}/\text{m}^3$]	26.2	20.5	23.1	32.6	24.7	30.6	21.7	32.2	30.3
25%-quantile [$\mu\text{g}/\text{m}^3$]	19.9	13.8	14.8	20.1	15.4	18.0	11.7	19.4	12.7
75%-quantile [$\mu\text{g}/\text{m}^3$]	43.3	34.0	33.7	48.2	37.1	46.4	34.5	44.7	41.4
Exceedance events > 50 $\mu\text{g}/\text{m}^3$	35			18		17		14	
Exceedance events (extrapolation)	69			84		80		66	

Table 3: Characteristic data on PM mass concentrations
^{*)}given are total periods of the intense campaigns; only days with complete PM₁₀ data sets have been evaluated

No exceedance of the PM₁₀ annual limit value for PM₁₀ (40 $\mu\text{g}/\text{m}^3$ by 2005) could be observed and is not to be expected in future. Contrarily, more than the 35 allowed exceedance events per year could be extrapolated for the daily limit (PM₁₀ > 50 $\mu\text{g}/\text{m}^3$ by 2005) for all sites (Table 3) and may also be expected for 2005. Most days of exceedance of the limit value occurred between Tuesday and Friday.

It should be noted that the measurement period did not cover a calendar year and thus comprised two phases (late winter 2002 and spring 2003) with high numbers of days with exceedance. These periods presumably are among the reasons for the unexpected increase of PM₁₀ concentrations that has been observed in Germany and adjacent countries (Belgium, The Netherlands, Switzerland and Czech Republic) in 2002 and 2003 (CAFE 2004) compared to the decreasing trend of the years 1991-2001.

Annual mean particle number concentrations at the central site amounted to 16.700 N/cm³ and 14.100 N/cm³ for the ultra-fine fraction. Comparable values were also determined for the satellite sites. This is to compare with figures of 3.000-28.000 N/cm³ and 2.000-25.000 N/cm³, respectively, given for urban and suburban sites in a „European aerosol phenomenology” study by Puteaud et al. (2003). From this data it follows that the three measurement sites have characteristics similar to other European cities.

Figure 3 shows the chemical composition of PM₁₀ as obtained for the central site (UNI) as an average of the whole campaign period. Accordingly, PM₁₀ comprises ca. 24% carbonaceous compounds, ca. 40% secondary ions (nitrate, sulphate, ammonia), approximately 5% sea salt components (Na, Mg, Cl), about 8% soil elements and metals as well as an unidentified residue of 23% (composed of silicates and water mainly). The chemical composition of PM₁ and PM_{2.5} is also shown in this figure for the purpose of comparison.

