Validation of POP Emission Estimates with Environmental Data

A limited validation of emission estimates is possible by comparing air concentration with emission data for well documented pollutants such as SO_2 and NO_2 and applying the ratio between observed atmospheric concentrations to accounted emissions to POPs. In applying this ratio, data for rural areas reflects long-range transport better than data from urban areas. Problematic is the accounting for import and export of pollutants.

The emission patterns of SO_2 and NO_2 are characterized by a wide variety of sources:

- large point sources (power plants, industrial facilities)
- residential heating
- diffuse emissions from vehicles

It is assumed that the ratio of rural air concentrations to total emissions account for mid-range transport processes. Without accounting for imports and exports, Table 1 contains the pertinent data for Germany in for selected years in the time period 1975-1992 data (UBA&StBA, 1995). Figure 1 provides a graphical display of the relationship between source data and air concentrations in rural areas.

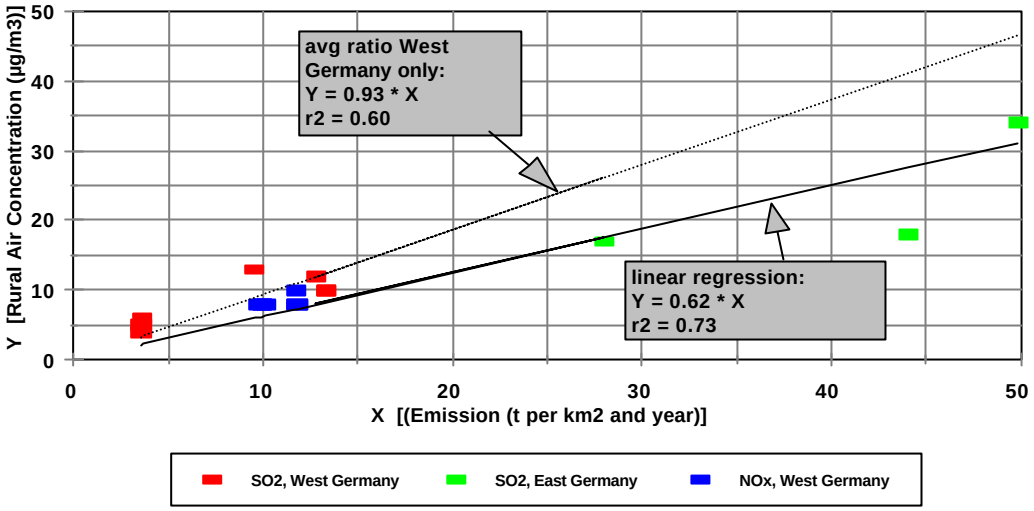
Table 1 Emissions of SO2 and NOx from all sources, East and West Germany (1974-1992) and air concentrations in rural areas (source: UBA&StBA, 1995)

Year	1975	1980	1985	1990	1991	1992
SO_2 emissions, West Germany, kt	3,308	3,166	2,369	878	896	875
SO_2 emissions, East Germany, kt	4,111	4,320	5,385	4,755	3,534	3,021
SO_2 in rural areas, West Germany, µg/m^3	10	12	13	5	6	4
SO_2 in rural areas, East Germany, µg/m^3			34	18		17
NO_x emissions, West Germany, kt	2,511	2,926	2,908	2,460	2,460	2,426
NO_2 in rural areas, West Germany, µg/m^3	8	8	10	8	8	8

Despite many compounding factors (emission height, import and export, averaging over large areas), there is a reasonable correlation (r^2=0.73) between the emission rate per km^2 and the observed average rural air concentration. The linear regression analysis is indicated in Figure 1 as well as the average ratio just for the West German data points which cover a larger geographical area.

Assuming that the average annual air concentration is known, and that the geographical distribution other emission characteristics are similar, the calculated relationship can be used to infer a source term. The relationship was used in the calculations presented in Table 2.

Figure 1 Emissions of SO_2 and NO_x in East and West Germany (1975-92) versus rural air concentrations of SO_2 and NO_2



The air concentration data in Table 2 was estimated from a variety of sources and does not necessarily reflect true averages. The range of emissions was calculated by multiplying the air concentrations with the average ratio determined for West German data points.

