Chapter 2

COMPARISON OF CALCULATION RESULTS WITH MEASUREMENTS

In this Chapter the comparison of air concentrations and depositions for the selected three POP species: B[a]P, PCB-153 and 2,3,4,7,8-PeCDF calculated by regional version of MSCE-POP model with available measurements is given.

Monitoring data. For the comparison available data from EMEP monitoring network were collected from CCC reports and web-site. In addition data from national measurements and episodic campaigns was obtained from different literature sources. The list of monitoring sites measuring POPs in air and precipitation under EMEP is displayed in Table 2.1.

Table 2.1. *EMEP measurements sites for POPs in 2003*

Sites	POPs in air	POPs in precipitation
CZ3	PAHs, PCBs, pesticides, HCHs	
FI96	PAHs, PCBs, pesticides, HCB	PAHs, PCBs, HCB
DE1		PAHs, PCBs, pesticides, HCB, HCHs
DE9		PAHs, PCBs, pesticides, HCB, HCHs
IS91	PCBs, pesticides, HCB, HCHs	PCBs, pesticides, HCB, HCHs
IE02		PCBs, pesticides, HCB, HCHs,
LT15	B[a]P	
NO42	PAHs, pesticides, HCHs, HCB, PCBs	
SE2/SE14	PAHs, PCBs, pesticides	PAHs, PCBs, HCHs
SE12	PAHs, PCBs, pesticides	PAHs, PCBs, HCHs

Almost all EMEP monitoring sites (except for CZ3) are located in the northern part of Europe. To enlarge the base of the comparison, additional data from the following monitoring sites and campaigns are included:

- The results of the joint Canadian/German Project “Quality of measuring data on atmospheric inputs of POPs” [*Gusev et al.*, 2005b]. Within this project measurement data on deposition fluxes and concentrations in the atmosphere and precipitation at a lot of European sites for B[a]P were collected.
- The measurement data collected under POPCYCLING-Baltic project [*Pacyna et al.*, 1999]. Within this project a lot of measurement data are collected for locations close to Baltic Sea.
- Additional measurement data obtained at Czech site Kosetice (CZ3) both in air and precipitation.
- The measurements of POP concentrations in the United Kingdom from DETR report [*Coleman et al.,* 1998].
- The results of passive sampling campaign performed by Lancaster University and Meteorological Service of Canada in June – July 2002 [*Jaward et al.,* 2004].

The comparison of calculated PCDD/F concentrations in air and precipitation with monitoring data is based entirely on the results of non-EMEP measurements since measurements of PCDD/Fs are not yet included into the EMEP monitoring program (see Table 2.1).

In the comparison the emphasis is put on measurement results obtained at EMEP monitoring sites.

The usage of measurement data for the comparison requires the analysis of specific features of measurement sites. For this reason the corresponding information was collected from CCC reports and EMEP website (Annex C). The most important issues for the comparison of model calculations with measurements are:

- Sampling frequency and sampling periods. For example measurement programs at FI96, SE2 and SE12 include one-week sample per month. This hampers the comparison of measured values with monthly means calculated by the model.
- The information on surroundings of the site and land use. Such information is of use for evaluation of representativeness of the site with respect to model results, which have spatial resolution 50×50 km^2. The presence of strong emission sources in the same or neighboring grid cells can essentially influence results of the comparison.
- The information on a number of samples below the detection limit at measurement sites and values of the detection limit. The latter information is absent for almost all EMEP sites.
- Uncertainties in measurement data. These are formed by the uncertainties in sampling and the uncertainties of laboratory analysis. The latter source of uncertainty can be evaluated on the basis of laboratory comparison carried out by CCC [*Manø and Schaug*, 2003]. The comparison showed that the deviations of measurement results in national laboratories for the analysis of extracts of real samples of the ambient air were found to be 30% for B[a]P and 40% and more for PCB-153.

The obtained information is used in the report for the analysis of some discrepancies between measurements and calculations. In addition, in the course of the analysis of seasonal variations of concentrations in air and precipitation a procedure of separating outliers is used in this report. This procedure is as follows. For any period without pronounced trend mean value of measurements and their square root deviation are determined. All measured values lying outside 3σ-interval around mean value are considered as outliers.

More information on the measurement sites and methods are found in EMEP/CCC's data report on heavy metals and POPs [*Aas and Breivik*, 2004].

Modelling data. Simulations of long-range transport and accumulation of B[a]P, 2,3,4,7,8-PeCDF and PCB-153 were made for the period from 1990 to 2003 by regional version of MSCE-POP model with spatial resolution 50×50 km^2. In addition, for PCB-153 calculations for the same time period by hemispheric version of the model are used for evaluation of contributions of non-EMEP sources of the Norhtern Hemisphere. The description of MSCE-POP model together with the description of the input data (meteorology, land cover, leaf area index, organic carbon content in soil, physical-chemical parameters of the considered substances etc.) is given in EMEP/MSC-E Technical Report 5/2005 [*Gusev et al.*, 2005a]. Emission data for B[a]P and PCDD/F were compiled on the basis of official data submitted to UN ECE Secretariat by Parties to the Convention supplemented when necessary by expert estimates [*Pacyna et al.,* 1999; *Tsybulski et al.*, 2001; *Berdowski et al*., 1997]. Emission data for PCB-153 were taken from emission inventory by *K. Breivik* with co-authors [*Breivik et al.,* 2002b].

More detailed description of emission data used for modelling can be found below in the Annex A.

Methodology. Comparison of modelling data against measurements includes: comparison of concentrations in surface atmospheric layer, comparison of concentrations in precipitation and comparison of deposition fluxes. In each of these parts the comparison is performed into two stages:

- Comparison of calculated long-term trends at locations with long enough time series of measurements. At this stage measured and calculated annual means of the considered parameter is compared. Then on the basis of seasonal variations the analysis of the comparison results is performed including selection of outliers and explanation of most valuable disagreements between measurements and calculations.
- Comparison of modelling results with all available measurements. Here scatter plots of calculated and measured values of concentrations/fluxes together with cumulative distribution of calculated-to-measured factor are analyzed. In the analysis we use the median of distribution of calculated-to-measured factor and fractions of measurements, which agree with calculations within factors 2 and 3. The median of distribution of calculated-to-measured factor is such a value of the ratio that the numbers of measurements with higher and lower values of the ratio are equal. This characteristic shows overall underestimation/overestimation of measurements by the model. The fractions of calculated values, which agree with measurements within factors 2 and 3 characterize the scattering between monitoring and modelling results.

In addition, for air concentrations of B[a]P and PCB-153 the analysis of the agreement between measurements and calculations from the viewpoint of spatial distributions in a number of years is done.

An important part of the analysis of the agreement between calculations and measurements is the uncertainty analysis. Here the analysis of discrepancy between measured and modelled results are given taking into account uncertainties of model description, emissions and measurements.

2.1. Benzo[a]pyrene (B[a]P)

For the comparison calculation results of simulations of B[a]P transport within the EMEP region for the period from 1990 to 2003 are used. These calculations are made by the regional version of MSCE-POP model with 50×50 km resolution. Emission data for calculations were compiled on the basis of official emission data supplied by expert estimates [*Pacyna et al.,* 1999; *Tsybulski et al.*, 2001; *Berdowski et al*., 1997] when necessary. We remark insufficient data on seasonal variations of B[a]P emissions which, together with rough description of degradation process (for example, photodegradation of B[a]P both in particulate and gaseous phase is not included in the model due to the lack of necessary information) leads to the discrepancies between measurement and modelling results. Below we present the results of comparison of these calculations with available measurements. Measurements at 8 EMEP sites together with additional data from German, Polish, Czech and UK sites from 1992 to 2003 are used. The location of these sites is shown in Fig. 2.1, where EMEP sites are marked red.

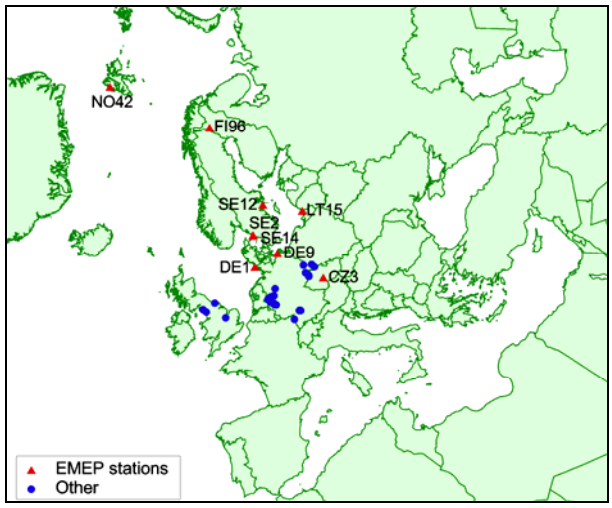


Fig. 2.1. *Location of measurement sites used for the comparison of calculations and measurements for B[a]P*

Air concentrations

Long-term trends of contamination will be considered first. Long enough time series of measurements are available at EMEP sites NO42, FI96, CZ3, SE2, SE12, SE14 and LT15. In the analysis we mainly concentrate at measurements in the period from 1997 to 2003 since the data obtained earlier are not so reliable.

EMEP sites. Let us begin with the background sites FI96 and NO42. These sites represent remote regions of Europe with rather low levels of concentrations in the atmosphere.

The plot of temporal trends of measured and calculated B[a]P air concentrations at NO42 for 1997 – 2003 is displayed in Fig. 2.2. According to the CCC data a lot of measurements at NO42 are below the detection limit. In 1997 27 samples of 51 are below detection limit, for 1998 – 22 of 38, and in 2002 – 34 of 58 (Annex C). So the data for these years are to be used for the comparison with caution.

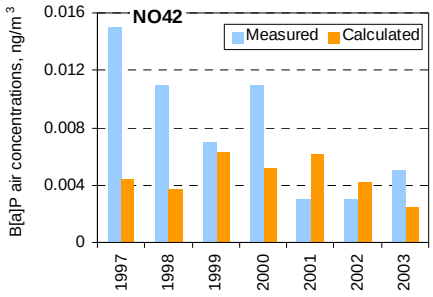


Fig. 2.2. *Measured and calculated temporal trends of B[a]P air concentrations at NO42 for the period 1997 – 2003, ng/m^3*

Low values of air concentrations (around 0.005 ng/m^3) are characteristic of this station. The agreement between measurements and calculations is mainly within a factor of 2.

More information can be obtained from the analysis of seasonal variations of measured and calculated air concentrations. The corresponding plot is presented in Fig. 2.3.

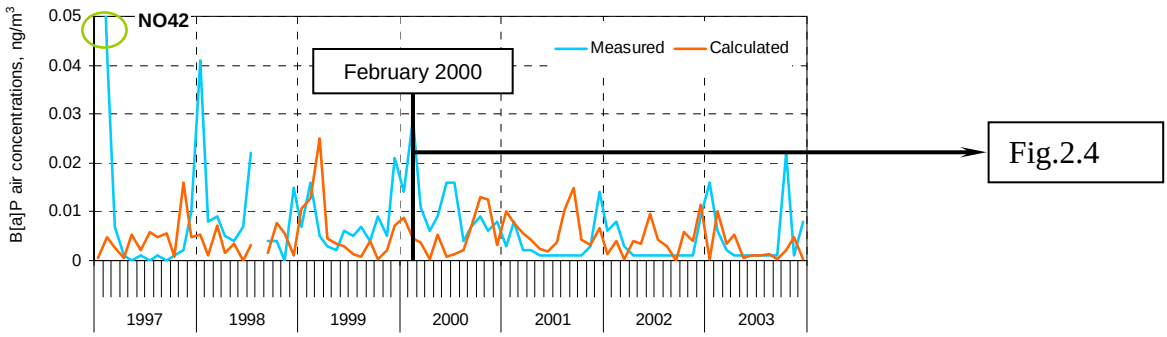


Fig. 2.3. *Seasonal variation of B[a]P air concentrations at NO42 in 1997 – 2003*

It is seen that in general the model follows concentration levels given by measurements. However, measurements show (at least for three last years) pronounced seasonal variations with high values of concentrations in cold season and low in the warm season. This can be caused by two possible reasons. First, emission seasonal variations used in the model need further refinement. The second reason is the roughness of model description of B[a]P degradation in the atmosphere. At present only chemical degradation of gaseous phase is realized in the model. The photodegradation both of particulate and gaseous phases is not included since there are no reliable data on the corresponding parameters. Later the underestimation of seasonal variations of air concentrations will be seen at other sites as well.

Further, seasonal variations of air concentrations at NO42 are characterized by sharp peaks, which are not reproduced by the model. The reason of this phenomenon can be that NO42 is located near

the model domain boundaries. Therefore significant episodic contribution to air concentrations measured at this site can be attributed to the emission sources located outside the model domain and thus not taken into account in modelling. This is illustrated by the peak value in February 2000 (see Fig. 2.3). The two maps with backward air mass trajectories reflecting atmospheric transport from industrial regions of Asian part of Russia in February 2000 are displayed in Fig. 2.4. This explains the peak value of air concentrations observed at NO42 in this period.

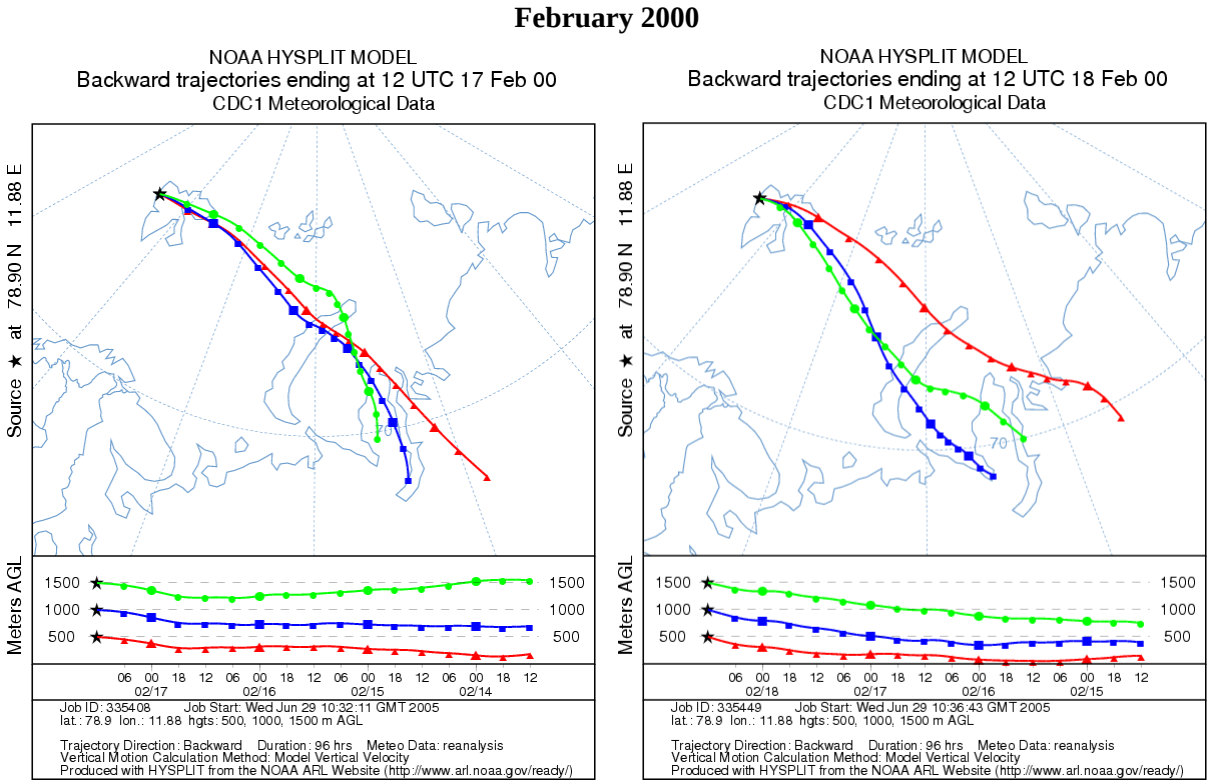


Fig. 2.4. *Backward trajectories of air masses for the site NO42 in February 2000*

For further refinement of the agreement between calculations and measurements proper definition of contributions of external sources is needed.

The levels of measured and calculated concentrations at FI96 are rather low (about 0.001 – 0.03 ng/m^3). For almost all years the agreement between measurements and calculations is within a factor of 1.4, Fig. 2.5. The only exception takes place for 2000, where calculated-to-measured ratio equals about 3 and measured annual mean of air concentrations is about four times lower than in 2001–2003. On the other hand, calculated concentrations agree well with official emission data for Finland (total emission values and their spatial distribution) in the considered period. The discrepancy in 2000 needs further examination together with experts on measurements and emissions.

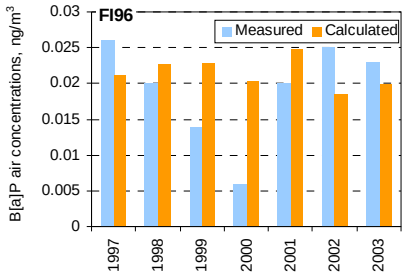


Fig. 2.5. *Measured and calculated temporal trends of B[a]P air concentrations at FI96 for the period 1997 – 2003, ng/m^3*

Seasonal variations of calculated and measured air concentrations at this site are shown in Fig. 2.6. The outliers (that is, values of measured air concentrations lying outside 3σ-interval around mean value) are marked green in the diagram.

