Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen

Quantifying the Emissions of Stationary Industrial Sources

Using PM10 Monitoring Data

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Aims of monitoring air quality at industrially influenced sites

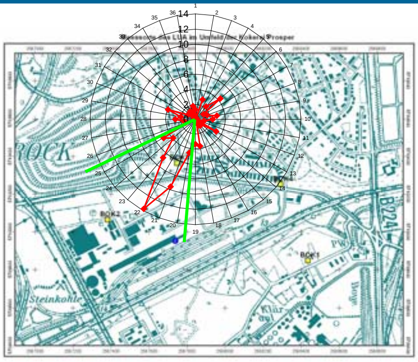
- Determine exceedances of limit and target values of the EU, in case of exceedances
- Identify sources of pollution
- Quantify the contribution of sources to the annual mean values

A simple example:

In Bottrop the target value of Benzo[a]pyrene (BAP) was exceeded in 2004. A pollution rose simply shows the reason

Bottrop-Welheim 2004

Pollution rose for 24 h values of BAP



BAP concentrations 2004:

Bottrop:

3,4 ng/m³

Northern Ruhr-region:

0,3 – 0,5 ng/m³

Contribution of the Coking plant:

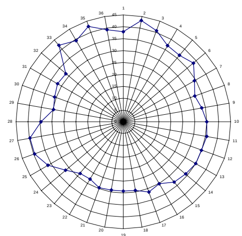
3 ng/m³

A more difficult case: Duisburg-Bruckhausen

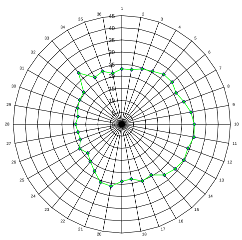
- Number of days with PM10 > 50 µg/m³ higher than 35 during many years (2008 was the first year without an exceedance of the EU limit value)
- 4 blast furnaces, 3 oxygen steel works, a sinter plant, a coking plant and many other facilities in a distance of less than 2 kilometers
- A PM 10 pollution rose does not seem to be helpful

PM10 in Duisburg-Bruckhausen 2008

data base: 0,5h values of wind direction and PM10

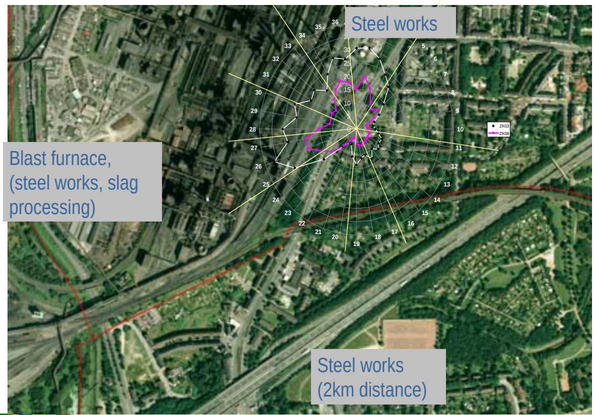


PM10 Duisburg-Bruckhausen



PM10-Background

Mean of 4 stations in the Duisburg agglomeration



Some definitions

- Pollution rose: graphic figure of mean values of pollant concentrations at different wind directions (called *i*)
- Surplus concentration (*SC*): difference of measured PM10 and background PM10 concentrations

Pollution roses of PM10 SC often give hints to stationary sources

Metal surplus concentrations

- Only 24 h values available
- Background concentrations of metals are mesured every second day only
- Use average background aerosle composition and daily PM10 concentration

Accuracy of estimated metal backgrund concentrations is low, but good enough for further calculations

D. Gladtke, W. Volkhausen, B.Bach, Atmospheric Environment 43, 4655 – 4665 (2009)

PM10 speciation: a tool to identify single facilities

- Fe: blast furnaces, steel works, sinter plant (20 - 40 % of PM10SC)
- Zn: steel works (3 – 5 % of PM10SC, origin: scrap)
- Ca: slag processing (~ 30 % of PM10SC), sinter plant (~ 10% 0f PM10SC)
- Cr, Ni: stainless steel production

Origin of PM10 SC in Duisburg-Bruckhausen, with wind blowing from south west:

10 – 20 % steel works (Zn), 10 – 20 % slag processing (Ca), 60 – 80% blast furnace