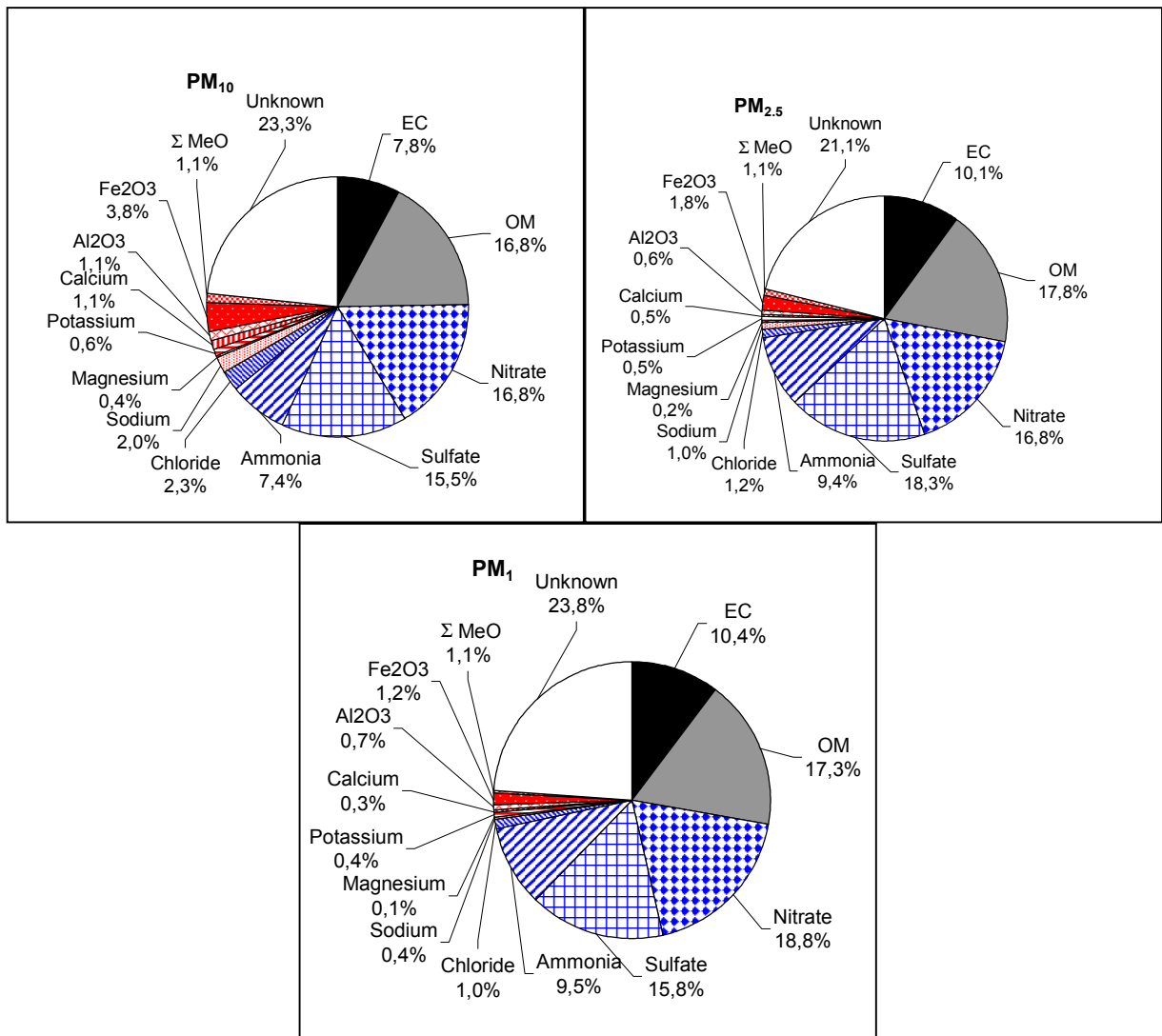


Figure 3: Chemical composition of PM₁₀, PM_{2.5} and PM₁, UNI whole measurement period

1.4. Site comparability

In general, a high degree of similarity was found for the three sites concerning the parameters PM₁₀, PM_{2.5}, chemical components, number concentration and particle size distribution. However, detailed analyses showed for the sites located in the urban agglomeration (UNI, STYR) area a slightly better comparability to each other than to the more Western suburban site KALD. Anyhow, each of the urban sites may be taken as representative for the larger Duisburg area with respect to particle characteristics.

Concentration differences of chemical components observed for the three sites were marginal and could be mainly found for trace compounds. In particular, at KALD elevated concentrations of titanium and zinc and lower levels of V, Mn, Co, Ga, Se, Rb, Sr, Sn, Ba were obtained compared to the UNI site. At STYR, higher shares of Cr, Ni, Zn and lower contributions of Ti, Mn, Co and Rb were observed.

1.5. *Source apportionment*

Five different approaches were applied to evaluate contributions of sources and source types to the PM₁₀ concentrations:

- Wind direction analyses
- Concentration related evaluation
- Episode analysis
- Analysis of diurnal variation
- Positive Matrix Factorisation (PMF)

From a detailed **wind direction analysis** of particular compounds or their statistically elaborated cluster a clear separation into three groups was obtained: sea salt emission, secondary particles and locally/regionally influenced side components. Some cases (cluster) could be assigned to specific industrial emission sources when compared to data taken from the State emission register. This concerned for example sources of manganese in the North-East of site UNI or a titanium source located in south direction from site KALD.