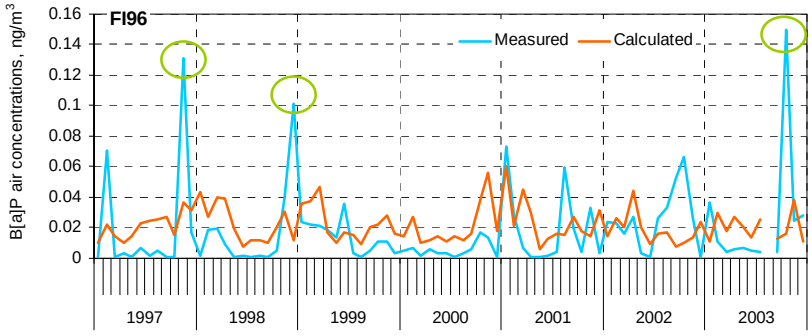


Fig. 2.6. *Seasonal variation of B[a]P air concentrations at FI96 in 1997 – 2003. Outliers are marked green.*

Excluding outliers, model calculations in general follow the trend of measured concentrations (especially for the period from 1998 to the first half of 2001). Some exceptions can be explained by the fact that measurements at this site are performed within one week each month (see Annex C) whereas the model represents monthly means of air concentrations.

Let us proceed now with the analysis of sites located in more contaminated parts of Europe.

Seasonal variations (measured and calculated) of air concentrations at CZ3 are presented in Fig. 2.7. Concentration levels at this site are about 0.2 – 1 ng/m^3.

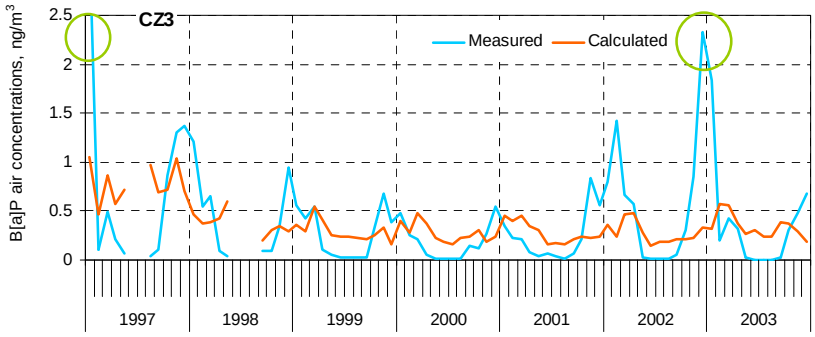


Fig. 2.7. *Seasonal variations of B[a]P air concentrations at CZ3 in 1997 – 2003. Outliers are marked green*

It is seen that there exist very sharp peaks of concentrations in January 1997, December 2002 and January 2003. These peaks can be viewed as outliers since they are outside 3σ-interval around mean value of air concentrations for the considered three years. Besides, for July and August 2003, zero values of concentrations are reported. Excluding these values, we come to the plot of the comparison of measured and calculated B[a]P air concentrations at CZ3 (Fig. 2.8).

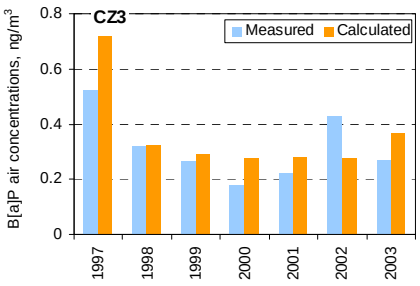


Fig. 2.8. *Measured and calculated temporal trends of B[a]P air concentrations at CZ3 for the period 1997 – 2003 (improved), ng/m^3*

The agreement of air concentrations at CZ3 is within a factor of 1.5 for all considered years.

Another important conclusion, which can be derived from this comparison is that measurements show strong difference between values of air concentrations in cold and warm seasons. This once more shows that the information on seasonal variations of B[a]P emissions and the description of degradation process can be rather essential for modelling of contamination levels of the pollutant.

Non-EMEP sites. The following non-EMEP sites Hazelrigg, Stoke Ferry, High Muffles (the United Kingdom), Cherniawa (Poland) and Zinnwald (Germany) are included into the comparison. It is worth to mention that two of these locations (Stoke Ferry – GB4 and High Muffles – GB14) are included into the EMEP measurement network but the data on POPs are not included into the CCC database.

Fig. 2.9 presents the comparison data at three locations in the United Kingdom: Hazelrigg, Stoke Ferry and High Muffles for various time periods. These sites are not influenced essentially by emission sources of Europe except for the United Kingdom. The emissions of the United Kingdom are presented by the country officially for all years of the calculation period. So, the comparison of calculated and measured values at these sites could be considered as rather reliable.

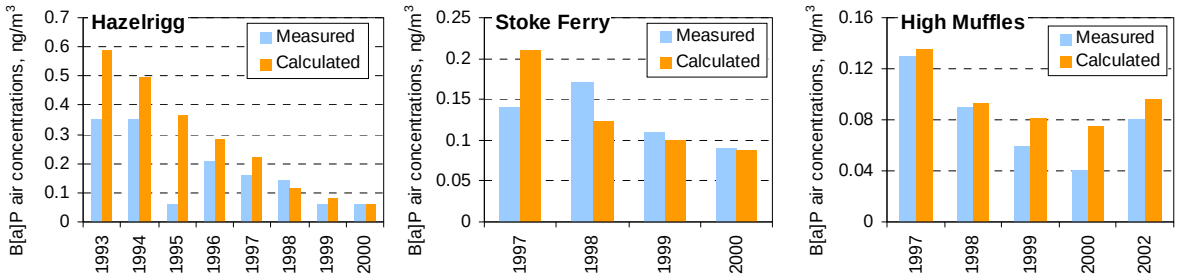


Fig. 2.9. *Measured and calculated temporal trends of B[a]P air concentrations at three locations in the United Kingdom, ng/m^3*

It is seen that the agreement between calculations and measurements at these locations is mostly within a factor of 1.5. High discrepancy between measurements and calculations takes place at Hazelrigg in 1995. At the same time, decreasing trend of calculated concentrations agree well with official emission data. Besides, in two of four quarters of this year measured values are below detection limit. The comparison of measured and calculated long-term trends of air concentrations show that the model correctly describes temporal trends of contamination in the United Kingdom. It is important to stress that the model not only describes general decrease during 8 years (1993 – 2000) but also reproduces the increase of concentration level at High Muffles in 2002. Thus, using reliable emissions for the United Kingdom, the model is able to predict correctly air concentration levels in this country. Unfortunately, the absence of monthly averages of air concentrations at these sites do not allow analyzing seasonal variations of contamination generated by the model.

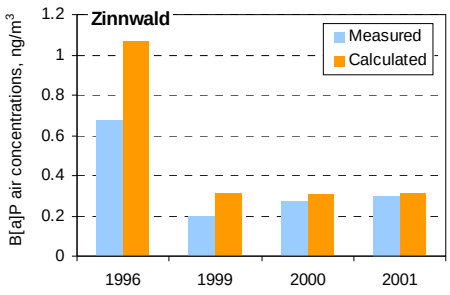


Fig. 2.10. *Measured and calculated B[a]P air concentrations at Zinnwald (Germany) for the period from 1996 to 2001, ng/m^3*

Similar situation takes place also in some other parts of Europe. The comparison of measurements and calculations at site Zinnwald (Germany) for the period from 1996 to 2001 is displayed in Fig. 2.10. Here calculated air concentrations agree with measurements within a factor of 1.3 on the average.

Measured and calculated seasonal variations of air concentrations at this site are available for 1999 and 2000 (Fig. 2.11).

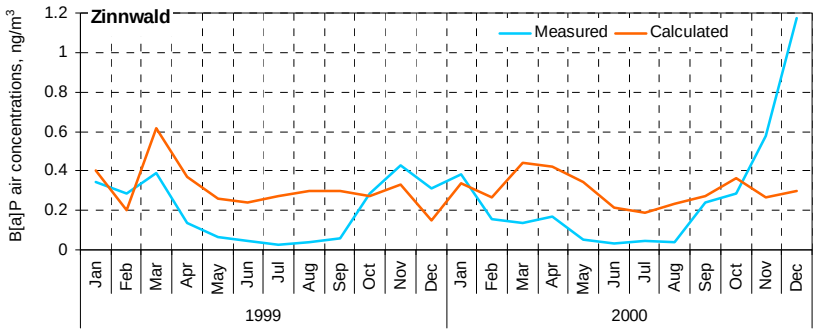


Fig. 2.11. *Seasonal variations of B[a]P air concentrations at Zinnwald in 1999 – 2000*

The comparison of seasonal variations again shows that seasonal variations of emissions seem to be more pronounced than that accepted in the model. At the same time annual averages for calculated and measured air concentrations are in a good agreement.

The plot of temporal trends of measured and calculated air concentrations at Cherniawa (Poland) is presented in Fig. 2.12. The agreement between measurements and model results at Cherniawa is again mostly within a factor of 1.5.

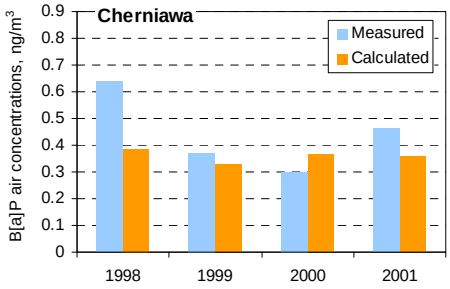


Fig. 2.12. *Measured and calculated B[a]P air concentrations at Cherniawa (Poland) in 1998 – 2001, ng/m^3*

Measured and calculated seasonal variations of air concentrations at this site are displayed at the plot in Fig. 2.13.

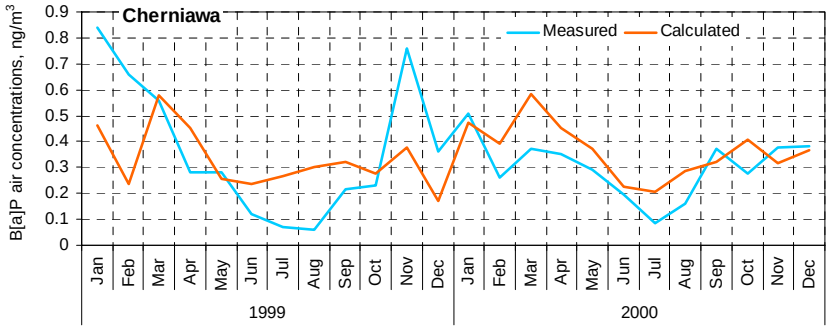


Fig. 2.13. *Seasonal variations of B[a]P air concentrations at Cherniawa in 1999 – 2000*

At the considered site model calculations correlate with measurements. However, comparison measurements and calculations in 1999 shows, as above, that model can underestimate seasonal variability of B[a]P air concentrations.

So, the comparison of calculated air concentrations with measurements obtained at EMEP sites and within national measurement campaigns show that the model reproduces air concentrations in various locations in Europe mainly within a factor of 1.5 for a number of years.

Spatial distribution of B[a]P air concentrations (for 2003 – the end of calculation period) obtained by calculations together with long-term trends of concentrations (measured and calculated) at EMEP sites for a number of years is shown in Fig. 2.14. The calculations allow evaluating spatial distribution of contamination and temporal trends at particular locations.

Spatial distribution of calculated air concentrations agree with available measurements. Measurements at the remote sites NO42 and FI96 show very low concentration levels 0.002 – 0.03 ng/m^3. Calculations present the same concentration levels. Good agreement is obtained at site FI96 (mostly within a factor of 1.5). Some discrepancies between calculations and measurements at NO42 are due to small values of concentrations and, possibly, the influence of emission sources outside the EMEP region.

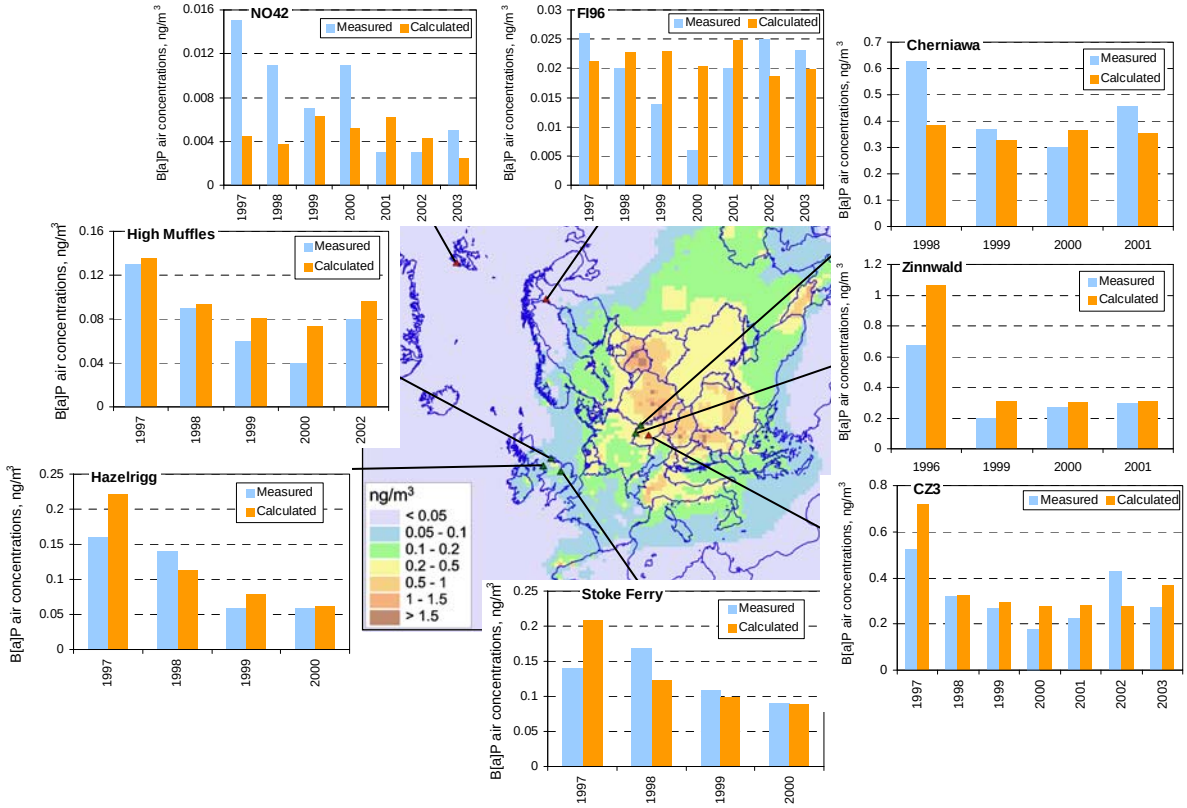


Fig. 2.14. *Measured and calculated B[a]P air concentrations, ng/m^3*

According to measurements, concentration levels at site CZ3 located in a contaminated part of Europe are about 0.3 – 0.5 ng/m^3 and higher. Same values are generated by model calculations. The agreement of air concentrations at this site is within a factor of 1.5 for all years.

Similar levels of air contamination are obtained at Zinnwald (Germany) and Cherniawa (Poland) both by calculations and measurements. The agreement between measurements and modelling results at these sites is mostly within a factor of 1.4.

For the United Kingdom (sites Hazelrigg, Stoke Ferry and High Muffles), where official emission data are used and the influence of other emission sources to air contamination is small, the model correctly predicts long-term tendencies of contamination. Typical levels of concentrations at these sites (both measured and predicted by the model) are around 0.1 ng/m^3. The agreement between calculations and measurements at all three sites is mostly within a factor of 1.4. The model reproduces general

decrease of air concentrations at Hazelrigg and Stoke Ferry and the growth of air concentrations in 2002 at High Muffles.

So, it can be concluded that the model correctly describes spatial distribution of concentration levels in different parts of Europe and long-term trends of contamination.

Specific cases. Here we consider the comparison of measured and calculated air concentrations for the cases that require special consideration.

The comparison of measured and calculated B[a]P air concentrations at site SE12 is shown in Fig. 2.15.

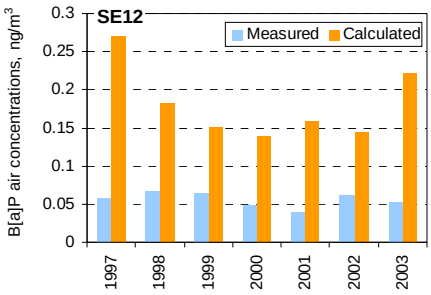


Fig. 2.15. *Measured and calculated temporal trend of B[a]P air concentrations at SE12 for the period 1997 – 2003, ng/m^3*

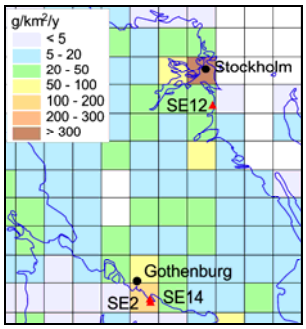


Fig. 2.16. *B[a]P emission distribution in Southern part of Sweden and location of Swedish measurement sites SE2, SE12 and SE14*

The comparison shows that model calculations based at expert emission estimates overestimate measured concentrations at this site 3 times on the average. The reason of such discrepancy is large value of emissions in a neighboring cell containing Stockholm (Fig. 2.16). It seems that spatial distribution for emissions in Sweden are to be refined on the basis of official data. This could improve the agreement of measured and calculated air concentrations at the considered site.

Additionally, the discrepancy between measured and calculated values can be caused by rough model description of local meteorological situation near zone where SE12 is located.

Seasonal variations of B[a]P air concentrations at SE12 are shown in Fig. 2.17.

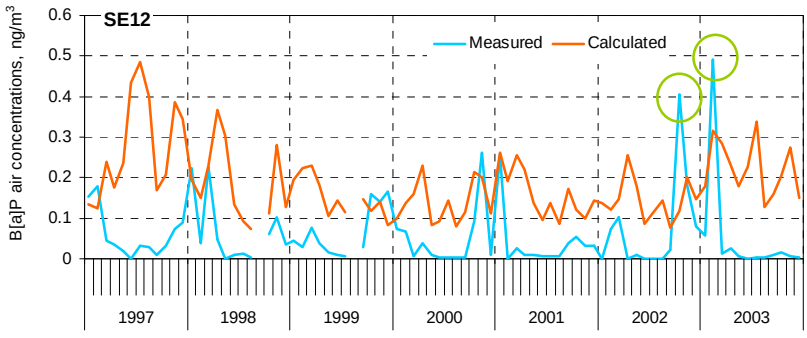


Fig. 2.17. *Seasonal variations of B[a]P air concentrations at SE12 in 1997 – 2003. Outliers are marked green.*

It is seen that, in spite of general overestimation, values of measured and calculated air concentrations correlate in some periods. The seasonal variations of B[a]P air concentrations at SE12 are characterized by sharp peaks of concentrations mainly in the winter period. Similar to earlier considered sites, the most probable reason for this can be underestimation of B[a]P emission seasonal variations.