Table 2 Estimate of POP emissions in Germany from observed air concentrations in rural areas

Substance, Location, Year	Air concentration	Emission
POP emissions estimated from observed avg. SO_2/NO_2 ratios		
PCDD/F, Germany	20 - 50 fg TE/m^3 (est. rural avg.)	8 - 20 kg TE/a
PCB [6 Con.], Germany	50 - 150 pg/m^3 (est. rural avg.)	20 - 60 t/a
B[a]P, Germany	30 - 100 pg/m^3 (est. rural avg.)	10 - 40 t/a
HCB, Germany	50 - 150 pg/m^3 (est. rural avg.)	20 - 60 t/a
PCP, Germany	100 - 200 pg/m^3 (est. rural avg.)	40 - 80 t/a
By comparison: Emission estimate this study (1994)		
PCDD/F		0.33 kg TE/a
PCB [6 Con]		21 t/a
HCB		10 - 50 t/a
B[a]P		71 t/a
PCP		~ 100 t/a (?)

The largest discrepancy was observed for PCDD/F where the total estimate for the identified sources described in this study is a factor of 24 below the range of emissions estimated from annual average concentrations. In other words, would the total inventory for Germany indeed be 330 g TE/a, and the ratio between emissions and air con-

centrations which was established for SO_2 and NO_x also be attributable to PCCD/F, one would expect an annual average air concentration of ~1 fg TE/m^3.

There are several possibilities to explain the apparent discrepancy:
1. the source characteristics differ distinctly for PCCD/F on one side and for SO_2 and NO_x on the other side,
2. net import of PCDD/F exceeds national emissions by an order of magnitude,
3. releases from any of the known and described sources are underestimated, or
4. there may be large sources which were not considered thus far.

An insight into the nature of the sources is possible by analyzing the seasonal trends in ambient air concentrations. If a substance shows a marked peak in the summer, it is likely to be affected with temperature related release mechanisms such as evaporation. Peak concentrations in the winter months, on the other hand, are most likely to be associated with residential and industrial combustion for heating purposes. If several pollutants are measured at the same time, the correlation between observed concentrations can help in the assessment.

In this context, Figure 2 provides some insight into primary POP sources in Southern Germany[1]. The results represent representative measurements over an entire year at a suburban location in the Northeast of Munich. The intent of the program was to determine an impact of a large 550,000 t/a municipal waste incinerator. Such an impact could not be determined. The following trends were observed:

- Air concentrations of PCDD/F (TE) and the PAH/B(a)P show a clear winter peak and thus appear to be related to residential combustion.
- The following positive correlation with $r^2 > 0.5$ was found: PAH to B(a)P (r^2=0.93), PCDD/F to PAH (r^2=0.73), PCDD/F to B(a)P (r^2=0.77).
- Concentrations of PCB are larger in the summer months and support emission estimates that the major source is loss from capacitors, expected to be increase with temperature.
- Concentrations of HCB are inconclusive. If the January peak is determined an outlier, the data may suggest a seasonal trend supporting the hypothesis of remobilization from soil to be the major source.
- Concentrations of Chlorophenols show a mild seasonal trend with a summer peak which interestingly is not visible for PCP. The hypothesis that the major source for PCP is treated wood would suggest a clear summer peak .

[1] Franke B., Franke A. (1997), Umweltverträglichkeitsuntersuchung zum Müllherizkraftwerk München-Nord, ifeu-institut für Energie- und Umweltforschung Heidelberg GmbH, im Auftrag der Stadtwerke München, im Druck

Figure 2 Seasonal variation of POP concentrations in ambient air in Aschheim near Munich, Germany, 1995/96