Based on a **concentration-related evaluation** of the PM₁₀ chemical composition applied to days with PM₁₀ above 50 µg/m³, between 30 and 50 µg/m³ and below 30 µg/m³, respectively, it could be concluded that ammonia and nitrate are indicator components for days of exceedance. These secondary compounds are either ubiquitously formed or subject to long range transport mechanisms since they contribute equally to the increase of PM₁₀ at all sites. On the other hand, concentrations of the sea salt components decrease with increasing PM₁₀ mass concentrations. This may be seen as an indication for continental air masses flowing from south or eastern directions and/or stagnant meteorological conditions.

By means of detailed statistical **episode analysis** for days with limit value exceedance three episode types could be differentiated which however are not clearly separated from each other due to the limited data set. All days with PM₁₀ exceedance exhibited very short back trajectory distances that indicate stable weather conditions and slow mixing processes.

For episode **type A** which covered winter and springtime days elevated values for Al and Ca indicate soil materials or processes used in stone and earth industries. Hence this type may be denoted „transitional period/re-suspension“.

Regarding **type B**, elevated concentrations of vanadium in connection with predominant western wind direction (which however are not consistently supported by the backward trajectories) lead to the assumption of an influence by oil refineries or fuel oil combustion located in the Netherlands. Presumably very stable high-pressure summertime weather conditions caused the low trajectory distances for this episode type. Hence this episode type could be denoted „summer/high pressure“.

A lowered concentration of secondary aerosols correlating with also less global radiation is characteristic for episode **type C**. This type mainly covers winter days with changing wind directions. Elevated contributions of many metals indicate a higher influence of local or re-

gional emission sources. This might likely be due to lower atmospheric mixing heights during wintertime. According to these characteristics, this episode type is denoted "winter/local influence". In Table 4 some features of the main episode types are given; Figure 4 presents the relative contribution of the main episode types that are further split into sub-groups according to a more detailed cluster analyses.

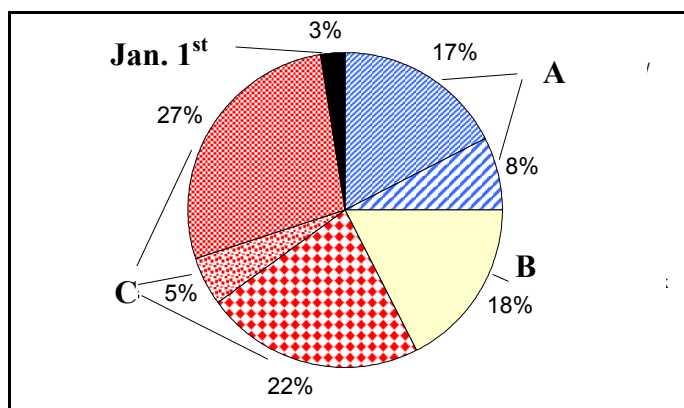


Figure 4: Percentage distribution of main episode types ($PM_{10} \geq 50 \mu g/m^3$)

	Season	Elevated chemical compounds	Mean trajectory distance [km]			Predominant wind direction	Global radiation [W/m^2]
			24h	48h	72h		
A	Winter/spring	Sec., Al, Ca	340	700	1000	easterly.	100
B	Early summer + other	Sec, Mn, V	260	500	700	westerly.	90
C	Winter + other	metals, OM, EC	290	900	1300	East./west.	56

Table 4: Characteristics of main episode types ($PM_{10} \geq 50 \mu g/m^3$)

Diurnal variations of the continuously determined particle parameters were used (after correction to the filter based data) to quantify the contribution of local to regional sources with regular fluctuating emission activities. All analysed parameters revealed significant diurnal and weekly profiles. A summary of this evaluation is given in Table 5.

	local contribution		Fraction of local contribution	
	Tue – Fri $\mu g/m^3$	relative	PM_{10}	$PM_{2.5}$
PM_{10}	8-10	27-31%		
$PM_{2.5}$	4-6	19-24%		
Nitrate + NH_4^+	1.8-2.3	27-31%	18-29%	30-58%
Soot+OC	1.6-2.0	37-43%	16-25%	27-50%
20-40 nm		30-36%		
50-100 nm		23-30%		
150-300 nm		22-31%		
400-600 nm		22-33%		