Similar situation takes place at sites SE2/SE14 located in one and the same grid cell. The comparison of measured and calculated values of B[a]P air concentrations at sites SE2/SE14 for the period from 1997 to 2003 is shown in Fig. 2.18.

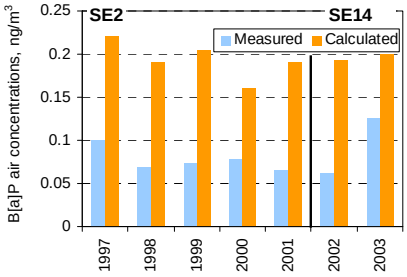


Fig. 2.18. *Measured and calculated temporal trend of B[a]P air concentrations at SE2/SE14 for the period 1997 – 2003, ng/m^3*

Model calculations represent in general temporal trend of measured air concentrations but overestimate measured values 2.6 times on the average. The reason of this underestimation is spatial variability of concentrations within a grid cell. The cell with sites SE2/SE14 contains also Gothenburg (see Fig. 2.16), located near the boundary of the cell – city with relatively high level of emissions. The emissions in this cell equal 0.25 t/y in 2003 whereas emissions in the neighboring cells do not exceed 0.05 t/y. In model calculations, emissions of Gothenburg are spread over the considered cell, which leads to high values of air concentrations there. Such values are not characteristic of the considered measurement sites.

Seasonal variations of B[a]P air concentrations at SE2/SE14 are shown in Fig. 2.19.

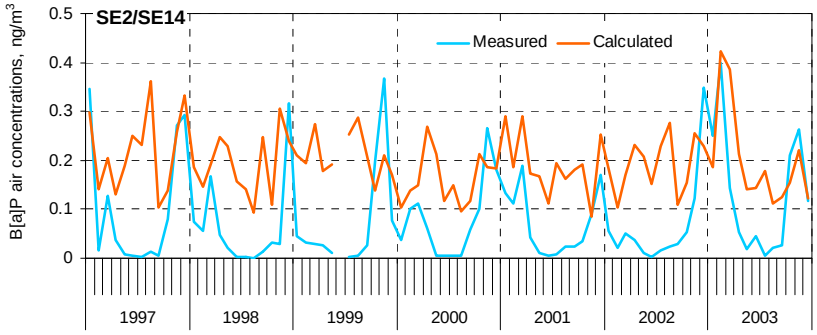
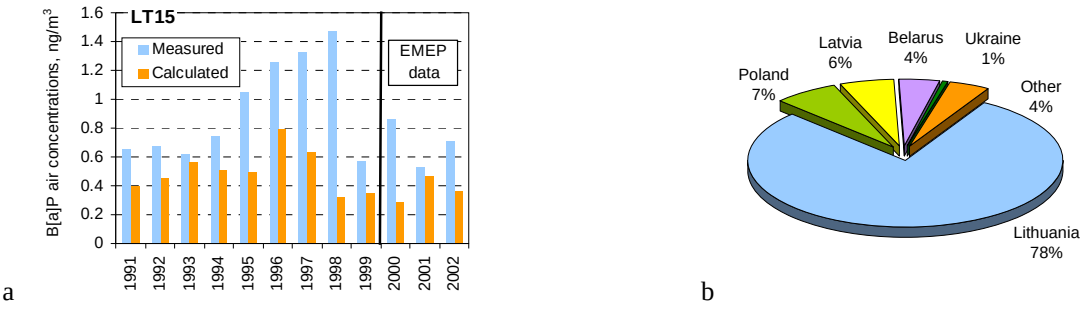


Fig. 2.19. *Seasonal variations of B[a]P air concentrations at SE2/SE14 in 1997 – 2003. Outliers are marked green.*

Some correlations between measured and calculated values take place in 1998, 2000, 2001 and 2003.

So, overestimation of air concentrations at SE2/SE14 is caused by the same reasons as for SE12. Seasonal variations of air concentrations at these sites again show a pronounced tendency of low values in warm seasons and high values in hot seasons. The most probable reason of this is underestimation of seasonal variations of emissions.

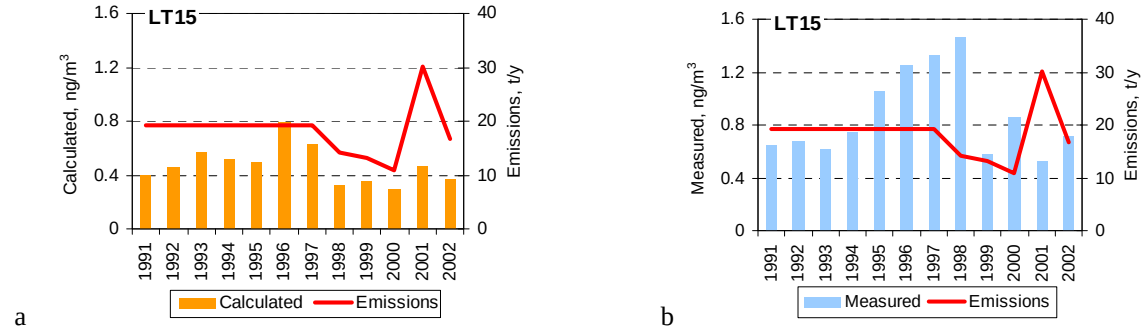
Temporal trends of measured and calculated air concentrations at LT15 for the period from 1991 to 2002 are displayed at Fig. 2.20a. It must be noticed that only the data for 2000 – 2002 are included into the EMEP database.



a b

Fig. 2.20. *Measured and calculated temporal trends of B[a]P air concentrations at LT15 for the period 1991 – 2002, ng/m^3(a). Export diagram of B[a]P air concentrations for Lithuania in 2003 (b)*

At this site model underestimates measurements about 1.7 times on the average, and the underestimation reaches 4.5 times in 1998. For the analysis of the obtained disagreement, the trend of B[a]P emissions in Lithuania for the considered period will be used. Calculation of source-receptor relationships for B[a]P show that about 80% of air concentrations in the country are determined by domestic B[a]P sources (Fig. 2.20b). Comparison of calculated and measured B[a]P air concentrations at LT15 with emission trend used in calculations is shown in Fig. 2.21a and b, respectively. We remark that no official data on B[a]P emissions in Lithuania are submitted to UN ECE Secretariat for 1991 – 1999.



a b

Fig. 2.21. *Comparison of calculated (a) and measured (b) values of B[a]P air concentrations at LT15 with emissions of Lithuania for the period 1991 – 2002*

It is seen that trend of emissions used in modelling cannot explain the obtained measurements whereas model calculations generally follow the changes in the period 1996 – 2002. So, it seems that the discrepancy between measurements and calculations at LT15 can be explained by uncertainties of emission data or of measurements. It should be noticed that “a relatively higher concentration of benzo(a)pyrene at the Preila station may be attributed to the influence of domestic heating in the nearest villages and increased traffic on the road Klaipeda-Kaliningrad”. Besides, “The Preila background station may be influenced not only by close permanent sources but also by different occasional sources, which are usually a result of urbanization on the Curonian Spit” (the report by A. Milukaite at the final Workshop on RBA PTS Project, Brno, November 2003). So, the comparison between measured and calculated air concentrations at LT15 is not reliable and only indicates similar measured and calculated contamination levels.

Seasonal variations of calculated and measured B[a]P air concentrations at LT15 are shown in Fig. 2.22.

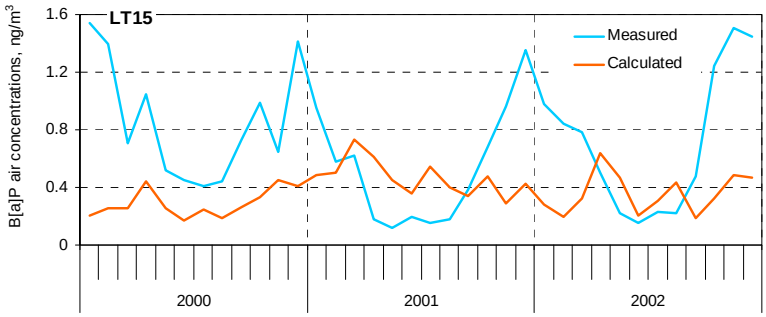


Fig. 2.22. *Seasonal variations of B[a]P air concentrations at LT15 in 2000 – 2002*

The comparison of calculated and measured seasonal variations at this site shows again that the model underestimates the difference between concentrations in cold and warm seasons.

General results. The scatter plot of all results of the comparison (including the above analyzed results, specific cases and measurements made at locations where the analysis of the comparison is complicated by the absence of necessary information) is given in Fig. 2.23a. For grid cells containing more than one measured value the average between measurements in this cell is used.

This comparison gives an impression of the overall uncertainties that is uncertainties caused by model, measurements and emission estimates altogether.

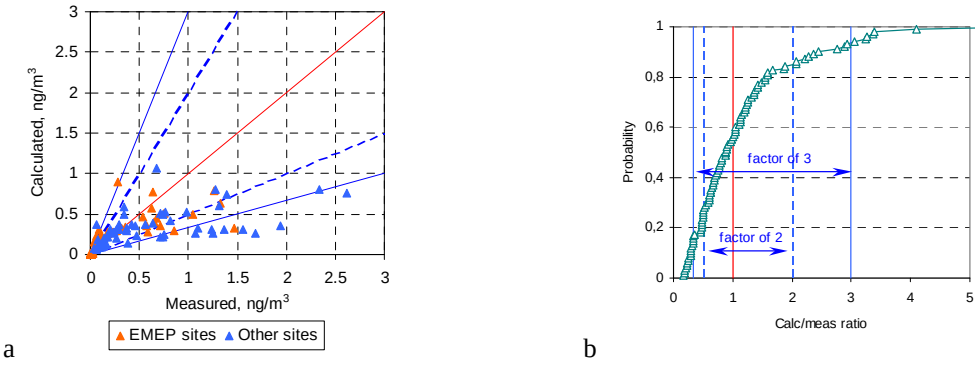


Fig. 2.23. *Scatter plot of measured and calculated annual means of B[a]P air concentrations in Europe 1991 –2003 (annual averages) (a). EMEP sites are marked red. Cumulative distribution of calculated to measured factor (b)*

The range of measured values of air concentrations is from 0.03 to 2.5 ng/m^3. The range of calculated values is from 0.02 to 1 ng/m^3. For over 60% of calculated values the agreement is within a factor of two, and in most cases measured and calculated air concentrations agree within a factor of three (over 80%). This shows that the model describes satisfactorily temporal and spatial variations of B[a]P air concentrations in surface atmospheric layer. The cumulative distribution of calculated to measured factor is presented in Fig. 2.23b. The median of the distribution is 0.88. This means that on the average the model slightly underestimates air concentrations of B[a]P.

Concentrations in precipitation and deposition fluxes

The amount of measurements of concentrations in precipitation and deposition fluxes is much more limited than for concentrations in the atmosphere.

Long-term trends. Long-term series of measurements of concentrations in precipitation and deposition fluxes are available at the following EMEP sites: DE1, DE9 and CZ3 (concentrations in precipitation) and FI96, SE2, SE12 and SE14 (deposition fluxes).

Data on measurements of B[a]P concentrations in precipitation in 1999 – 2002 were kindly put at our disposal by Dr E Bieber (Germany). The comparison of measured and calculated values of concentrations in precipitation at DE1 (annual averages) is shown in Fig. 2.24 for the period 1997 – 2003. For all years except for 1998 and 2001 calculations agree with measurements within a factor of 1.5.

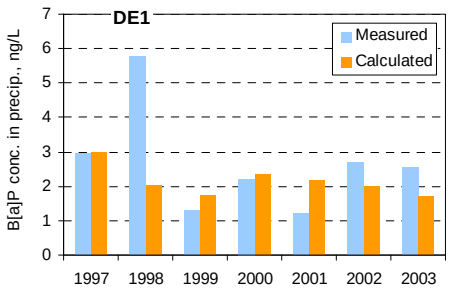


Fig. 2.24. *Measured and calculated B[a]P concentrations in precipitation at DE1 in 1997 – 2003, ng/L*

For the analysis of the obtained discrepancy, the plot of seasonal variations of B[a]P concentrations in precipitation at DE1 for the considered period is presented in Fig. 2.25.

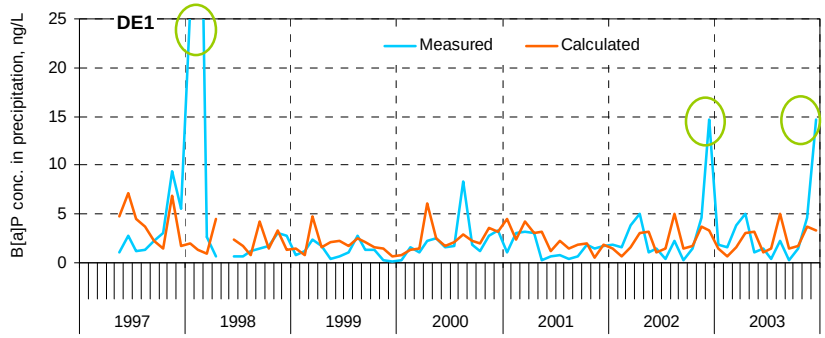


Fig. 2.25. *Seasonal variations of B[a]P concentrations in precipitation at DE1 in 1997 – 2003. Outliers are marked green*

The peaks marked green in the diagram can be viewed as outliers since they are outside 3σ-interval around mean value of concentrations in precipitation for the considered years. Calculation-to-measured ratio for 1998 and 2002 excluding these values are within a factor of 1.3. Besides, except for outliers, there is seen correlation between measured and calculated values of concentration in precipitation at the site. So, the model is not able to reproduce peak values in concentrations in precipitation. Possibly, this is caused by rough description of precipitation rates used in the model.

The comparison of measured and calculated values of concentrations in precipitation at DE9 (annual averages) is shown in Fig. 2.26.

The agreement between calculations and measurements at DE9 is within a factor of 1.5 except for three years: 2000, 2001 and 2003. The values of measurements for 2000 and 2001 are essentially lower (2 times and more) than the average concentrations within the considered period. The reason of discrepancies in these years is a topic for further discussion together with experts in measurements. To analyze the discrepancy in 2003, we consider the plot of seasonal variations of B[a]P concentrations in precipitation at DE9 for the considered period (Fig. 2.27).

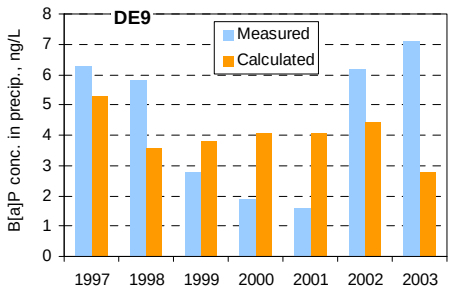


Fig. 2.26. *Measured and calculated B[a]P concentrations in precipitation at DE9 in 1997 – 2003, ng/L*

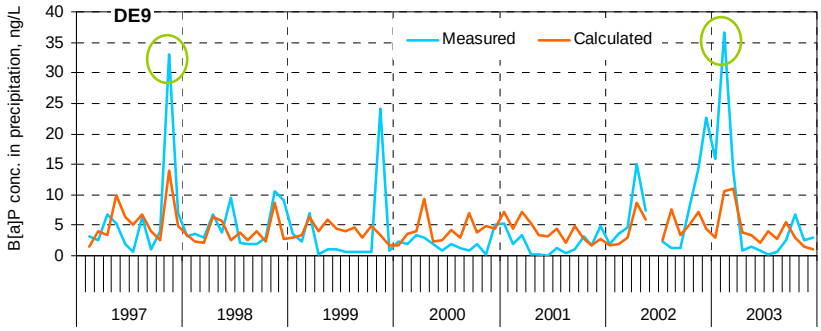


Fig. 2.27. *Seasonal variations of B[a]P concentrations in precipitation at DE9 in 1997 – 2003. Outliers are marked green*

Calculation-to-measured factor computed for 2003 without the outlier is around 1. For some periods there is seen correlation between calculated and measured values. Very good correlation takes place in 1998. However, the analysis of the agreement between calculation and measurement results again shows that the model does not reproduce well seasonal variations of B[a]P concentrations in precipitation. It is concerned with the absence of seasonal variability of official emission data for Germany.

The comparison of annual averages of concentrations in precipitation at CZ3 is shown in Fig. 2.28. We remark that these data are not included into EMEP database.

The model generally overestimates the values of concentrations in precipitation given by measurements. Strong overestimation takes place in 1997, 2000 and 2001. In 1999 calculated-to-measured factor equals 1.7. For the rest years the agreement between measurements and calculations is within a factor of 1.4. Model calculations show decreasing trend of air concentrations at CZ3 for all considered period. This corresponds to the trend of emission totals used in calculations, which are decreasing from 12.4 t/y in 1997 to 6.4 t/y in 2003. We remark that official emission data for Czech Republic are reported only for 2002 and 2003. For the rest years in the model interpolation between

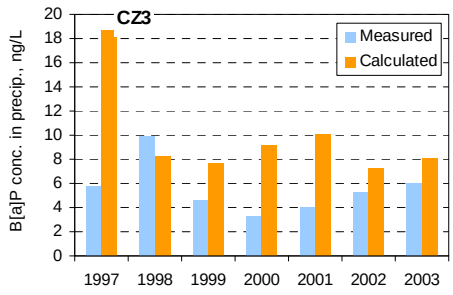


Fig. 2.28. *Measured and calculated B[a]P concentrations in precipitation at CZ3 in 1997 – 2003, ng/L*

expert estimates by [*Pacyna et al.,* 1999] and official data of 2002 are used. Refinement of emission data could improve the agreement between calculations and measurements as it is seen for 2002 and 2003.