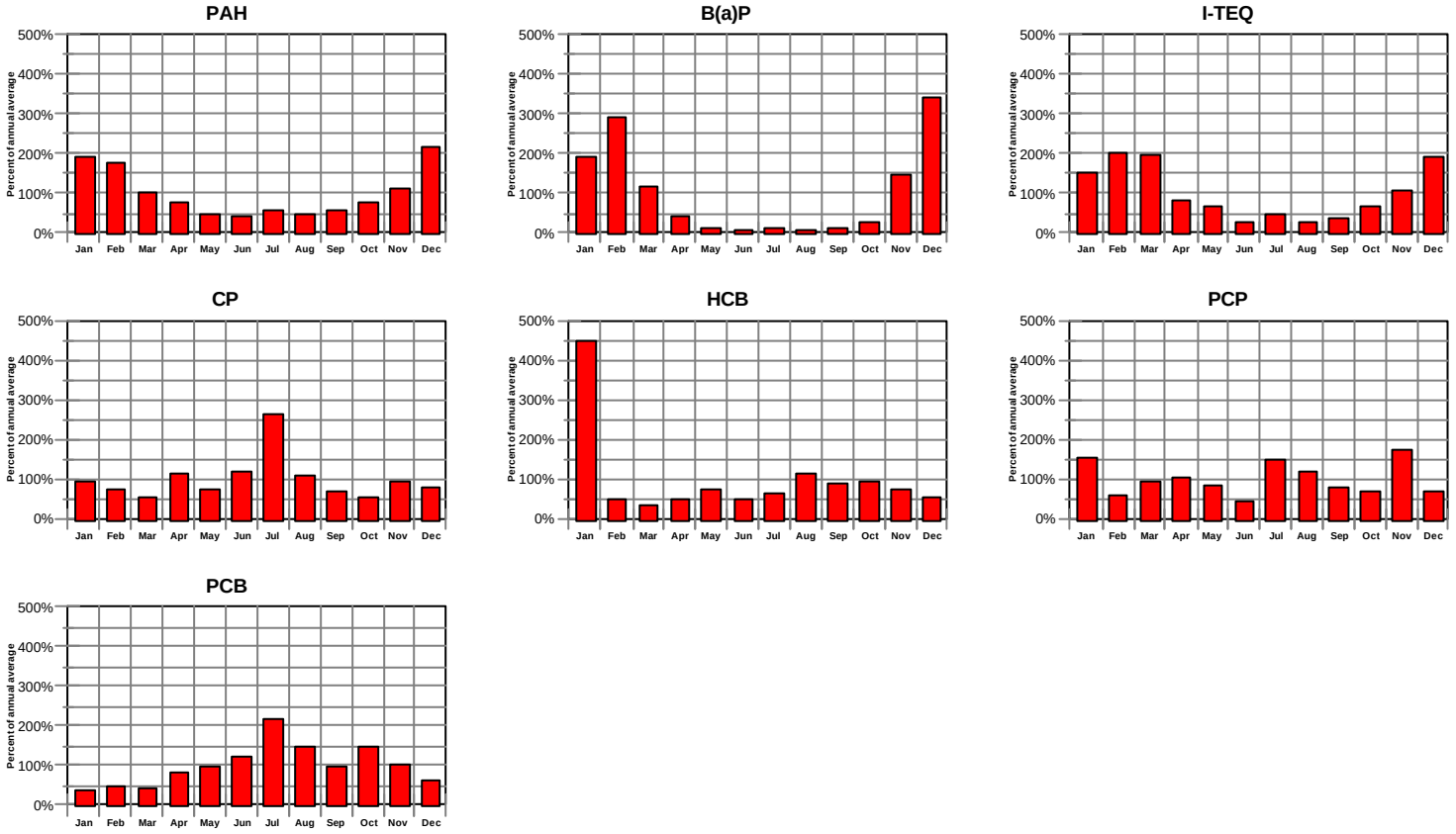


Figure 3 Correlation between concentrations of PCDD/F (TE) and B(a)P in ambient air in Aschheim near Munich, Germany, 1995/96

