

# Item 6. Progress in activities in 2011 and future work

*a) Measurements and modelling*

*(Persistent Organic Pollutants)*

Victor Shatalov

on behalf of CCC and MSC-E

# Main CCC/MSC-E activities on POPs in 2011

EMEP Work-Plan for 2011 [ECE  
CLRTAP long-range strategy [E  
HTAP Assessment 2010

## ➤ Routine activities

- ✓ Input data for POP mo
- ✓ Monitoring data for 20
- ✓ Evaluation of pollution  
for PAHs, PCDD/Fs and

## ➤ New developments

Convention on Long-range Transboundary Air Pollution

emep  
Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe

TECHNICAL REPORT  
4/2010 July 2011

STATUS REPORT  
3/2011 June 2011

Assessment of environmental contamination by heavy metals and persistent organic pollutants: New developments

EMEP/MSC-E Technical Report 4/2011

Hg concentration, ng/m<sup>3</sup>

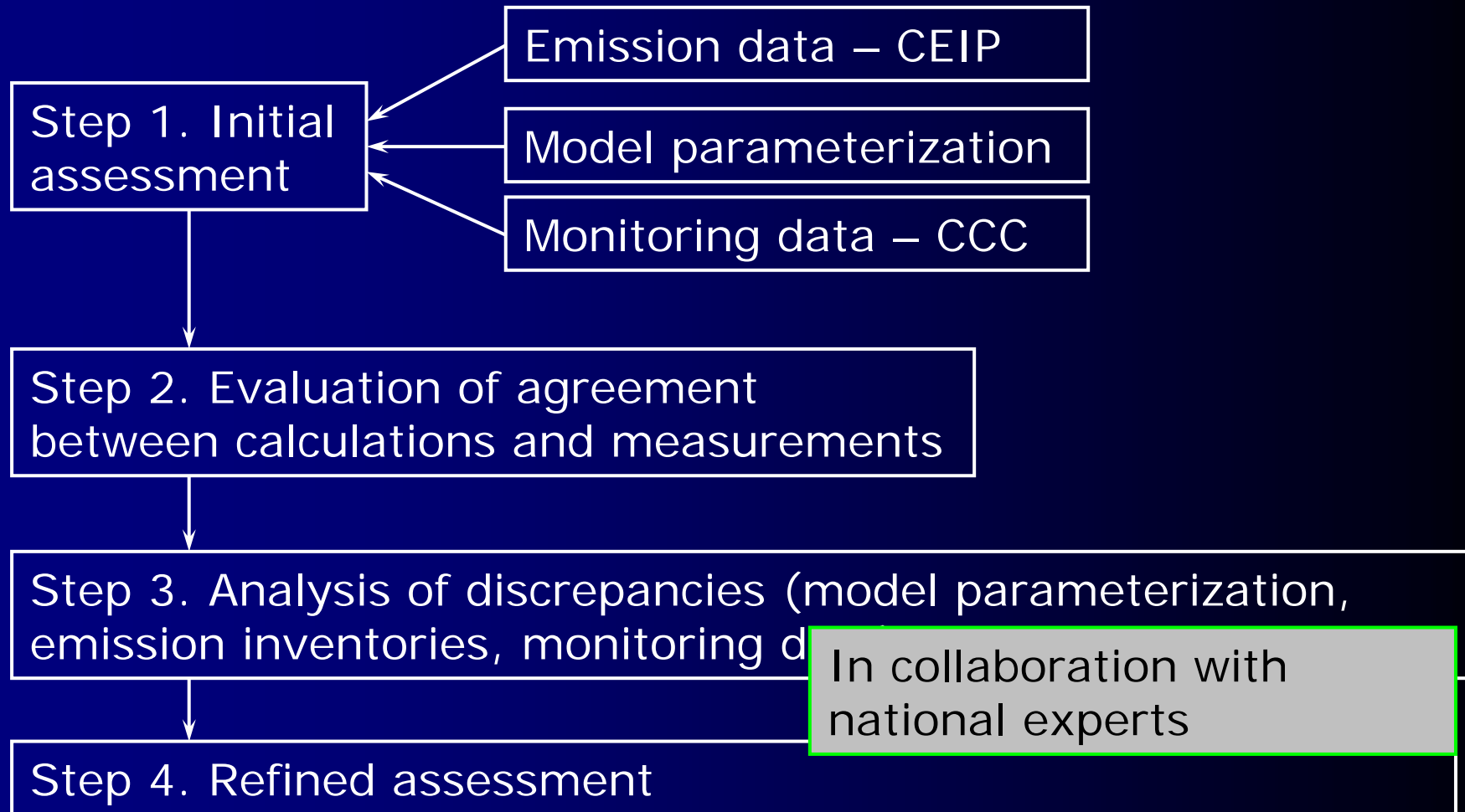
— Measurements  
— Model (no AMDEs)  
— Model (AMDEs & re-emission)