Seasonal variations of concentrations in precipitation are shown in Fig. 2.29.

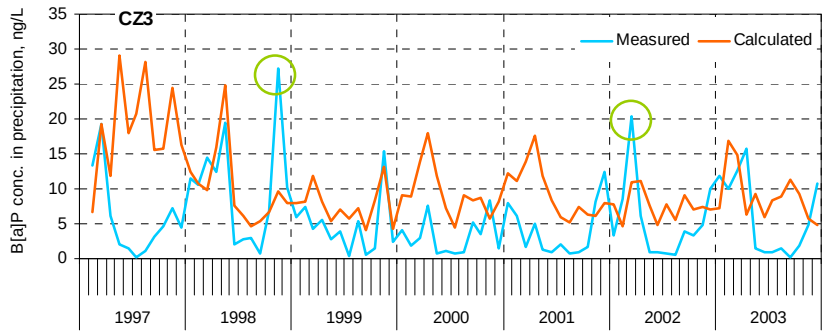


Fig. 2.29. *Seasonal variations of B[a]P concentrations in precipitation at CZ3 in 1997 – 2003. Outliers are marked green*

At the considered site some correlation between measurements and calculations is seen in the period from 1998 to the beginning of 2003. Seasonal variability of concentration in precipitation for measured values is much stronger than given by calculations. Similarly to the case of air concentrations, this shows the necessity of more precise model description of seasonal variation of emissions for refinement of the agreement between measurements and calculations.

The values of deposition flux are measured at four EMEP sites – FI96, SE2, SE12 and SE14. Two of these sites are located in one and the same grid cell and will be considered together.

The measurements at these sites are carried out with the help of precipitation + dry deposition samplers. The model evaluates values of wet depositions and the values of dry depositions at different types of underlying surface. After consultations with CCC (*Wenche Aas, private communication*) it was decided to compare the values of deposition flux measured at these sited with the sum of wet depositions and dry depositions to open areas (grass) calculated by the model. Since an unknown part of dry deposition is collected by sampler the comparison is of indicative character. Here we present the comparison of annual means for the period from 2000 to 2003.

The plot of comparison of measured and calculated values of deposition flux at FI96 is displayed in Fig. 2.30.

It is seen that for all years except for 2000 calculated values agree with measurements within a factor of 2 and better. Low value of measured deposition flux in 2000 agree with low value of air concentration, measured for the same period (Fig. 2.5).

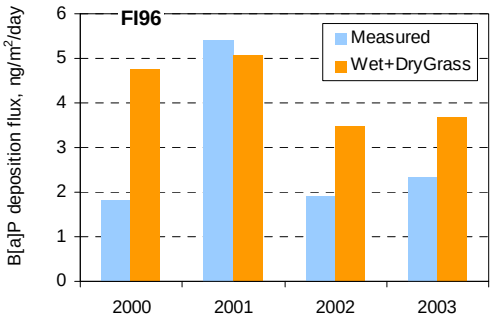


Fig. 2.30. *The comparison of measured and calculated deposition flux (wet+dry) at FI96 in 2000 – 2003*

The comparison of measured and calculated deposition flux at SE2/SE14 is shown in Fig. 2.31.

With the exception of 2001, all calculations agree with measurements within a factor of 2. In general, the model overestimate deposition flux at these sites. The reasons of such overestimation were analyzed above in the course of the consideration of air concentrations.

The plot of comparison of calculated and measured values of deposition flux at SE12 is demonstrated in Fig. 2.32.

It is seen that the model overestimates deposition flux at this location from 2 to 6 times. This in general corresponds to the overestimation of air concentrations at this site. The reasons of this overestimation were analyzed above.

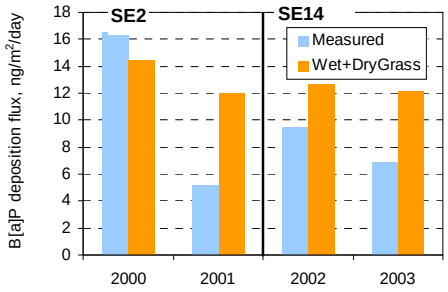


Fig. 2.31. *The comparison of measured and calculated deposition flux (wet+dry) at SE2/SE14 in 2000 – 2003*

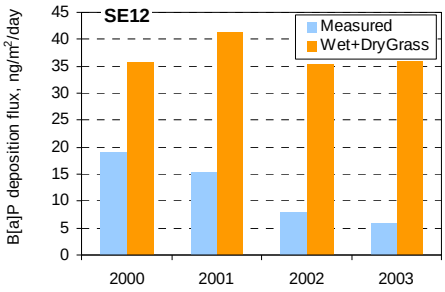
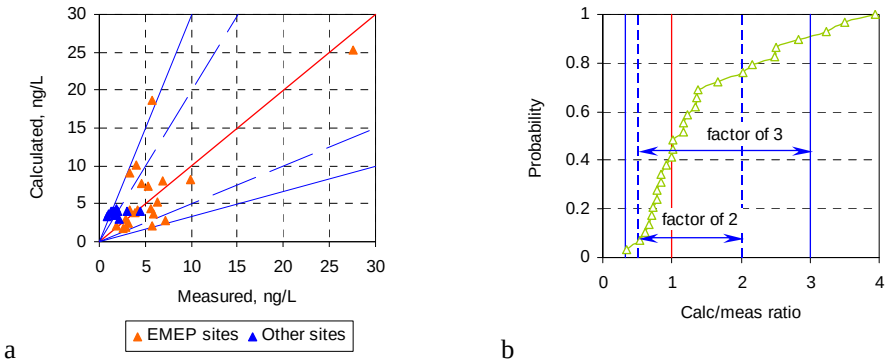


Fig. 2.32. *The comparison of measured and calculated deposition flux (wet+dry) at SE12 in 2000 – 2003*

General results. Scatter plot of the comparison of calculated and measured concentrations in precipitation for all available measurements are given in Fig. 2.33a. Figure 2.33b shows the cumulative distribution of calculated to measured factor.



a b

Fig. 2.33. *Scatter plot of measured and calculated annual means of B[a]P concentrations in precipitation in 1997 –2003 (annual averages) (a). EMEP sites are marked red. Cumulative distribution of calculated to measured factor (b)*

The comparison of calculated values of concentrations in precipitation with available measurements lead to the conclusion that about 70% of measured concentrations in precipitation agree with calculations within a factor of two and over 80% – within a factor of three.

Scatter plot of calculated and measured deposition fluxes together with cumulative distribution of calculated to measured factor for all available measurements are given in Fig. 2.34.

The comparison of calculated and measured values of deposition flux shows that about 70% of measured concentrations in precipitation agree with calculations within a factor of two and over 80% – within a factor of three.

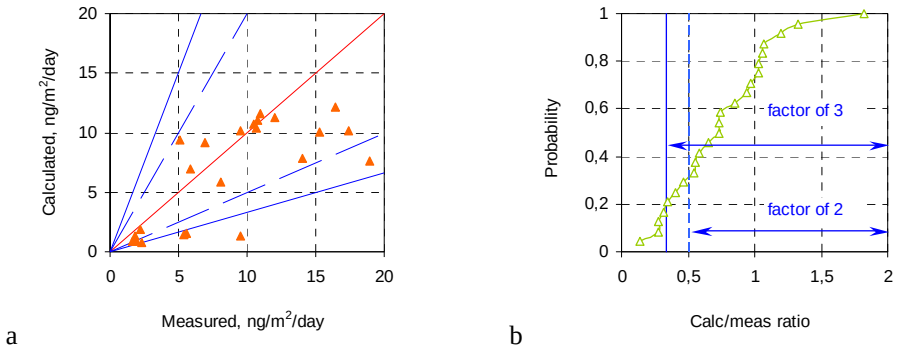


Fig. 2.34. *Scatter plot of measured and calculated annual means of B[a]P deposition flux in Europe 1997 – 2003 (annual averages)(a). Cumulative distribution of calculated to measured factor (b)*

Washout ratio

Simultaneous measurements of concentrations in air and precipitation are available at EMEP sites CZ3 and SE14 (107 monthly averages altogether). These data allows validating model from the viewpoint of washout ratio calculated for total (gas + particles) concentrations. To do that the values of washout ratio were calculated for all available data on the basis of calculations and measurements. The cumulative distribution function of calculated-to-measured factor for this parameter is displayed in Fig. 2.35.

It is seen that about 40% of calculated values agree with measurements within a factor of two and over 60% – within a factor of three. The median of this distribution is 0.91. This mean that the model underestimates measured concentration in precipitation by 10% on the average.

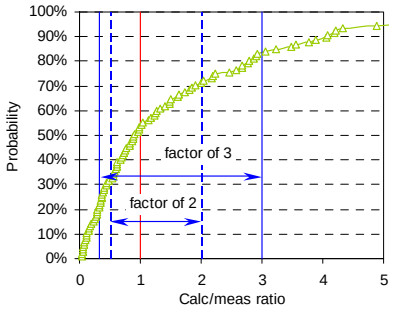


Fig. 2.35. *Cumulative distribution of calculated to measured factor for washout ratio*

2.2. Polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls

This section of the report is devoted to the comparison of modelling results with available measurements for the group of the following chlorinated chemicals, namely, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs). PCDD/Fs and PCBs congeners have similar physical-chemical properties and thus their fate in the environment can be evaluated using similar modelling approaches. It should be noted that at the moment more information is available on observed atmospheric levels of PCBs in comparison to

measurements of PCDD/Fs. Therefore, taking into account that PCDD/Fs are close in their physical-chemical properties to PCBs, the comparison of measured and calculated values for PCBs can to some extent confirm the ability of the MSCE-POP model to describe the behavior of PCDD/Fs in the environment.

2.2.1. Polychlorinated biphenyls (PCBs)

PCBs are the pollutants of global dispersion due to their properties, comparatively long period of application, and wide distribution of their emission sources. To describe correctly the level of pollution by PCBs within the EMEP region there is a need to take into account the influence of remote emission sources. For this reason modelling approach for PCBs is based on the usage of regional MSCE-POP model for the EMEP region along with its hemispheric version which allows to obtain contributions of remote sources.

For the comparison of PCB modelling results against measurements one of PCB congeners – PCB-153 was chosen. The choice of the congener was conditioned by the following reasons. First of all, this congener is one of the most investigated PCB congeners, which was used for the evaluation of environment pollution by PCBs in various monitoring and modelling studies. There is a set of its physical-chemical properties along with their temperature dependencies. PCB-153 is found mainly in the particulate phase at low temperatures. At the same time at elevated temperatures it can have significant fraction of gaseous phase. The combination of properties of this congener permits to study how the model reproduces spatial and temporal variations of its measured levels in the environment.

The calculations were made for the period 1990-2003 by the regional version of MSCE-POP model with 50×50 km^2 resolution. To take into account the contribution of the sources outside the EMEP region, the modelling of PCB-153 transport over the northern hemisphere was performed to supplement the results of regional calculations. The data on emissions of PCB-153 congener were obtained from the global PCB emission inventory [*Breivik et al.,* 2002a; *Breivik et al.,* 2002b] which covers the period of time from 1930 to 2000. The inventory includes three datasets corresponding to minimum, default, and maximum level of PCB emission. Maximum expert estimates were selected for modelling since model results obtained with their use were closer to measurements. For the period 2001-2003 the level of PCB emissions in 2000 was prolonged.

These expert estimates do not include an evaluation of the seasonal variation of PCB emissions which is an important factor for modelling of monthly variations of concentrations and depositions [*Breivik et al.,* 2002b].

It can be supposed that PCB emissions vary seasonally having higher values in summer due to more active volatilization in accordance with individual PCB congener volatility. At present, however, quantifying seasonal variations is difficult because of uncertainties in emission factors, the absence of necessary data and peculiarities of contributions made by various source categories to PCB emissions in specific countries. Therefore, in model calculations seasonal variations of PCB emissions were not taken into account.

Measurement data from different sources were used for the comparison with model results. First of all these are the data obtained at 9 EMEP monitoring sites in period from 1990 to 2003. Additional data from 16 monitoring sites across the Baltic Sea area for the period 1990-1993 [*Agrell et al.*, 1999] were obtained from the database of POPCYCLING-Baltic project [*Pacyna et al.*, 1999] and included in the analysis. The location of measurement sites included into the comparison is shown in Fig. 2.36, where EMEP sites are marked red. These data cover mostly the northern part of Europe. Better coverage of

European territory was obtained in the POP monitoring campaign carried out using passive samplers in summer 2002 [*Jaward et al.,* 2004].

The analysis of an agreement between observed and computed levels of pollutions by PCB-153 was performed for the concentrations in air and in precipitation, and for deposition fluxes. Spatial and temporal trends in measured and computed values were considered.

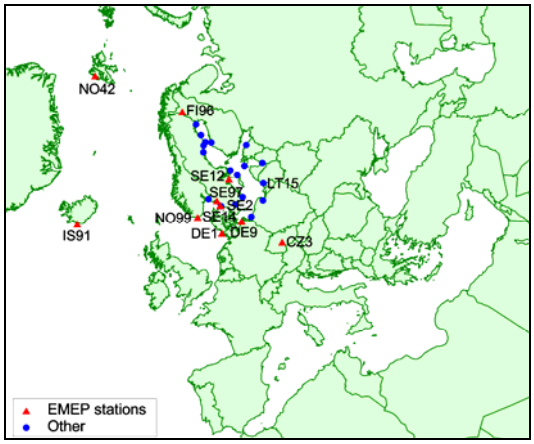


Fig. 2.36. *Location of measurement sites used for the comparison of calculations and measurements for PCB-153*

Air concentrations

Temporal variations of computed air concentrations of PCB-153 were compared with measurements of 7 EMEP sites, namely, NO42, IS91, FI96, SE2, SE12, SE14, and CZ3. Time-series of PCB-153 concentrations in air are presented starting from 1997. Some monitoring sites provide longer period of measurements, nevertheless, to give more uniform set of data the comparison is performed for the period 1997-2003.

Since seasonal variations of emission were not taken into account in modelling the comparison with measurements is focused mainly on annual mean concentrations of PCB-153. Variations of monthly mean air concentrations are also given for illustration however it should be taken into account that in the areas with moderate and high levels of emission computed concentrations might be overestimated in winter time and underestimated in summer time to some extent. For the remote areas in absence of significant local emission sources this effect is not important.

EMEP sites. In Fig. 2.37 the comparison of annual mean measured and calculated air concentrations of PCB-153 for the remote site FI96 is presented. It can be seen that model results are consistent with the observed concentrations. The agreement between computed and measured values is within a factor of 1.4. The largest discrepancy is found for 2001 which is caused mainly by the overestimation of observed concentrations in winter time (Fig. 2.38).

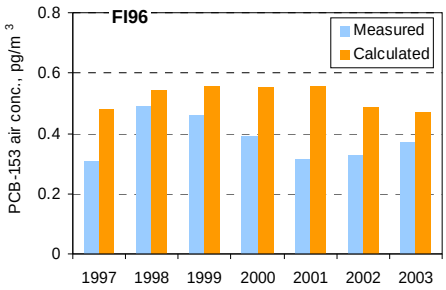


Fig. 2.37. *Measured and calculated annual mean air concentrations of PCB-153 at FI96 for the period 1997 – 2003, pg/m*^{3}

Calculated seasonal variations of PCB-153 concentrations are close to the observed with the exception of peak values measured in summer time of 1999, 2002, and 2003 which are not captured by the model. The reason of these differences can be connected with the influence of emission sources not included in the emission inventory. In other periods, in particular, in 1998, model predictions correlate with measured values of concentrations. Higher concentrations comparing to the observed values were also obtained for the winter time. Taking this into account it can be concluded that the model is capable to reasonably characterize seasonal variations of PCB-153 air concentrations if the emission data include correctly defined variation of emission fluxes depending on ambient temperature.

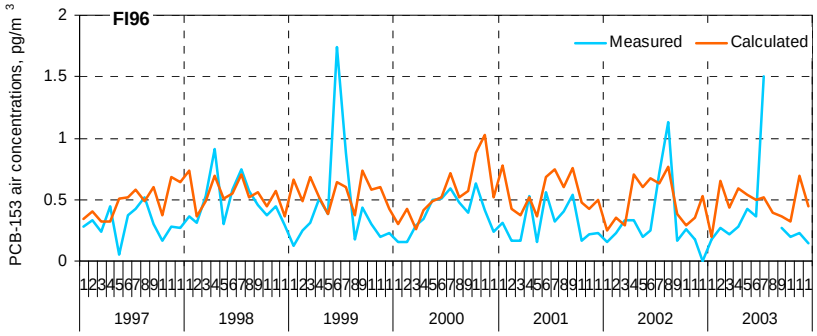


Fig. 2.38. *Measured and calculated seasonal variations of PCB-153 air concentrations at FI96 for the period 1997 – 2003, pg/m*^{3}

Time series of the computed and measured air concentrations of PCB-153 at the site NO42 are given in Fig. 2.39. This site is located in the vicinity of model domain boundaries and thus measured concentrations are influenced by the emission sources located outside the model domain. As it was mentioned above for the evaluation of pollution levels in the remote areas of EMEP region modelling approach is based on the usage of regional MSCE-POP model along with its hemispheric version. The contribution of sources outside the EMEP region to calculated air concentrations at this site obtained by the hemispheric model reaches 50%.