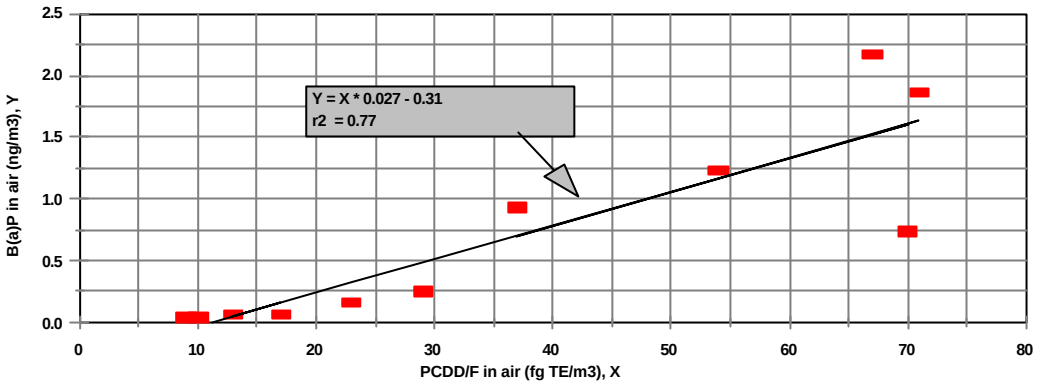


Figure 3 display the correlation between B(a)P and PCDD/F (TE) observed near Munich.

The pronounced seasonal variation of PCDD/F, PAH and PCB concentrations of are corroborated by observations in other locations as well:

- Swerev et al. report results from ambient air measurements in Augsburg (1992-93, 1994-96) and Burgkirchen (1993-95) that PCDD/F and PAH concentrations raise by a factor of 5 to 10 during the winter months whereas PCB concentrations are higher by a factor of 4 in the summer[2]
- The Swedish Environmental Research Institute reports for the sampling period 1988-1994 an increase of PAH during winter months and a peak of PCB concentrations in summer months[3]
- The seasonal variation was also observed for the City of Hamburg[4]

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2 Swerev M., Nordsiek H., Pawlik V., Hutzinger O. (1996). Impact of emissions of modern municipal waste incinerators on atmospheric concentrations of PCDD and PCDF, in: Organohalogen Compounds, Volume 28, p.134-139; (Dioxins 96, 16th Symposium on Chlorinated Dioxins and Related Compounds, Amsterdam August 12-16, 1996)

3 Brorström-Lundén E. (1996), Persistent organic pollutants in air and deposition, unpublished manuscripts, Swedish Environmental Research Institute

4 Lau C. et al. (1996). Dioxin mass balance for the City of Hamburg, Germany: Part1: objective of the study and emission inventory, , in: Organohalogen Compounds, Volume 28, p.83-88; (Dioxins 96, 16th Symposium on Chlorinated Dioxins and Related Compounds, Amsterdam August 12-16, 1996)

- A seasonal trend was observes near Eging am See (Eastern Bavaria, Germany) with markedly increased concentrations in the winter (Table 3) during two one-week sampling periods[5]. PCB concentrations were higher in the summer months.
- Strong seasonal trends for PCDD/F were also observed in several locations in Austria (Figure 4)[6].

The composite of these observations suggest the following hypothesis:

1. The primary PCCD/F emissions in Germany are currently associated with heating during the winter months.
2. The major sources are residential heating as well as smaller commercial heating plants.
3. The evaluation of emission factors suggests that prime candidates for large emissions are wood and lignite coal combustion, especially if waste materials are added.
4. The absolute emissions from these sources are likely to be in the order of 10 kg TE per year.