# Main CCC/MSCE activities on POPs in 2011

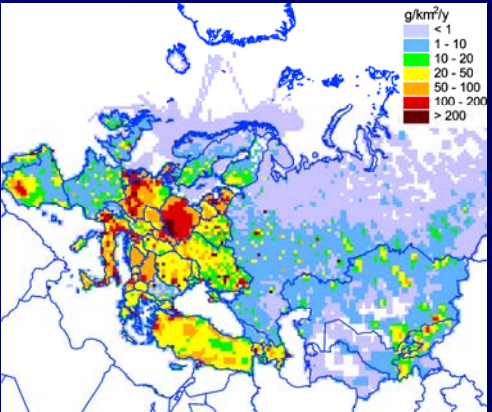
- New developments
  - ✓ Application of integrated monitoring/modelling/emission approach.
  - ✓ Global transport of POP pollutants (oceanic transport).
  - ✓ Climate change and POP inter-linkages (influence of meteorological parameters on POP fate).



# Integrated monitoring/modelling/emission approach

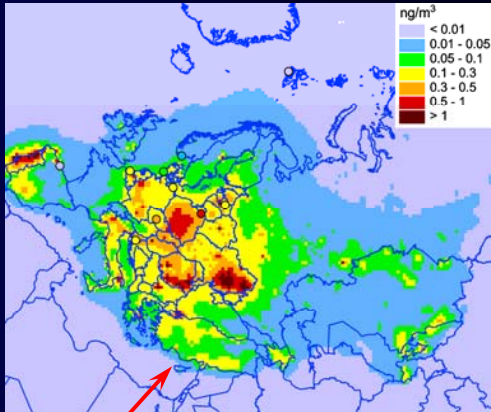


# Step 1: Preliminary assessment (B[a]P)

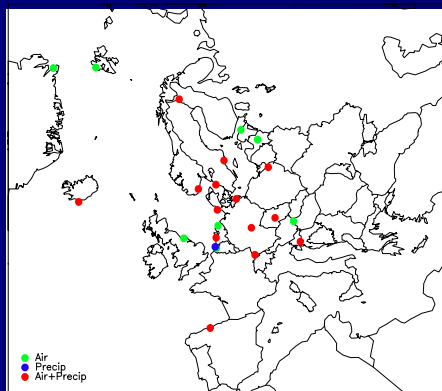


Emissions of B[a]P in the EMEP domain in 2009

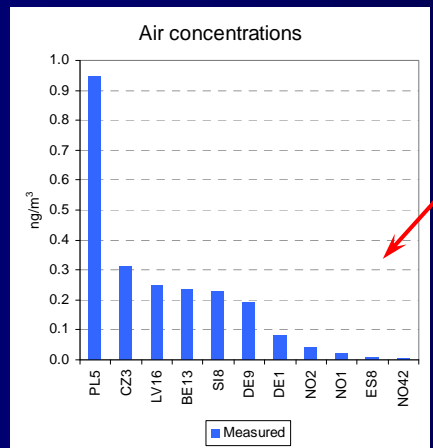
Model calculations



Calculated B[a]P air concentrations in 2009



Monitoring data



Evaluation of agreement (step 2)