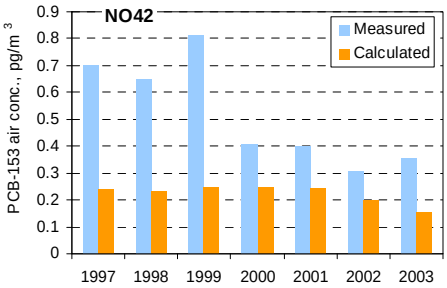


Fig. 2.39. *Measured and calculated temporal trends of PCB-153 air concentrations at NO42 for the period 1997 – 2003, pg/m*^{3}

Model results underestimate measured levels of concentrations at this site especially in period 1997-1999. Relatively high values of air concentrations measured at this site, comparable with levels measured at SE12 and SE2 in 1997-1999, might be connected with on-site contamination taking place in 1994-1997 and possibly in subsequent years [*Berg and Hjellbrekke*, 1999]. Starting from 2000 observed annual mean concentrations are significantly lower and are comparable with the computed concentrations. Some underestimation of measurements by the model (about 50%) is likely caused by the influence of underestimated emission of remote sources. Variations of computed and observed monthly mean air concentrations are presented in Fig. 2.40. It can be seen that with the exception of peak concentrations measured in several months from 2000 to 2003 computed concentrations are rather close to the observed ones.

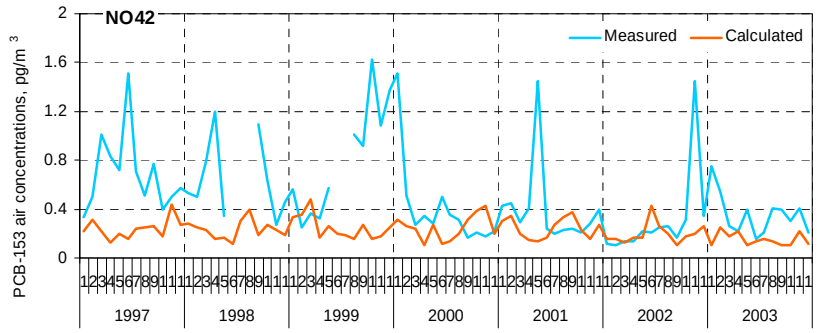


Fig. 2.40. *Measured and calculated seasonal variations of PCB-153 air concentrations at NO42 for the period 1997 – 2003, pg/m*^{3}

The comparison of measured and calculated annual averages of PCB-153 air concentrations at site IS91 for the period from 1997 to 2003 is shown in Fig. 2.41.

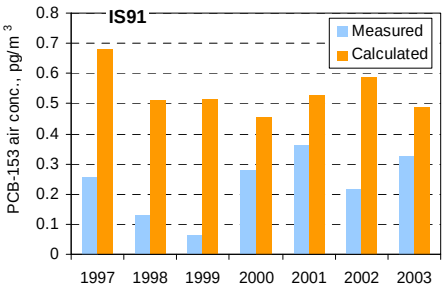


Fig. 2.41. *Measured and calculated temporal trends of PCB-153 air concentrations at IS91 for the period 1997 – 2003, pg/m^3*

Measurements made at this site in period 1997-1999 differ from the ones for 2000-2003 in that they are generally lower and contain zero values (Fig. 2.42). This difference can be connected with possible changes in sampling and analysis methods. Therefore the comparison of model results with these data is indicative and requires further analysis.

Computed annual mean concentrations slightly overestimate measured values in period 2000-2003 by 40% on average with the exception of 2002 where the difference is about a factor of 3. Air concentrations measured at this site in 2002 distinctly differ from measurements for other years by the absence of seasonal variations (Fig. 2.42). It is seen that measured concentrations are basically at one and the same level varying from 0.20 to 0.23 pg/m^3. The discrepancy between measured and calculated values of air concentrations in 2002 can be caused by some measurement problems and low values of concentrations which are often bellow detection limit.

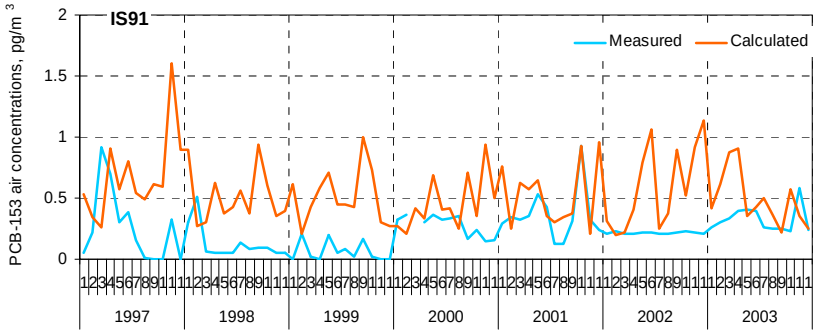


Fig. 2.42. *Measured and calculated seasonal variations of PCB-153 air concentrations at IS91 for the period 1997 – 2003, pg/m^3*

The comparison of measured and calculated values of PCB-153 air concentrations at sites SE2 and SE14 for the period from 1997 to 2003 is shown in Fig. 2.43a. These two sites are located close to each other and therefore in one and the same model grid cell. Similar to the results obtained for B[a]P, computed values for these two sites overestimate measured concentrations due to the location of emission source associated with Gothenburg within the same model grid cell and in the neighbouring cell (Fig. 2.43b). The value of emission in these two cells is almost 9 times higher comparing to the level of emission in surrounding cells. Since spatial distribution of PCB emission for Sweden was obtained on the basis of population density, the emission of these two cells might be overestimated that possibly leads to the overestimation of PCB-153 air concentrations observed at the sites SE2 and SE14.

In spite of these differences some correlation can be noted between the model results and monthly mean concentrations measured at the site SE2 in period 1997-2001 (Fig. 2.44). It can be seen also that due to the absence of seasonal variations in emissions the model tend to overestimate measured concentrations at SE14 in winter time and to underestimate in summer time in 2002-2003.

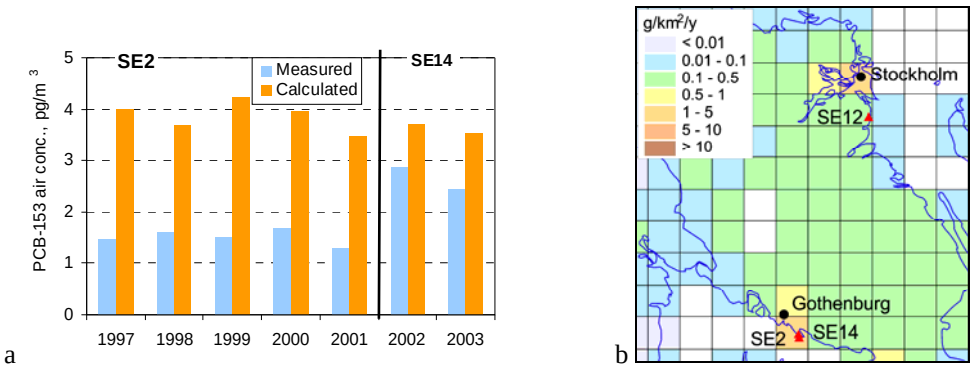


Fig.2.43. *Measured and calculated temporal trends of PCB-153 air concentrations at SE2/SE14 (a) for the period 1997 – 2003 (pg/m^3) and spatial distribution of PCB emission over southern Sweden (b) with the location of the sites SE2, SE14, SE12*

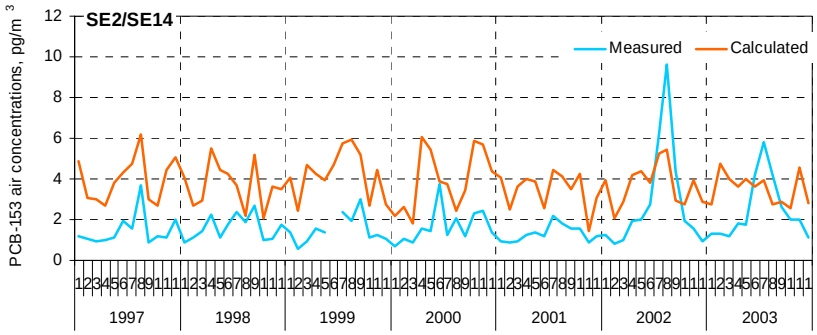


Fig. 2.44. *Measured and calculated seasonal variations of PCB-153 air concentrations at SE2/SE14 for the period 1997 – 2003, pg/m^3*

The comparison of calculated annual averages of PCB-153 air concentrations with measured at the site SE12 for the period from 1997 to 2003 is presented in Fig. 2.45. It can be seen that measured annual mean concentrations in this period are overestimated by the model about factor 2-3.

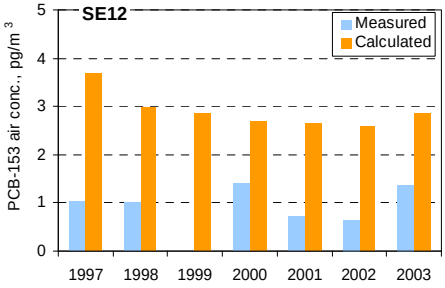


Fig. 2.45. *Measured and calculated temporal trends of PCB-153 air concentrations at SE12 for the period 1997 – 2003, pg/m^3*

Similar to the situation discussed above for SE2 and SE14, the overestimation of observed PCB-153 air concentrations is likely caused by the uncertainties in spatial distribution of PCB emission. In particular, this site is located in the model grid cell next to the cell with the significant emission source associated with Stockholm (Fig. 2.43b). Emission of this cell is about 8 times higher than level of emissions of nearby cells. Due to disaggregation of total emission of Sweden on the basis of population density this value might be overestimated. It should be mentioned that seasonal variations of observed concentrations are reasonably reproduced by the model as it can be seen from Fig. 2.46. Similarly to the case of SE2 and SE14 there is some correlation between measured and calculated seasonal variations of air concentrations at the considered site.

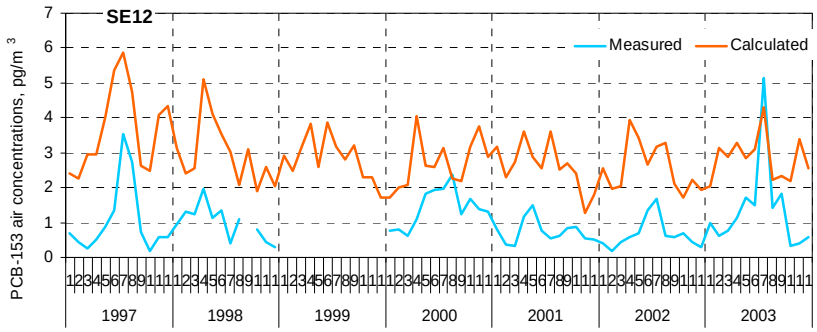


Fig. 2.46. *Measured and calculated seasonal variations of PCB-153 air concentrations at SE12 for the period 1997 – 2003, pg/m^3*

In Fig. 2.47 and 2.48 computed concentrations are compared with the observed ones at the site CZ3. Model results underestimate measured concentrations. The reason of the underestimation might be connected with the underestimated emission of PCBs in this region. In particular, in course of preparation of the inventory of global use and emission of PCBs [*Breivik et al.*, 2002] there was a deficiency of information on production of these substances produced on factories of Poland, East Germany and Austria.

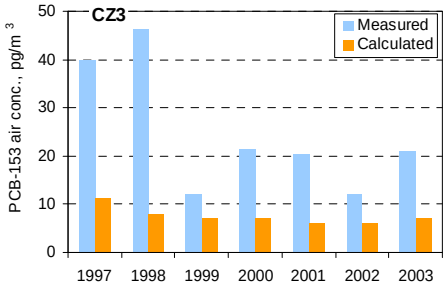


Fig. 2.47. *Measured and calculated temporal trends of PCB-153 air concentrations at CZ3 for the period 1997 – 2003, pg/m^3*

Higher values of concentrations were obtained by the model for the central France and western Germany in comparison to concentrations in Czech Republic and southern Poland. However, monitoring campaign on the basis of passive samplers [*Jaward et al.,* 2004] obtained elevated level of concentrations at sites in Czech Republic comparing to other regions.

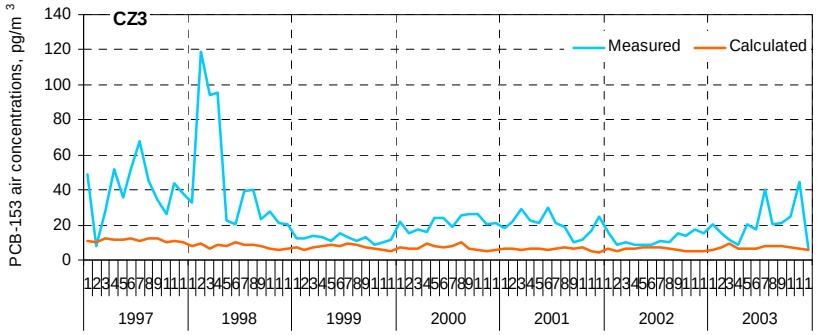


Fig. 2.48. *Measured and calculated seasonal variations of PCB-153 air concentrations at CZ3 for the period 1997 – 2003, pg/m^3*

Spatial distribution of computed annual mean air concentrations for 2003 along with the time-series of measured concentrations at EMEP monitoring sites is shown in Fig. 2.49. The model reasonably reproduces spatial distribution of annual mean PCB-153 air concentrations in the remote regions and in the vicinity of emission sources. The pattern of average air concentrations calculated by the model is close to the observed values. Though the number of sites is limited relatively high spatial correlation between observations and model results obtained for 2003 can be noted. Elevated air concentrations

of PCB-153 about 20 pg/m^3 were measured in central Europe (CZ3) in comparison to northern Europe and remote areas where levels of concentrations were about 0.3-0.4 pg/m^3. Relatively higher values about 1-2 pg/m^3 were observed in Sweden at SE12 and SE14 sites.

Considering the model results obtained for these sites it can be seen that values of air concentrations computed for the remote sites (IS91, FI96, NO42) differ from measured ones by 30-60%. Computed air concentrations for southern Sweden overestimate measurements of sites SE14 and SE12 by 30-50%. This difference is likely caused by the uncertainties of spatial distribution of PCB emission for Sweden obtained on the basis of population density.

Relatively higher level of annual mean air concentrations (7 pg/m^3) is obtained by the model for the site CZ3 in central Europe in comparison to other regions. However, the model underestimates measured level of air concentrations at this site by a factor of 3. The reason of the underestimation might be connected with the underestimated emission of PCBs in this region. In particular, as it was mentioned in [*Breivik et al.*, 2002a] information on PCB production in Poland, Eastern Germany, and Austria was insufficient.

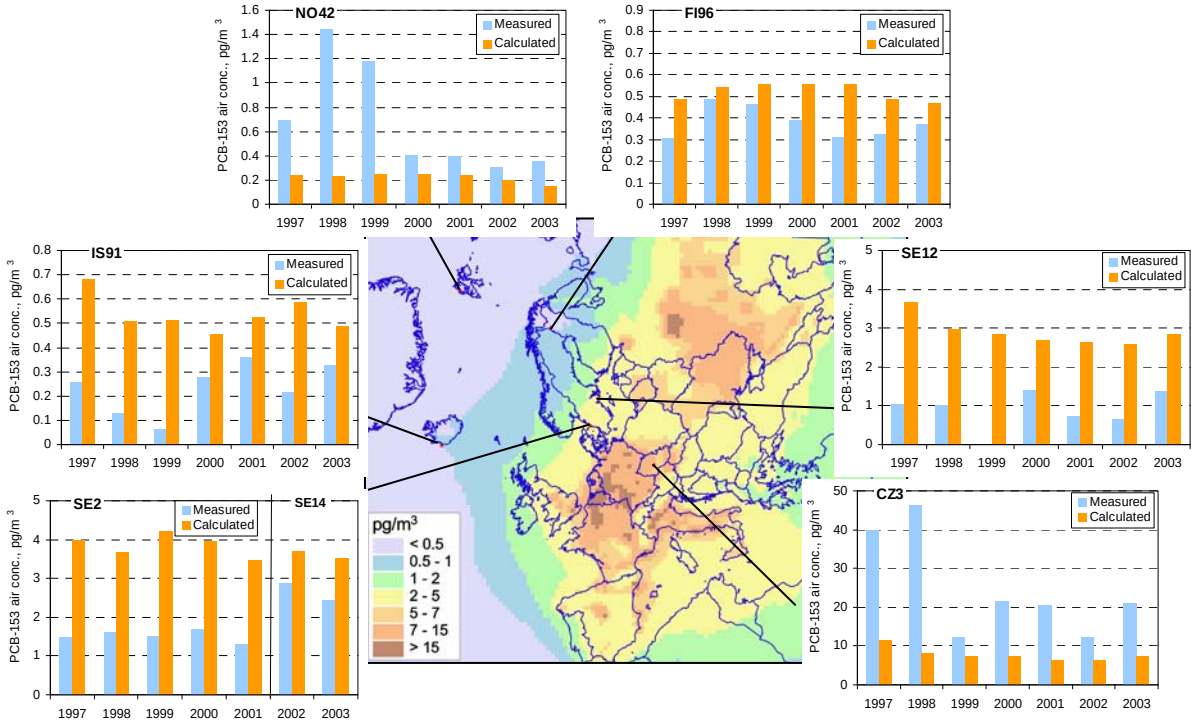


Fig. 2.49. *Spatial distribution of calculated annual mean PCB-153 air concentrations for 2003 and comparison of calculated annual mean PCB-153 air concentrations with measured at EMEP monitoring sites, pg/m^3*

Non-EMEP sites. Model results for the period 1990-1993 were compared with air concentrations observed during the monitoring study carried out at 16 monitoring sites across the Baltic Sea [*Agrell et al.*, 1998]. Data on concentrations were obtained from the database of the POPCYCLING-Baltic project [*Pacyna et al.*, 1997]. During this study relatively higher levels of PCB concentrations (2-4 pg/m^3) were obtained at the sites in the southern part of the Baltic Sea area. Measured air concentrations show some decrease in northern direction along the Baltic Sea western coast. Similar

pattern of PCB-153 air concentrations was obtained by the model as it can be seen from the Fig. 2.50. In general the level of computed air concentrations is close to the observed. The overestimation of measured air concentrations at the sites in southern Sweden, Poland, Lithuania, and Latvia by the model can be noted. Some deviations between temporal variations of observed and computed concentrations can be explained by the lack of seasonal variations of PCB emission used for modelling.