Quantification

- Surplus burden (SB) of a single facility
- Calculate the SC of a pollutant in the wind direction sector corresponding to the plant
- Multiply it with the relative frequency of the wind direction
- Formula: $SB = SC * ai / \Sigma ai$

ai: number of 0,5 or 24 h values at wind direction *i*;

Σai: total number of wind direction values

Contribution of single plants to PM10 in Duisburg-Bruckhausen 2008

- Blast furnace 9 — 0,8 µg/m³
- Slag processing — ~0,2 µg/m³
- Steel works Beeckerwerth — ~0,2 µg/m³
- Steel works Bruckhausen — 0,4 µg/m³

Duisburg - Untermeiderich

Results at Duisburg-Bruckhausen: With wind blowing from southern directions

- High concentrations of lead (0,2 to > 0,5 µg/m³)
- Concentrations of nickel > 20 ng/m³
- Probable sources far away (2 km)

New sampling site: Duisburg-Untermeiderich

Results 07.07 – 07.08

PM10 µg/m³	Number of Days with PM10 > 50 µg/m³	Ni ng/m³	Cr ng/m³	Pb µg/m³	Fe µg/m³	Zn µg/m³
33	42	24,4	25,9	0,15	1,7	0,17

Fe, Zn: steel works;

Pb: special steel

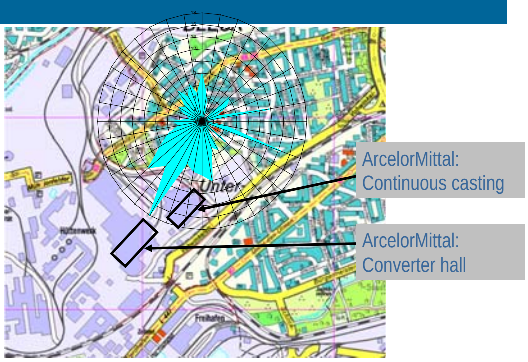
Ni: ?? Often: high quality steel production, but no steel with high amount of Ni and Cr is produced, the ratio of Cr/Ni is unusual (for stainless steel: 2)

Identification of sources with pollution roses

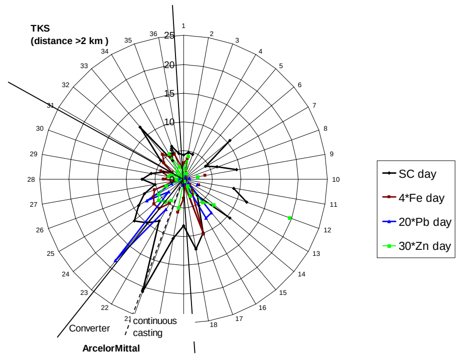
Data

- 24 h values of PM10 and metals in PM10
- 0,5 h values of wind direction, 24 h values of wind direction
- 24 h values of background PM10
- 24 h values of metals in background PM10 estimated using the average composition of the background aerosol

Pollution rose of PM10 SC



Pollution rose of PM10 and metals in PM10



Different sources

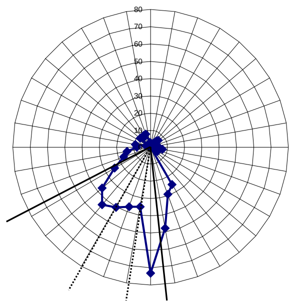
- A source with a high content of lead in the discharged dust (continuous casting?)
- A source discharging high amounts of iron and zink (converter?)

The peak of lead points into a direction not fitting to the position of the sources: are the 24 h wind directions wrong? Do unknown sources of lead exist?

Wind direction in case of high concentrations of lead

- Highest concentrations of lead are measured at daily vector means of 220°
- The direction of the most important source of lead is the continuous casting hall in direction 180 to 200°
- Distribution of 0,5 h wind directions at days with high lead concentrations: most frequent wind directions: 180° (south) and 220 (south west)

Number of 0,5 h-values of wind direction at days with Pb >0,5 µg/m³



Methods to combine 24 h analysis results with 0,5h meteorological data

- Look at **days** with 0,5 h values of the wind direction preferently from the direction of the facility, estimate SC
- Perform a linear zero order **regression** of the daily number of 0,5 h values at different wind direction sectors corresponding to facilities or groups of facilities (as x values) and the daily SC (as y values). The constants of the regression are the new values of wind direction dependent SC (often works well using SC and using large wind direction sectors, well fitting to the position of facilities)
- Use the PRP method described by Cosemans, Kretzschmar and Mensink:

Atmospheric Environment 42, 6982-6991 (2008)

Days with wind preferently from the wind direction sector of CC and converter

	CC	Converter
SC µg/m³	9 - 12	9 - 11
Fe µg/m³ (%)	1,2 – 2 (10 – 20)	2,5 – 3,2 (25 – 35)
Pb µg/m³ (%)	0,4 – 4 (4 – 35)	0,4 – 0,6 (~5)

Linear regression (smoothed)

	CC	Converter
SC µg/m³	13 - 14	10 - 13
Fe µg/m³ (%)	1,5 – 2 (11 – 15)	2,2 – 2,6 (17 – 26)
Pb µg/m³ (%)	0,4 (3) Sd of slope: >50%	0,4 (4) Sd of slope: >30%

Problems

Results coincide, but their uncertainty is high because

- Plumes of the two facilities overlap at wind direction 200°, therefore two calculations were performed: one with wind direction sector 200° attached to the plume of CC, the other one with the sector attached to the converter hall
- Extremely high scattering of Pb SC, Pb rich steel alloys are not produced daily

At days with the highest Pb SC, wind blew dominantly from CC (30 -50%) and the converter (~40%)

PRP-roses (Cosemans, Kretzschmar, Mensink)

- Look at the data set, eliminate outliers
- Divide the wind direction in e. g. 10° sectors
- Perform a linear least square regression of numbers of 0,5 h values of each sector and daily analysis data
- Calculate a power rose
- Combine the constants of the power rose and the equation system of the linear regression using the ridge regression method (power ridge pollutant rose)

PRP roses, linear regression

For each day ***j*** and wind direction sectors ***i***:

$$\sum_{i=1}^{36}(aijxi) = \left(\sum_{i=1}^{36} aij\right)Cj$$

xi: constants of regression, mean concentration of pollutant at direction ***i***

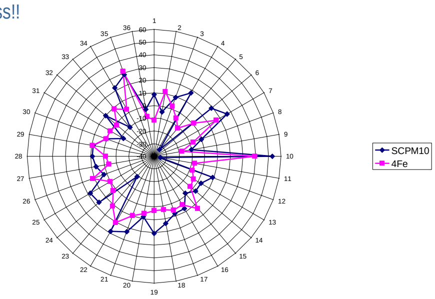
ai: number of 0,5 h values of wind direction ***i*** at day J

Cj: pollutant SC at day ***j***

The method often results in highly oscillating constants, if the wind direction sectors are small

Least square zero order regression

Quite a mess!!



PRP roses, power rose

The components of the power rose (p) are calculated using the equation system:

$$pi = \alpha\lambda i$$

pi: average pollutant concentration at Wind direction ***i***

$$\alpha = \frac{\sum_{j=1}^{Ndays} observed}{\sum_{j=1}^{Ndays} predicted}$$

observed: Cj

$$predicted(dayj) = \frac{\sum_{i=1}^{36}(ai\lambda i)}{\sum_{i=1}^{36} ai}$$

$$\lambda i = \frac{\sum_{j=1}^{N} aijCjCj^{m}}{\sum_{J=1}^{N} aij}$$

Cj = pollutant concentration at day ***j***

aij = number of 0,5 h values of wind direction ***i*** at day ***j***

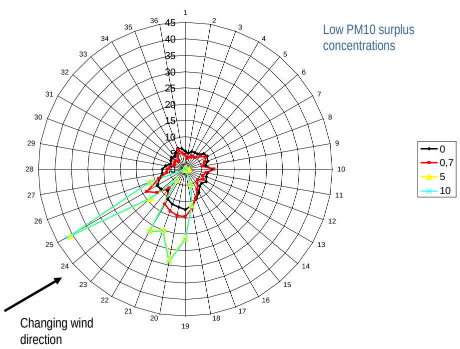
m, the most important variable

What happens if ***m*** grows?