Table 5: Relative local contribution due to sources with regular activity fluctuations

Local to regional sources with regular activity fluctuations contributed 8-10 $\mu\text{g}/\text{m}^3$ (termed excess concentration) to the PM_{10} mass concentration. This comprises about 20-30% of ammonium nitrate and 15-25% of soot plus organic carbon. The weekly variation of the excess concentrations correlates well with the weekly variation of the exceedance of the PM_{10} daily limit value. Further, the diurnal profiles of soot and PM_{10} exhibit a clear time-correlation with rise and drop of traffic activities; on the opposite, in case of nitrate a time delay of ca. 1 day appears to occur.

The calculations reveal maximum excess concentrations for soot and for particle number concentration in the size range of 20-40 nm. Taking into account the site location and the observed diurnal/weekly profiles this is most likely due to traffic emissions, maybe partly also due to domestic heating.

The excess concentration shares of ammonia nitrate and soot were calculated to be 30-60% and 30-50%, respectively, of the $\text{PM}_{2.5}$ fraction and are considerably higher than in PM_{10} . This agrees well with the mass size distribution for these compounds. These compounds are found mainly in the $\text{PM}_{2.5}$ fraction. It is concluded that different compounds are responsible for the excess concentrations of $\text{PM}_{2.5}$ and PM_{10} ; the overall excess concentration in PM_{10} are due to approximately equal part of increase of $\text{PM}_{2.5}$ and of $\text{PM}_{2.5-10}$.

For all parameters it was found that the concentration increase due to local to regional sources with regular activity fluctuations is higher on days with limit exceedance than for the yearly average. Moreover, the excess peak is superimposed to a significantly elevated baseline concentration on these days.

Finally, the relative excess input as calculated from the diurnal variations was compared to the “urban contribution to PM_{10} ” that was evaluated according to Lenschow et al. (2001) for measurement data obtained at Ludwigshafen and Koblenz (Kuhlbusch et al., 2003) and at Berlin (John and Kuhlbusch, 2004). This “urban contribution” has been shown to be about 40-45% for Ludwigshafen and Koblenz and 50% for Berlin and thus are higher than the relative excess input observed at Duisburg based on the diurnal variation analysis. This is as expected since the relative excess input based on diurnal variations covers only a part of the “urban contribution” as determined with the Lenschow approach. Therefore the relative excess input calculated for Duisburg appears to be plausible.

Positive-Matrix-Factorisation (PMF) was applied to resolve sources and source groups from PM_{10} and $\text{PM}_{2.5}$ chemical composition data. In case of PM_{10} eight different factors could be resolved whereas for $\text{PM}_{2.5}$ only six factors were obtained. Based on their chemical composition in connection with wind direction dependency and inter-site-correlation it was possible to assign source groups and in some cases to identify source regions. In particular, factors denoted “industry” and “zinc/iron” could be assigned to specific local industrial sources. Quantitative factor distributions related to PM_{10} and $\text{PM}_{2.5}$ are shown in Figure 5.