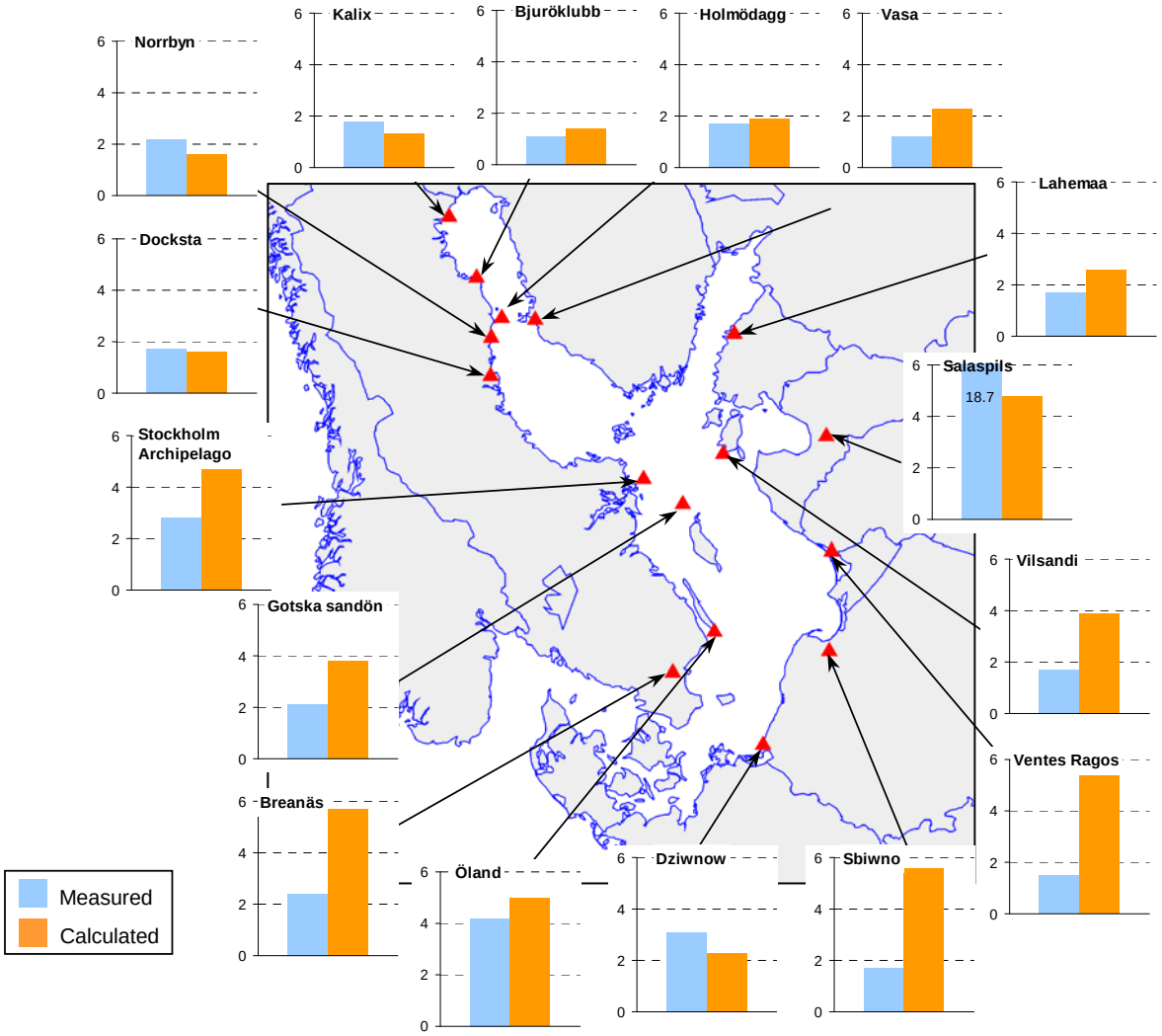


Fig. 2.50. *Comparison of PCB-153 air concentrations measured during the period 1990 – 1993 across the Baltic Sea with the results of MSCE-POP model computations , pg/m*^{3}

General results. Summarizing the results of the comparison of calculated and measured air concentrations it can be mentioned that model results slightly overestimate available measurements. The median of the distribution is 1.23. Scatter plot of calculated and measured PCB-153 air concentrations for all measurements at EMEP monitoring sites together with cumulative distribution of calculated-to-measured factor is given in Fig. 2.51. More than 40% of calculated air concentrations are within a factor of 2 with respect to observed values and about 70% – within a factor of 3.

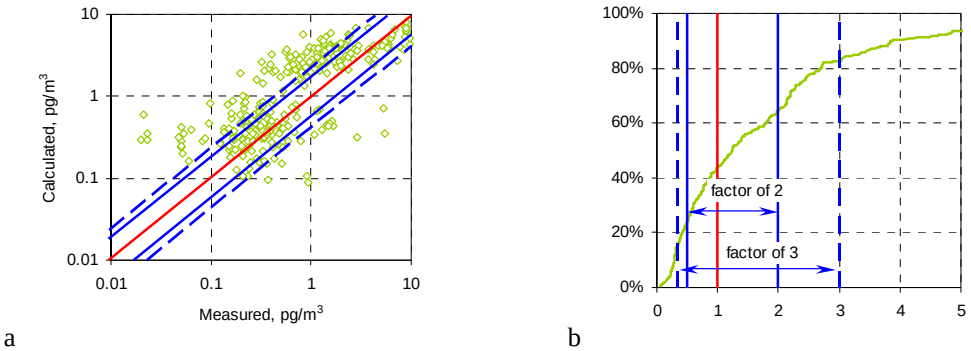


Fig. 2.51. *Scatter plot of measured and calculated PCB-153 air concentrations at EMEP monitoring sites (a); cumulative distribution of calculated to measured factor (b)*

Additional information on spatial distribution of atmospheric levels of PCB-153 is obtained from the results of measurement campaign performed by Lancaster University in summer 2002 [*Jaward et al.,* 2004]. During this study 71 passive air samplers were deployed throughout the European territory across 22 countries in the remote, rural, semi-rural, suburban, and urban sites. Spatial distribution of obtained air concentrations was compared with the calculated PCB-153 air concentrations for June and July of 2002. In Fig. 2.52 both sets of information are shown, namely, spatial distribution of PCB-153 air concentrations obtained by the MSCE-POP model and levels of PCB-153 in air measured by passive air samplers.

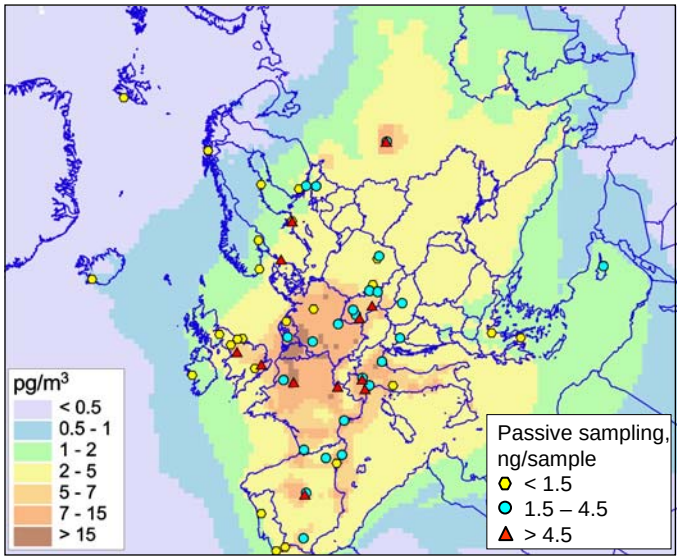


Fig. 2.52. *Comparison of calculated spatial distribution of PCB-153 air concentrations with the results of passive sampling campaign in summer 2002*

It can be seen that spatial distribution of calculated PCB-153 air concentrations is consistent with the measurements made by passive samplers. Elevated levels of contamination (marked with black squares and red circles) coinciding with the model results can be indicated in central part of France, northern Italy, central part of Spain and of European Russia (Moscow region). Measurements with moderate values of contamination (marked with gray squares) are mainly located in the regions where the model predicts moderate contamination as well. Samples with low content of PCB-153 (marked with white squares) are located as a rule in regions where model concentrations are also low.

It should be noted that in some regions model predictions do not follow measurement results. The discrepancies might be caused by the uncertainties of emission data. For instance, high values of PCB-153 concentrations were measured in the Czech Republic. At the same time, the model predicts moderate levels of concentrations for its territory probably due to some underestimation of emissions for this region. This is also indicated in the comparison of computed and measured PCB-153 air concentrations at Kosetice (CZ3) presented in Fig. 2.47.

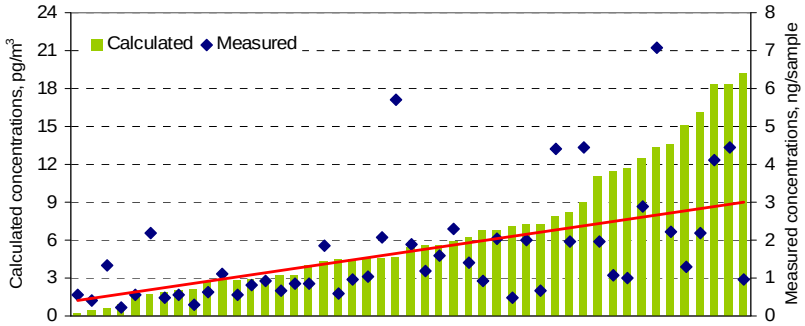


Fig. 2.53. *Comparison of calculated PCB-153 air concentrations sorted by their magnitude with passive sampling measurements. Red line shows linear trend of measured air concentrations*

In spite of these differences the spatial distribution of calculated air concentrations is consistent with the measured one. In particular, it can be seen from Fig. 2.53 that model reasonably reproduced the spatial trend in measured concentrations of PCB-153. It should be noted that for this analysis data of passive samplers in urban sites were not taken into account. In general, it can be concluded that model results obtained on the basis of PCB emission expert estimates of *Breivik et al.* [2002] are rather consistent with spatial distribution of PCB atmospheric levels observed during the passive sampling study.

Concentrations in precipitation and deposition fluxes

In comparison with measurements of PCB air concentrations less information is available for their concentrations in precipitation and deposition fluxes. Computed concentrations of PCB-153 in precipitation were compared with available measurements of EMEP monitoring sites, namely, DE1, DE9, and CZ3. Data on observed concentrations at these sites were obtained from CCC and from national experts (Dr. E. Bieber; Prof. Dr. I. Holoubek). PCB-153 deposition fluxes obtained by the MSCE-POP model were compared with the measurements of SE2, SE14, SE12, and FI96.

The comparison of calculated and measured concentrations in precipitation is complicated by several factors and should be considered as indicative. In particular, differences can be connected with the description of wet deposition process in the model, where precipitation is equally distributed in each model grid cell while in reality rainfall is restricted to rather limited area. Additional discrepancies can be caused by different amount of precipitation used in the model and obtained at monitoring sites. Therefore the model, operating with spatial resolution 50x50 km^2, cannot reproduce in some cases significant peaks of concentrations in precipitation obtained in measurements.

Fig. 2.54 shows the plots of annual averages of calculated and measured concentrations in precipitation at DE1 and DE9 for the period 2001–2003. Measured PCB-153 concentrations in precipitation at the sites DE1 and DE9 were available for the period 1996-2003. However, for the

comparison with the computed concentrations the period 2001-2003 was selected because this set of data is uniform with respect to the applied sampling and analysis methods (*Dr. E. Bieber, private communication*).

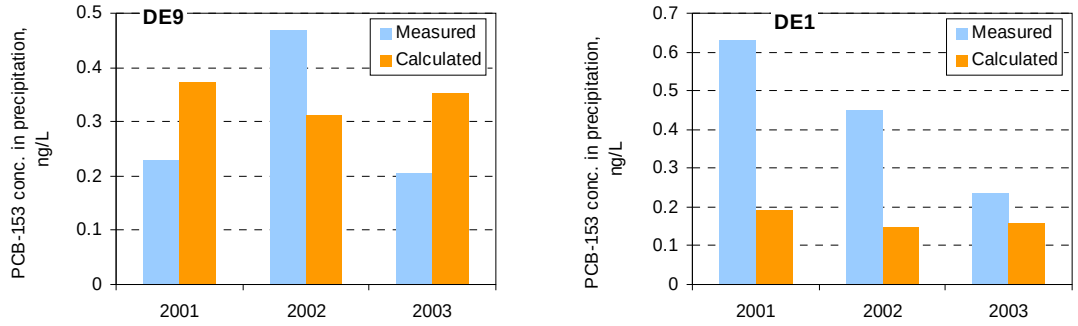


Fig. 2.54. *Measured and calculated PCB-153 concentrations in precipitation at DE9 and DE1 for the period 2001 – 2003, ng/L*

As it can be seen from the Fig. 2.54 computed annual mean concentrations for the site DE9 agree with measured within a factor of 1.6. Larger differences were obtained for the site DE1 especially in 2001 and 2002. At the same time measured and computed concentrations for 2003 agree within a factor of 1.6.

As it can be seen from Fig. 2.55, differences obtained between the computed and observed annual mean concentrations at the sites DE1 and DE9 are mostly connected with significant peak concentrations measured in several months which were not captured by the model. This underestimation of peak values can be caused by the factors mentioned above.

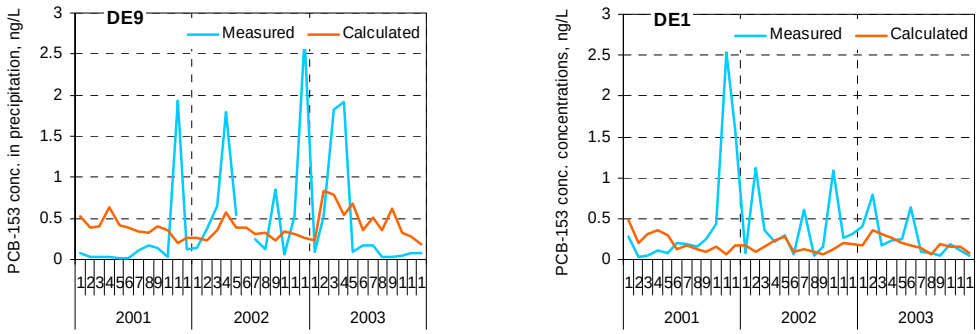


Fig. 2.55. *Measured and calculated seasonal variations of PCB-153 concentrations in precipitation at DE9 and DE1 for the period 2001 – 2003, ng/L*

Seasonal variations of measured and calculated monthly mean concentrations in precipitation at the Czech site CZ3 for the period 1997 – 2003 are displayed in Fig. 2.56.

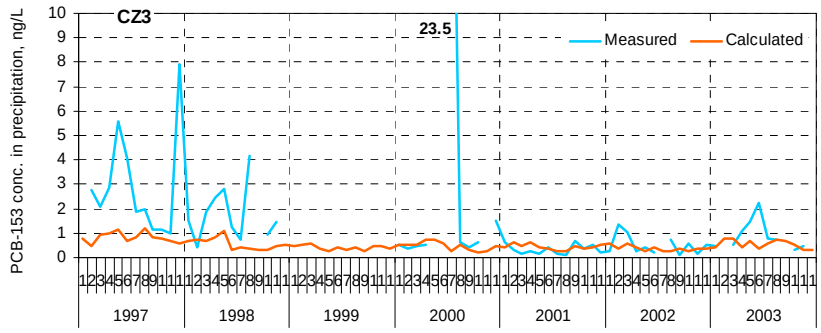


Fig. 2.56. *Measured and calculated seasonal variations of PCB-153 concentrations in precipitation at CZ3 for the period 1997 – 2003, ng/L*

It can be seen that computed PCB-153 concentrations in precipitations are close to the observed in period 2000-2003 with the exception of several peaks. Computed concentrations in precipitation for 1997 and 1998 underestimate measured concentrations at this site more significantly. The reason of this underestimation can be connected with the uncertainties of temporal variations of emission in the Czech Republic. In particular, from the analysis of the computed and measured air concentrations at the site CZ3 similar temporal variations in observed air concentrations can be seen (Fig. 2.56) with higher level of air concentrations in 1997 and 1998.

Comparison of calculated values of PCB-153 deposition fluxes was carried out with measurements of made at 4 EMEP sites, namely, SE2, SE14, SE12 and FI96. Measurements at these sites were carried out using bulk samplers which collect both wet deposition and some part of dry deposition of POPs [*Aas and Breivik*, 2004]. Measured values were compared with the sum of computed wet and dry deposition of PCB-153, where dry deposition was represented by deposition of particle-bounded phase to open (grass covered) areas. For these reasons total deposition fluxes calculated by the model can be higher than measured as the latter contain only part of dry deposition.

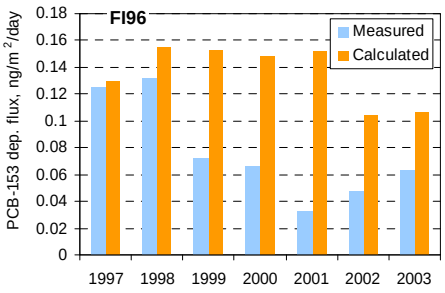


Fig. 2.57. *Measured and calculated temporal trends of PCB-153 deposition flux (wet+dry) at FI96 for the period 1997 – 2003, ng/m^2/day*

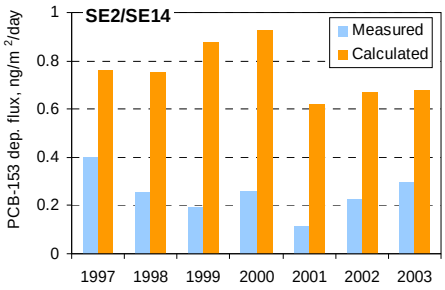
The comparison of annual means of calculated and measured deposition flux at Finnish site FI96 for the period from 1997 to 2003 is shown in Fig. 2.57.