Days with high pollutant concentration and one dominating wind direction are preferred, resulting in high ***pi*** at that wind direction

Days with low pollutant concentrations and changing wind directions are more and more neglected

p-rose for PM10 SC with different values for *m*



Power rose, variable m

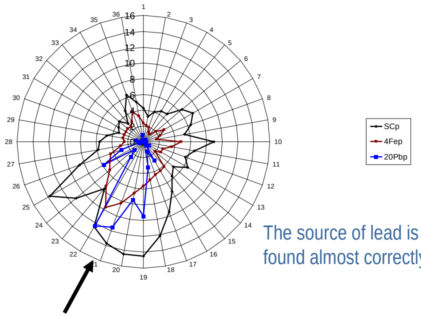
Find ***m*** by iteration

Look for

- Either a maximum of the correlation between observed and predicted values
- Or a minimum of the absolute difference between observed and predicted values

Keep m as small as possible!!!

Power roses of DUUM 07-08



The source of lead is found almost correctly

PRP-rose

- Use the matrices of the linear regresion
- Add 36 lines to the ***aij*** matrix: ***ϕWi***
- Add 36 values to the ***Cj*** vector: ***ϕWipi***

	aij		*Cj*
a1 1	a2 1 ....a35 1	a36 1	C1
a1 2	a2 2.........a35 2	a36 2	C2
.		.	.
.		.	.
.		.	.
a1 N	a2 N........a35 N	a36 N	C36
ϕw1	0.................0	0	*ϕw1p1*
0	*ϕw2*...............0	0	*ϕw2p2*
.		.	.
.		.	.
.		.	.
0	0................0	*ϕw36*	*ϕw36p36*

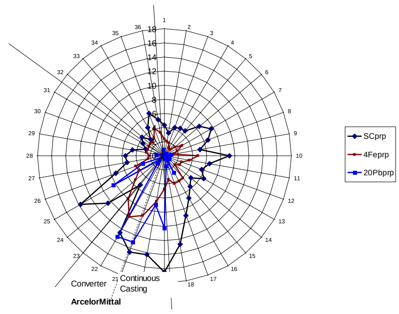
PRP rose

$$Wi = \frac{N * 48}{\sum_{j=1}^{N} aij}$$

N: total number of analysis days

- Take ***pi*** from the power rose
- Find ***ϕ*** iteratively: lowest value that correlation of p-rose and PRP-rose is more than 0,97

Power Ridge Pollutant Rose DUUM 2007/2008



Summary PRP-rose

	CC	Converter
SC µg/m³	15	13 - 14
Fe µg/m³ (%)	1,7 (11)	2,3 (18)
Pb µg/m³ (%)	0,5 (3)	0,6 (4)

Summary of all methods SC in µg/m³

	CC			Converter		
	days	Regression (smoothed)	PRP	days	Regression (smoothed)	PRP
SC	9-12	13-14	14-15	9-11	10-13	8-10
Fe	1,2-2,0	1,5-2,0	1,7	2,5-3,2	2,2-2,6	2,3
Pb	0,4-4	0,4	0,5	0,4-0,6	0,4	0,6

Summary: surplus burden

	CC			Converter		
	days	Regression (smoothed)	PRP	days	Regression (smoothed)	PRP
SC	1,1	1,4	1,6	0,9	1,1	0,9
Fe	0,12	0,2	0,2	0,3	0,2	0,2
Pb	0,04-0,44	0,04	0,06	0,05	0,04	0,05

Comparison of the methods

- Results only using 24 h values of wind direction are wrong
- Results of single days look reasonable, but at 3 days only the wind blew dominantly from the direction of the facilities, making the results very uncertain
- The uncertainty of results with the regression method is also very high
- The PRP-results look reasonable (source of lead is found with a ceviation of ~ 10°) and they are a good proof of the previous estimations

A kit for the analysis of data close to industrial facilities

1. Compute surplus concentration roses with daily values (if no 0,5 analysis data exist)
2. Look at the composition of the discharged aerosols
3. Look at days with wind dominantly blowing from the direction of facilities (if their position is known)
4. Try linear regressions (may be with smoothing) using sectors corresponding to groups of facilities
5. If all else fails: compute PRP-roses
6. Calculate SC and SB for the facilities of interest

Never forget to calculate the composition of discharged aerosols in order to verify your estimations!!!!!

Where is the nickel from ??

Only 24h data are used!!!!!

From a small factory in the west of the site