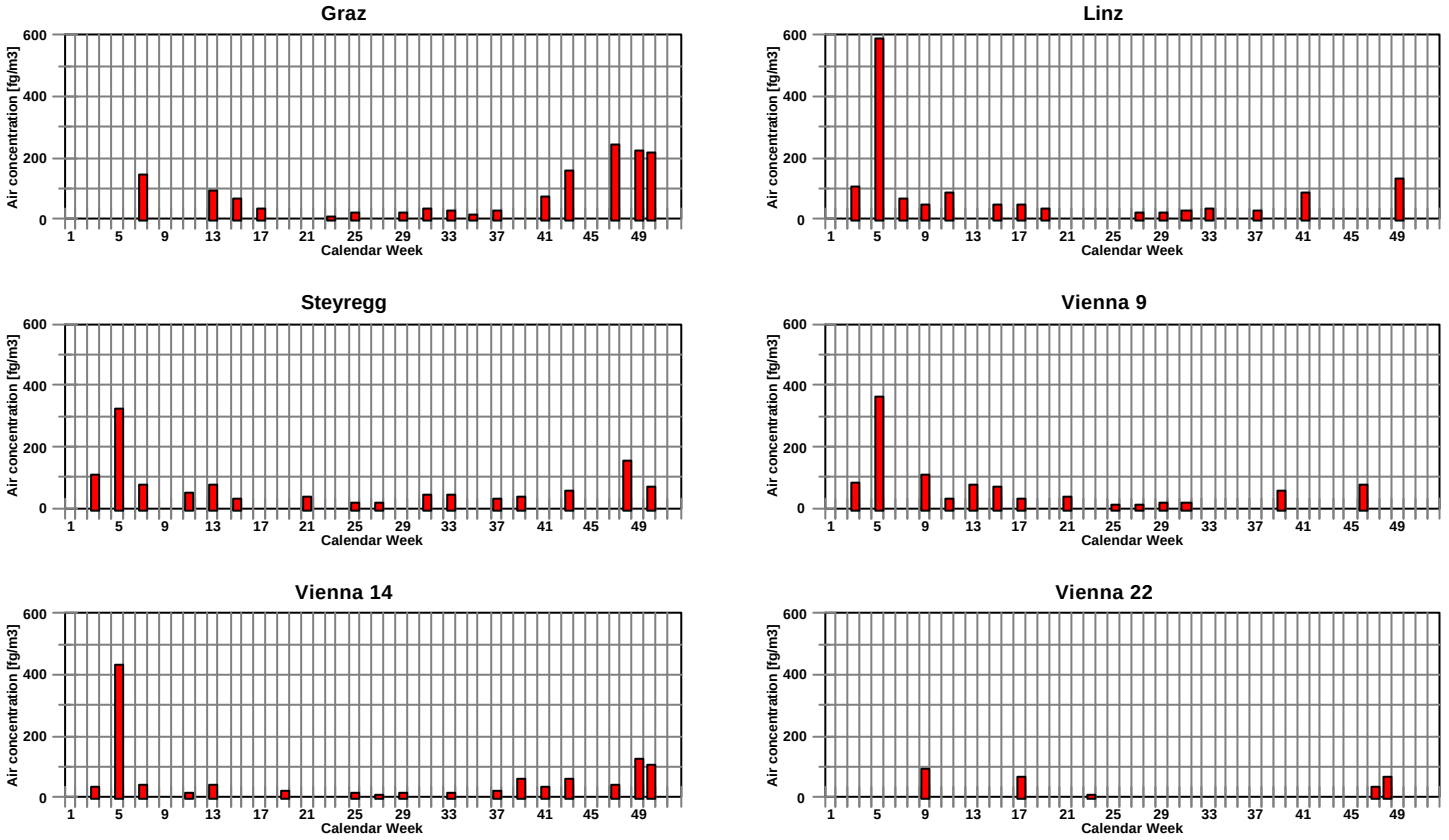
Table 3 Results of ambient air monitoring in rural Eastern Bavaria, 1995

	Winter (2/28 to 3/9,1995)		Summer (7/4 - 7/14, 1995)	
Chlorbenzenes (in ng/m³)	Außernzell	Eging am See	Außernzell	Eging am See
Trichlorobenzenes	0.766	0.646	1.080	1.14
Tetrachlorobenzenes	0.624	0.399	0.576	0.715
Pentachlorobenzenes	0.102	0.121	0.081	0.096
Hexachlorobenzene	0.163	0.174	0.235	0.239
Σ Chlorobenzenes	1.665	1.34	1.972	2.19
Dioxins and Furans (in fg/m³ I-TE)				
2,3,7,8-TetraCDD	4	3	<1	<1
PCDD/F (TE)	90	111	3.8	5.2
PCBs (in ng/m³)				
Total after DIN	0.21	0.111	0.222	0.558
Total DIN*5	1.05	0.555	1.11	2.79

[5] Franke B., Knappe F. et al. (1996). Umweltverträglichkeitsuntersuchung zur geplanten Thermischen Restmüllbehandlungsanlage (TRA) im ERZ Außernzell, ifeu-institut für Energie- und Umweltforschung Heidelberg GmbH, i im Auftrag der Abfallwirtschaftsgesellschaft Donau-Wald mbH

[6] Thanner G. & Moche W. (1996). Dioxine in der Luft von Ballungsräumen. Meßergebnisse aus Graz, Linz, Steyregg und Wien Teil 2. Monographien Bd. 76, Umweltbundesamt Wien

Figure 4 Results of ambient air monitoring for PCDD/F in Austria, 1992/93



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Source: IFEU, 1997