The agreement between measured and calculated values of deposition flux at this site is about a factor of 2, on the average, with the exception of the values for 2001 where the difference is about a factor of 4. It can be seen that in general model results follow the temporal variations of measured air concentrations (Fig. 2.37).

Annual means of measured and calculated deposition flux at Swedish sites SE2 and SE14 (located in one and the same grid cell) for the period 1997 – 2003 are displayed in Fig. 2.58. Calculated values of deposition fluxes similar to air concentrations (Fig.2.43a) overestimate measured values at these sites about a factor of 3.5. The reason of this overestimation is most likely connected with the uncertainties of spatial distribution of PCB emission which was discussed in section 2.2.1.

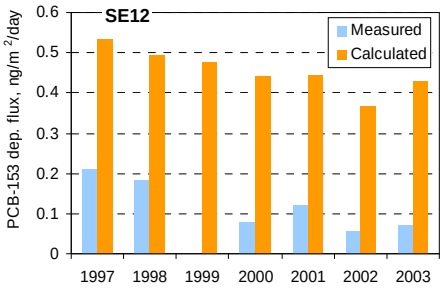
Similar situation is obtained for another Swedish site SE12. The comparison of calculated annual mean deposition fluxes with the results of measurements at this site is presented in Fig. 2.59.

Overestimation of measured values of deposition flux at SE12 (about a factor of 4.5) is conditioned by high values of emissions in a neighboring cell including Stockholm (see the discussion of comparison of calculated and measured air concentrations at SE12 in section 2.2.1). At the same time temporal variation of measured annual mean deposition fluxes are close to the observed ones.



a

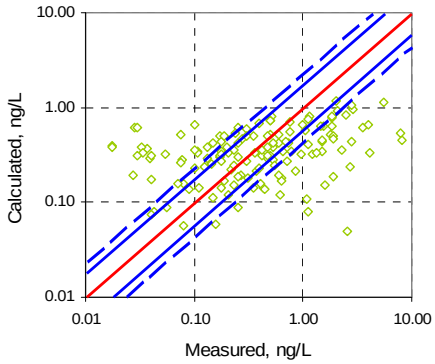
Fig. 2.58. *Measured and calculated temporal trends of PCB-153 deposition flux (wet+dry) at SE2 and SE14 for the period 1997 – 2003, ng/m^2/day*



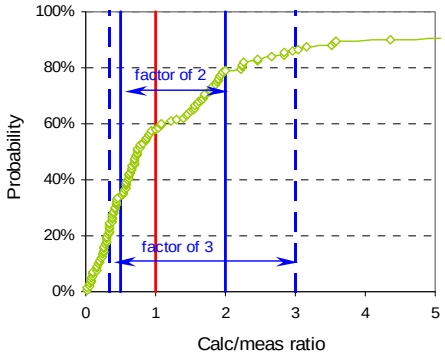
b

Fig. 2.59. *Measured and calculated temporal trends of PCB-153 deposition flux (wet+dry) at SE12 for the period 1997 – 2003, ng/m^2/day*

General results. Scatter plot of calculated and measured PCB-153 concentrations in precipitation for all measurements at EMEP monitoring sites together with cumulative distribution of calculated-to-measured factor is given in Fig. 2.60 *a* and *b*, respectively.



a

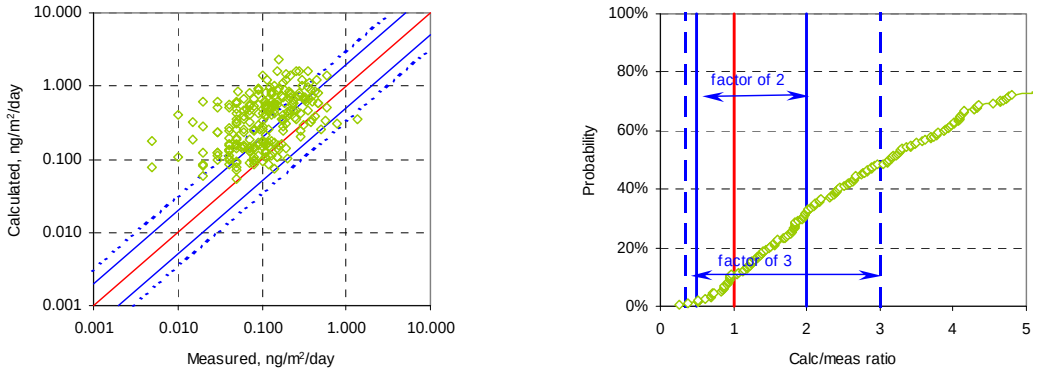


b

Fig. 2.60. *Scatter plot of measured and calculated PCB-153 concentrations in precipitation at EMEP monitoring sites (a); cumulative distribution of calculated to measured factor (b)*

For concentrations in precipitation the median of calculated-to-measured factor distribution is 0.74. About 45% of calculated values agree with measurements within a factor of 2 and 65% – within a factor of 3.

Scatter plot of calculated and measured monthly mean values of PCB-153 deposition flux for all measurements at EMEP monitoring sites together with cumulative distribution of calculated-to-measured factor are given in Fig. 2.61.



a b

Fig. 2.61. *Scatter plot of measured and calculated PCB-153 deposition flux (wet+dry) at EMEP monitoring sites (a); cumulative distribution of calculated to measured factor (b)*

For deposition fluxes the median of distribution of the ratio between calculated and measured values amounts to 3 which means that the model overestimates deposition fluxes observed at SE2, SE14, SE12, and FI96. The disagreement of measurements and calculations for deposition fluxes can be explained by the uncertainties in spatial distribution of PCB-153 emission and likely overestimated values of total PCB emission of Sweden which is also reflected in the comparison of model results with observed level of PCB-153 in air at Swedish sites (see section 2.2.1).

2.2.2. Dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)

For the verification of model results on PCDD/Fs against available measurements computations of transport and deposition of one of the toxic PCDD/F congeners – 2,3,4,7,8-PeCDF within the EMEP region in period 1990 - 2003 are used. Emission data for calculations were compiled on the basis of official emission data and expert estimates [*Pacyna et al.,* 1999]. The congener 2,3,4,7,8-PeCDF was chosen for calculations since it makes maximum contribution to the overall toxicity of PCDD/F emission (about 40%) and is characterized by essential part of the gaseous phase (about 30 – 40% on average in Europe, depending on the season). The calculations were made by the regional version of MSCE-POP model with 50×50 km^2 spatial resolution.

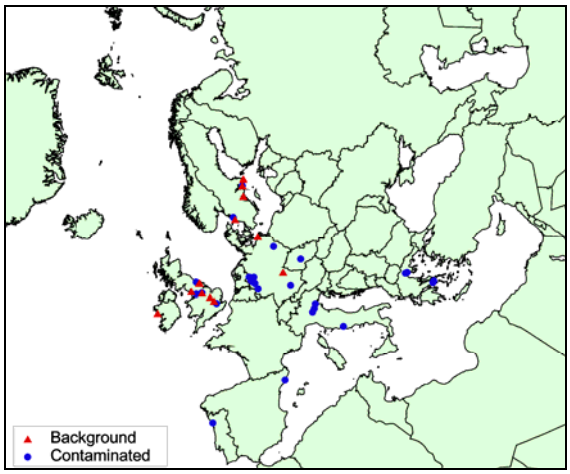


Fig. 2.62. *Location of measurement sites used for the comparison of calculations and measurements for 2,3,4,7,8-PeCDF*

PCDD/Fs are not currently included into the EMEP measurement programme. Therefore, for model validation the results of various measurement campaigns are used which include measurements made in background and contaminated regions of Europe (Fig. 2.62). In particular, these are the results obtained at two EMEP sites (SE2 and DE9) not included into the CCC database, and measurements carried out in Sweden, Germany, the United Kingdom, Portugal, Italy and Greece obtained in the framework of national measurement activities covering the period from 1990 to 2001.

As seen from the figure, the number of monitoring sites is rather scarce. Hence the comparison with measurements for PCDD/Fs presented here is of a preliminary character.

Air concentrations

For the comparison with model results over 100 individual measurements of PCDD/F air concentrations were used. These measurements were split into two parts: measurements in clear regions (background, rural and suburban) and measurements in contaminated regions. The comparison with calculations was carried out separately for these two groups of measurements.

Let us present the analysis of the comparison between measurements and calculations at particular locations for a number of years. All sites included into the comparison of measured and calculated values of toxicity in air are located in three countries: Sweden, Germany and the United Kingdom. Measured and calculated values of air concentrations at Swedish site SE2 for two periods in 1990 and for three locations in Sweden in April – June 1990 are presented in Fig. 2.63.

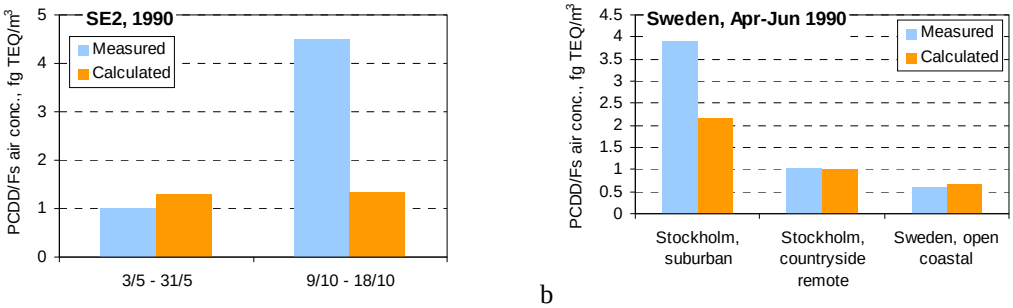


Fig.2.63. *Comparison of measured and calculated values of PCDD/F air concentrations at some Swedish locations in 1990*

The comparison of measured and calculated concentrations at SE2 for two time periods shows that in warm season the model correctly represents the levels of air concentrations. At the same time in the cold season model underestimates air concentrations.

Similar situation takes place in Bayreuth (Germany) in April – August 1995 (Fig. 2.64). It can be seen that calculations well agree with measurements. However, the comparison of measured and calculated concentrations in the atmosphere in cold season at two locations (site DE9 and Bayreuth) in the end of 1995 – beginning of 1996 (Fig. 2.65) again shows that the model underestimates air concentrations.

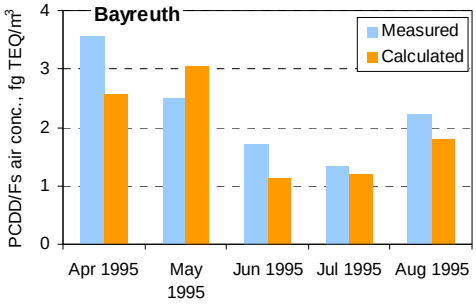


Fig. 2.64. *Comparison of measured and calculated values of air concentrations in Bayreuth (Germany) in April – August 1995*

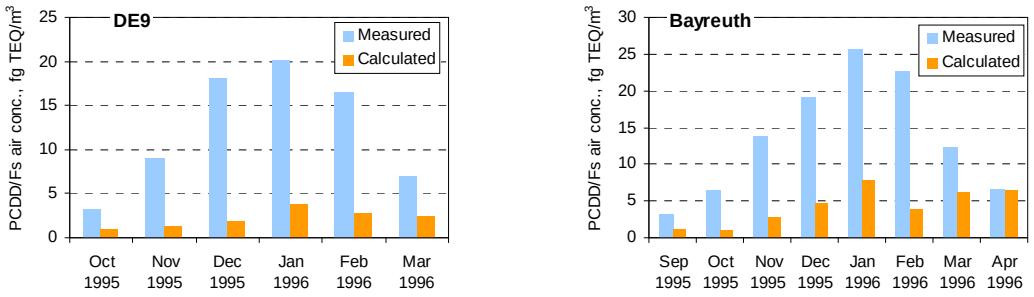


Fig. 2.65. *Comparison of measured and calculated values of air concentrations at DE9 and in Bayreuth in the end of 1995 – beginning of 1996*

The reason of discrepancies between measured and calculated values of air contamination in cold season can be connected with model evaluation of seasonal variations of emissions. Since no data on seasonal variations in emissions were reported by countries, in the model seasonal variations are taken to be the same as for B[a]P. So, the information on seasonal variations of PCDD/F emissions can be used for further refinement of the agreement between measurements and calculations. As a first step it is planned to perform a calculation run with conventional character of seasonal variations of PCDD/F emissions taking into account sharp distinctions between summer and winter concentration levels taking place in measurements.

Finally, the comparison of calculated and measured air concentrations at the site Hazelrigg in period 1994 – 1997 is demonstrated in Fig. 2.66.

The comparison shows a good agreement between measurements and calculations for three last years of the period.

Differences between model calculations and measurements are summarized as average calculated-to-measured factors for Germany, Sweden and the United Kingdom in Table 2.2.

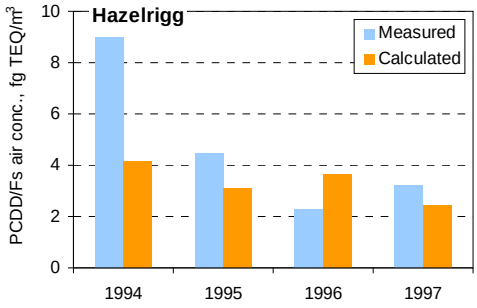


Fig. 2.66. *Comparison of measures and calculated values of air concentrations at Hazelrigg (the United Kingdom) for the period from 1994 to 1997*

Table 2.2. *Average calculated-to-measured factor in three European countries*

Country	Germany	Sweden	The United Kingdom	
Period	1995 – 1996	1990	1991 – 1997	1994 – 1997
Calculated-to-measured factor	0.45	0.83	0.71	0.96

For the analysis the diagrams of contributions to air concentrations of 2,3,4,7,8-PeCDF in these three countries originated from national emission sources and sources of other European countries can be considered (Fig. 2.67). These data were obtained on the basis of country-to-country matrix calculated using MSCE-POP model for 2003.

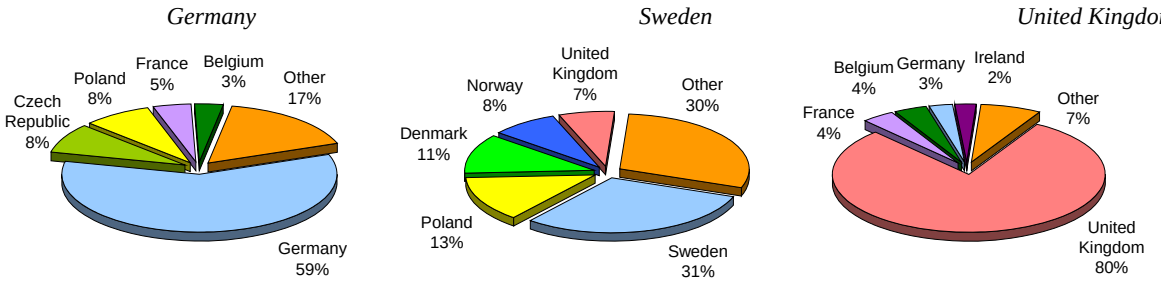


Fig. 2.67. *Contributions of countries to annual mean air concentrations of 2.3.4.7.8-PeCDF in Germany, Sweden, and the United Kingdom*

In Sweden calculated-to-measured factor is close to 1 (0.83 on the average with the range from 0.13 to 2.6). The same situation takes place in the United Kingdom where the average calculated-to-measured factor equals 0.71 with the range from 0.2 to 2 for the whole period (from 1991 to 1997) and even 0.96 for the recent period (from 1994 to 1997) with range from 0.5 to 2. Since most part of air pollution in the UK is determined by domestic emissions, it can be concluded that measured values of air concentrations correspond to emission data for the UK.

Main underestimation of measured values of the toxicity in the atmosphere takes place in Germany. Here the average value of calculated-to-measured factor equals 0.45 with range from 0.1 to 1.2. Calculated country-to-country matrix for 2,3,4,7,8-PeCDF shows that the levels of air concentrations in Germany are determined by domestic emission sources by about 60% (Fig. 2.67).

So, the underestimation of air concentrations in Germany can be partly explained by uncertainties of emission data in the country, at least for the period covered by measurements.

There exist about 50 individual measurements of 2,3,4,7,8-PeCDF toxicity in clear regions for the period from 1990 to 1997. The cumulative distribution of calculated-to-measured factor for the toxicity in surface atmosphere layer is presented in Fig. 2.68.

The median of the distribution is about 0.5. It is seen that for a lot of measurements the model underestimates measured values of air concentrations (for about 40% of measurements calculated-to-measured factor is less than 1/3). As it was discussed above, the reason of this discrepancy can be connected with the underestimation of of emissions in some regions of the Central Europe.

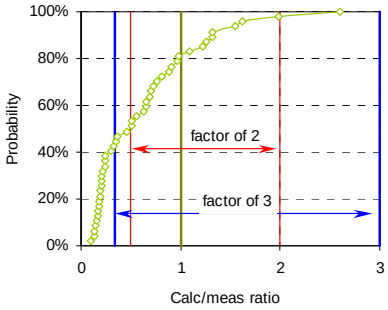


Fig. 2.68. *Cumulative distribution of calculated to measured factor for 2.3.4.7.8-PeCDF air concentrations in the surface atmosphere layer*

Let us now proceed with a short comparison of measured and calculated air concentrations in the contaminated regions. Of course, one cannot expect that calculated values will agree well with these measurements but such comparison can show the difference between measurements and calculations for contaminated regions (cities, places located near waste incinerators, etc). About 50 measurements in contaminated regions are included into the comparison. The cumulative distribution of calculated-to-measured factor is presented in Fig. 2.69.

It is seen that the distribution is shifted towards small values of the ratio. Almost all values of calculated-to-measured factor occur to be less than 1. The median of the distribution is 0.23. This means that measured values at contaminated locations are 4.3 times higher than values calculated by the model in corresponding grid cells. Such underestimation seems to be quite reasonable.