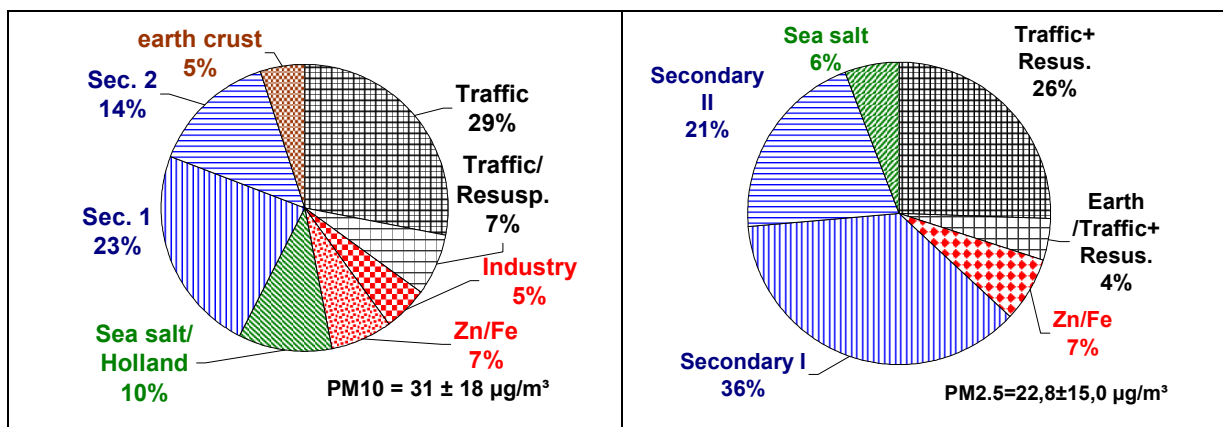


Figure 5: Source apportionment for PM₁₀ and PM_{2.5} by means of PMF (UNI, whole campaign period)

With respect to source regions the source types “secondary 1”, “secondary 2” and “sea salt/Holland” originate from long range transport, whereas “traffic”, “combustion/re-suspension” and “crustal material” are due to mixed super-regional and regional source areas. Contrarily, the factors “industry” and “zinc/iron” are clearly influenced by local processes. For the other sites a PMF analyses could be done only on basis of the shorter intense campaign periods. However, a comparison made for the UNI site between factor distribution obtained for the whole campaign period and the intensive campaign data showed good agreement. Hence the results obtained for KALD and STYR can be viewed as representative.

In general good agreement could be observed between the three sites also with respect to the PMF source apportionment results. Slightly increasing contributions of “traffic” in direction from KALD to STYR is in accordance with the related traffic densities and site-road distances. Higher industrial contributions at UNI (11%) and STYR (14%) compared to KALD (9%) originate from their location related to the most important industrial sites (distance as well as direction).

In PM_{2.5}, the factors “secondary 1”, “traffic”, “sea salt/Holland” and “zinc/iron” could again be resolved; however “traffic” was distributed to two highly correlating factors. The factors “industry” and “crustal material” were not resolved in the PM_{2.5} fraction; further, the factor “secondary 2” was found to be not robust.

Calculating the PM_{2.5}/PM₁₀ ratio for the assignable factors revealed a plausible picture with a ratio of nearly 1 for “secondary 1” and 0.3 for “sea salt/Holland”. This comparison also showed that the factor “zinc/iron” was related to the fine particle fraction (presumably due to a hot thermal source). Contrarily, from the impossibility to find the “industry” factor in PM_{2.5} it may be concluded that this factor is mainly influenced by “cold” sources emitting coarse particles.

Finally, a comparison of factor contributions of average with elevated PM₁₀ mass concentrations revealed a clear super-proportional influence of the factors “combustion/re-suspension”, “secondary 1” and “secondary 2” (actual ranking).

1.6. Conclusions

From the results of the investigations the following conclusions can be drawn with respect to the pollution by PM₁₀ in the area of Duisburg:

- PM₁₀/ PM_{2.5} mass concentrations and the chemical composition of dust particles are similar at all three measurement sites. Hence the airborne fine dust fraction originates mainly from regional (here: ca. 30 km surroundings) or super-regional processes and can be determined with sufficient reliability at any urban background site located in the regional area.
- Emission sources located in the regional area affect the PM₁₀ trace compound composition which in some cases allows to localise them.
- From the observation of time dependent variability of PM_x mass concentration and some compounds it can be concluded that a significant fraction of the atmospheric load is caused by traffic and other sources with weekly or diurnal activity fluctuations.
- Exceedance of PM₁₀ daily limit value is likely if the input by these variable sources occurs together with elevated baseline pollution due to super-regional processes and favourable meteorological conditions.
- Such episodes with elevated concentrations occur during all seasons; the relative importance of the super-regional and regional/time variable contributions appears to fluctuate with season resulting in increased relevance during the cold months.