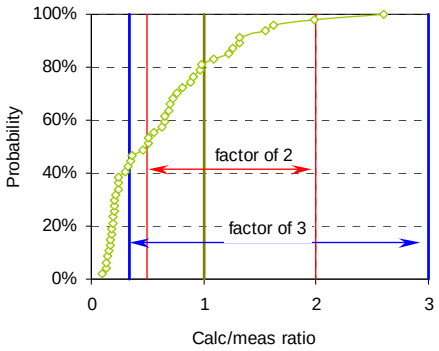


Fig. 2.69. *Cumulative distribution of calculated-to-measured factor for 2,3,4,7,8-PeCDF toxicity in the surface atmospheric layer in contaminated regions*

Deposition fluxes

There are very few data on deposition fluxes of PCDD/Fs in clear regions. Here we use the results of the measurement campaign in Bayreuth by [*Horstmann et al.,* 1997]. In the course of this campaign, measurements of deposition fluxes over the forest and to bare soil at adjacent locations for 12 periods from 1995 to 1996 were made. In particular, this allows comparing calculated and measured deposition fluxes to different types of the underlying surface.

The comparison of seasonal variations of measured and calculated deposition flux can be done on the basis of measurements in Bayreuth (Germany) in the end of 1995 – beginning of 1996 (Fig. 2.70).

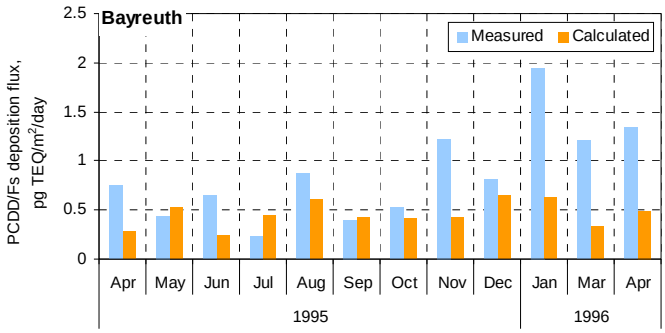


Fig. 2.70. *Comparison of measured and calculated values of (wet+dry) deposition flux in Bayreuth in the end of 1995 – beginning of 1996*

Similarly to the case of air concentrations, the agreement between measurements and calculations for the deposition flux, which includes wet deposition and dry deposition of pollutant associated with particles, is better in warm season. So, the refinement of seasonal variations of emissions can improve the agreement between measurements and calculations.

For the comparison it must be taken into account that the values of air concentrations at the same location were underestimated by the model on the average. The cumulative distributions of calculated-to-measured factor for air concentrations and deposition fluxes are presented in Fig. 2.71.

It can be seen that cumulative distributions of deposition flux looks quite similar to that of air concentrations. This means that the model correctly reproduces the relation between air concentrations and deposition fluxes.

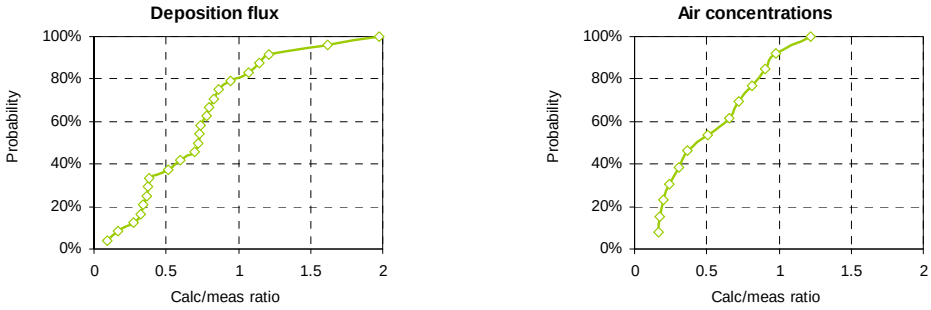


Fig. 2.71. *Cumulative distribution of calculated-to-measured factor for 2.3.4.7.8-PeCDF (wet+dry) deposition flux and air concentrations in Bayreuth*

To verify model calculations from the viewpoint of deposition to different underlying surfaces, ratios of deposition fluxes to forest and adjacent bare soil were calculated (both on the basis of measurements and calculations) for each observation period. The cumulative distribution of the corresponding calculated-to-measured factor is presented in Fig. 2.72.

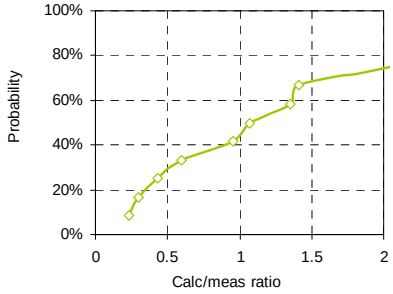


Fig. 2.72. *Cumulative distribution of calculated-to-measured factor for ratios of (wet+dry) deposition fluxes to forest and adjacent bare soil*

The median of the distribution is 1.1. This testifies that the model correctly reproduces the relations between deposition flux to the forest and bare soil.

2.3. Conclusions

Evaluation of MSCE-POP model performance was carried out on the basis of the comparison of model results on PAHs, PCBs, and PCDD/Fs with available measurements. For the comparison the following POP species were chosen: B[a]P as a representative of PAHs and PCB-153 and 2,3,4,7,8-PeCDF as a representatives of PCBs and PCDD/Fs. Modelling of long-range transport and accumulation of selected POPs was performed for the period from 1990 to 2003 by regional version of MSCE-POP model with spatial resolution 50×50 km^2. Modelling of PCB-153 was supplemented by calculations on the hemispheric level to take into account emission sources outside the EMEP region. Emission data for B[a]P and PCDD/Fs were compiled on the basis of official data submitted to the UN ECE Secretariat by Parties to the Convention and supplemented when necessary by expert estimates. In case of PCB-153 global PCB emission inventory [*Breivik et al.,* 2002] was used.

For the comparison of model results with measurements available data from EMEP monitoring network together with the data of national measurements and episodic campaigns were used. Analysis of agreement between model computations and observations was carried out for the concentrations in surface atmospheric layer, concentrations in precipitation, and deposition fluxes. Temporal variations of computed and observed values of concentrations and deposition fluxes were compared. In addition, the analysis of agreement between the spatial distribution of observed atmospheric levels of B[a]P and PCB-153 and obtained by the MSCE-POP model was carried out. In course of the analysis the emphasis was put on the comparison of annual means of calculated and measured values of air concentrations and depositions. To characterize the difference between the

model results and measurements the distribution of the ratio of calculated and measured values was analyzed and fractions of calculated concentrations and deposition fluxes, which agree with measured values within a factor of 2 and 3, were determined.

Polyaromatic hydrocarbons (B[a]P)

Measurements of B[a]P concentrations in air and precipitation and deposition fluxes performed at 9 EMEP sites, namely, FI96, SE2, SE12, SE14, NO42, CZ3, DE1, DE9, and LT15, were used for the comparison with model results. In addition, the results on B[a]P obtained in the framework of the Canadian/German project "Quality of measuring data on atmospheric inputs of POPs", measurements of B[a]P concentrations in the United Kingdom [*Coleman et al.,* 1998] were included into the comparison.

On the whole, the results of the comparison of computed and observed B[a]P concentrations and deposition fluxes show that about 60% of calculated values agree with measurements within a factor of 2.

The comparison of measured and calculated contamination levels in different parts of Europe reveals that the model correctly describes spatial distribution of contamination. Both in the background sites, where concentrations range from 0.002 to 0.03 ng/m^3, and in more polluted areas, where the concentrations range from 0.2 to 0.4 ng/m^3, the MSCE-POP model reproduces observed air concentrations mainly within an accuracy of 50%.

The comparison of time-series of measured and computed B[a]P content in air shows that temporal variations of concentrations obtained by the model are consistent with that observed at monitoring sites.

The discrepancies found between the measurements and model results can be partly explained by the uncertainties of emission data, in particular, spatial distribution and seasonal variability of B[a]P emission, and model description of B[a]P degradation in the atmosphere. Additional reasons of the discrepancies can be connected with the influence of emission sources outside the EMEP region and the quality of measurement data.

Air concentrations. Computed annual and monthly mean air concentrations of B[a]P were compared with measurements of the following EMEP sites: FI96, NO42, SE2, SE14, SE12, LT15, and CZ3.

- Reasonable agreement between annual means of calculated and measured air concentrations (mainly within an accuracy of 50%) takes place at monitoring sites FI96, SE2, SE14, and CZ3.
- At the background site NO42 the model underestimates air concentrations within a factor of 2. The underestimation can be connected with the influence of emission sources outside the EMEP grid not taken into account in modelling. The analysis of backward trajectories shows that level of air concentrations at this site is determined not only by European emission sources, but also by the sources of emissions located outside the model domain.
- The comparison of calculated air concentrations with measurements obtained in the framework of national measurement campaigns in the United Kingdom, Germany, and Poland shows that the model reproduces air concentrations in these countries within an accuracy of 50%. In the United Kingdom, the model reproduces measured values within an accuracy of 40% and correctly describes long-term trends of contamination.

- The analysis of seasonal variations of air concentrations at the considered sites shows that the model underestimates seasonal variations of air concentrations. To improve the agreement between calculated and measured values, the information on seasonal variations of B[a]P emissions in European countries is required.

Concentrations in precipitation and deposition fluxes. Computed concentrations of B[a]P in precipitation were compared with measurements of sites DE1, DE9, and CZ3. Model results on B[a]P deposition fluxes were compared with the data of the sites FI96, SE2, SE12, and SE14.

- Measurements of concentrations in precipitation at DE1 and DE9 agree with calculations for the period 1997 – 2003 mainly within an accuracy of 50%.
- The model generally overestimates the values of B[a]P concentrations in precipitation measured at the site CZ3. For 1998, 1999, 2002, and 2003 the agreement between measurements and calculations is within an accuracy of 70%.
- The comparison of annual means of measured and calculated deposition fluxes at the sites FI96, SE2, SE12, and SE14 shows that measurements agree with calculations mainly within a factor of 2. The disagreement between measured and calculated values of deposition fluxes correlate with disagreement in air concentrations.
- The comparison of measured and calculated washout ratio shows that the model reasonably describes the process of wet deposition for B[a]P.

Polychlorinated biphenyls (PCB-153)

Verification of MSCE-POP model results for PCBs was performed on the basis of the comparison with measurements from different sources. In particular, measurements of PCB concentrations and deposition fluxes at 9 EMEP monitoring sites in period from 1990 to 2003, data from 16 monitoring sites across the Baltic Sea area obtained in period 1990-1993, and the results of POP monitoring campaign carried out using passive samplers in summer 2002.

Comparison of model results with measurements reveals that MSCE-POP model reasonably reproduces spatial and temporal variations of PCB-153 air concentrations within the European region measured at the EMEP sites and obtained in the framework of monitoring campaigns. On the whole, over 40% of computed concentrations in air and in precipitation are within a factor of 2 with measurements. More significant differences are obtained between model computations and PCB-153 deposition fluxes observed at monitoring sites in Sweden and Finland. The discrepancies obtained are connected mostly with the uncertainties of PCB emission spatial distribution and the absence of seasonal variations in emission data used for modelling.

Air concentrations. Computed annual and monthly mean air concentrations of PCB-153 were compared with available measurements of 7 EMEP monitoring sites for the period 1997-2003, episodic measurements made at monitoring sites across the Baltic Sea in 1990-1993, and the results of passive sampling campaign performed in June and July 2002.

- Time-series of PCB-153 air concentrations measured at EMEP sites NO42, IS91, FI96, SE2, SE12, SE14, and CZ3 were compared with the results of MSCE-POP model. Temporal variations of air concentrations obtained by the model are close to the observed at remote sites (NO42, FI96, IS91) and the sites in Sweden (SE2, SE14, SE12). At the same time the model does not reproduce decrease of concentrations measured at CZ3 in period 1997-2003,

which is likely caused by the uncertainty of temporal variations of PCB emissions in central Europe.

- Comparison with long-term measurements of EMEP monitoring sites reveals reasonable agreement between the computed and measured annual mean air concentrations. Thus, model results are within a factor of 2 on average with measurements of the site FI96 and the sites NO42, IS91 in period 2000-2003. For the evaluation of PCB atmospheric levels at these sites there is a need to take into account the influence of emission sources outside the EMEP region, which contribution to concentrations can reach 30-50%.
- Computed air concentrations for SE2, SE14, and SE12 overestimate measured concentrations by a factor 2-3. The reason of the overestimation is possibly connected with the uncertainties in spatial distribution of PCB emission for Sweden. Model results for central Europe underestimate PCB-153 air concentrations obtained at Czech site CZ3 which is likely caused by underestimation of emission in this region.
- Comparison of monthly mean PCB-153 air concentrations obtained by the model and observed at EMEP monitoring sites reveals that the model is capable to reproduce seasonal variations of air concentrations. In particular, reasonable agreement is found for the remote site FI96, located distantly from PCB emission sources. Model results correlate also with measurements of SE2, SE14, and SE12 in some periods. The deviations between computed and measured values, in particular, some overestimation of observed concentrations in winter months and underestimation in summer months, are likely caused by the absence of seasonal variations in PCB emission data used for modelling.
- Spatial distribution of computed PCB-153 air concentrations was compared with the results of episodic monitoring campaign based on passive samplers deployed in 22 European countries. Good agreement is found between the distribution of atmospheric levels of PCB-153 obtained by the model and measured by passive samplers. In particular, low levels of concentrations in remote areas, moderate levels in northern and southern Europe, elevated levels in central and western Europe obtained by the model are generally consistent with the observed air concentrations.
- Reasonable agreement was also found between the model results and air concentrations measured during the monitoring study at 16 sites across the Baltic Sea area in 1990-1993. The model reproduced decreasing of PCB-153 air concentrations measured along the west coast of the Baltic Sea from south to north.

Concentrations in precipitation and deposition fluxes. Computed concentrations of PCB-153 in precipitation were compared with measurements of sites DE1, DE9 and CZ3. Comparison of calculated PCB-153 deposition fluxes was carried out with measurements of 4 EMEP sites SE2, SE14, SE12, and FI96. The comparison of calculated and measured concentrations in precipitation generally is more complicated since the description of wet deposition process in the model assumes that precipitation is equally distributed over model grid cell while in reality rainfall is often restricted to rather limited area. Additional discrepancies can be introduced by the uncertainties in emission data and differences between the precipitation amount used in the model and obtained at monitoring sites.

- The agreement between computed annual mean concentrations in precipitation and measurements of the site DE9 in the period 2001 – 2003 and the site DE1 in 2003 is within a factor 1.6. Larger differences were obtained between computed and observed concentrations for the data of the site DE1 for 2001 and 2002.

- The agreement between measured and calculated concentrations in precipitation at CZ3 for the period from 2000 to 2003 is within a factor of 1.8. Differences between computed and observed values for 1997 and 1998 are more significant. Most of the measured annual mean concentrations are underestimated by the model. The reason of the underestimation can be connected with underestimation of PCB emission in this region of Europe and the uncertainties in its temporal variations.
- Comparison of calculated and measured PCB-153 deposition fluxes at FI96, SE2, SE14, SE12 shows that the model overestimate observed values by a factor of 3 on average. At the same time model results, in general, follow temporal variations of observed deposition fluxes. The disagreement of measurements and calculations for deposition fluxes can be explained by the uncertainties in spatial distribution of PCB-153 emission and likely overestimated values of total PCB emission of Sweden, which is also reflected in the comparison of model results with observed level of PCB-153 in air at Swedish sites.

Dibenzo-p-dioxins and dibenzofurans (2,3,4,7,8-PeCDF)

PCDD/Fs are not currently included into the EMEP measurement programme. For this reason verification of the MSCE-POP model results for PCDD/Fs was based on the comparison with the data of various measurement campaigns, which include measurements for background and contaminated regions of Europe. Due to the limited information on measured atmospheric levels of PCDD/Fs and their temporal variations the comparison with the model results for this contaminant is of a preliminary character.

Air concentrations. Computed annual and monthly mean air concentrations of 2,3,4,7,8-PeCDF were compared with the concentrations observed at two EMEP sites SE2 and DE9 and measurements carried out in Sweden, Germany, the United Kingdom, Portugal, Italy and Greece in period from 1990 to 2001.

- The comparison of model results with measurements performed at the United Kingdom site Hazelrigg shows reasonable agreement between computed and observed annual mean concentrations.
- Seasonal variations of computed and observed air concentrations for Swedish and German sites were compared. Better agreement is found between the model results and measurements for the warm season of the year while in the cold season the model essentially underestimates PCDD/F air concentrations.
- In general, about 50% of calculated values of concentrations agree with measurements within a factor of 2 and about 60% – within a factor of 3. The model tends to underestimate observed PCDD/F air concentrations. The underestimation of observed concentrations is most likely connected with the uncertainties of PCDD/F emissions and their seasonal variations used for modelling.

Deposition flux. Comparison of computed PCDD/F deposition fluxes was carried out with the data of measurement campaign in Bayreuth (Germany). In the course of this campaign, measurements of deposition fluxes under the forest and to bare soil at adjacent locations for 12 periods from 1995 to 1996 were made. In particular, this allows comparing calculated and measured deposition fluxes to different types of the underlying surface.

- Similarly to the case of air concentrations, the agreement between measurements and calculations for the deposition flux is better in warm season (mainly within a factor of 2) while in cold season the differences can reach a factor of 3. The refinement of seasonal variations of emissions can improve the agreement between measurements and calculations.
- The probability distribution of calculated-to-measured factor for deposition fluxes is similar to that of air concentrations. This shows that the model correctly reproduces the relation between air concentrations and deposition fluxes obtained during the measurement campaign in Bayreuth.
- The relation between values of deposition fluxes to forest and to adjacent bare soil is reasonably reproduced by the model. The median of the calculated-to-measured factor for ratios of deposition fluxes to forest and adjacent bare soil is 1.1.