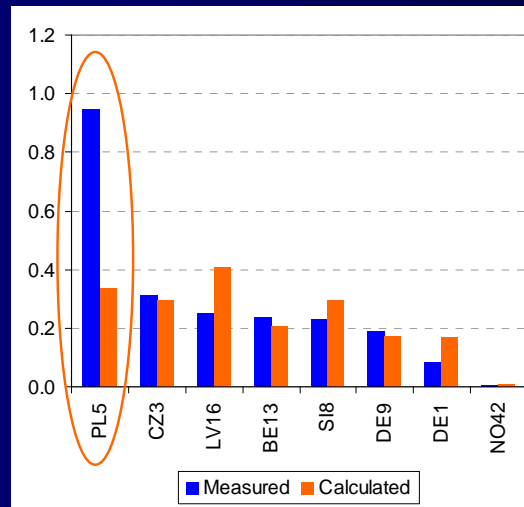
Statistical indicators



## Statistical indicators

Indicator	Meaning	Threshold
FAC2	Fraction of agreements within a factor of 2	> 50%
Correlation coefficient	Agreement of variability	> 0.6
Regression coefficient		$1 \pm 0.3$
Normalized mean bias	Characterization of systematic error	< 0.2
Student ratio		95% confidence level

## Step 2: Evaluation of agreement

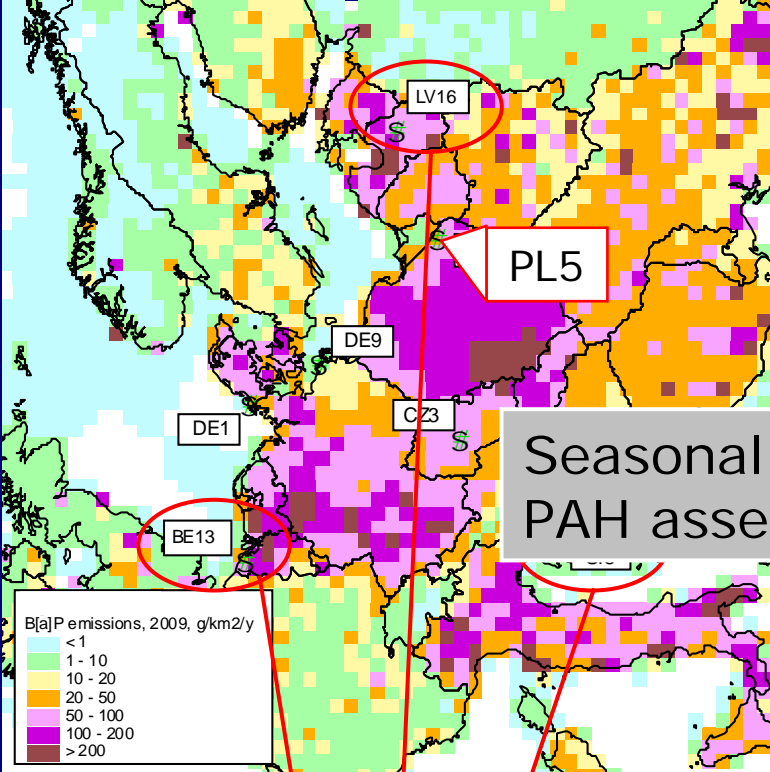


Comparison with measurements

Indicator	All sites	Without PL5	Threshold
Fac 2	75%	85.7%	> 50%
Correlation	0.57	0.84	> 0.6
Regr.	1.32	0.70	$1 \pm 0.3$
NMB	0.16	- 0.19	< 0.2 (abs.val)
Student Ratio	0.56	- 1.31	< 2.36 (abs.val)

# Step 3: analysis of discrepancies

Comparison with measurements

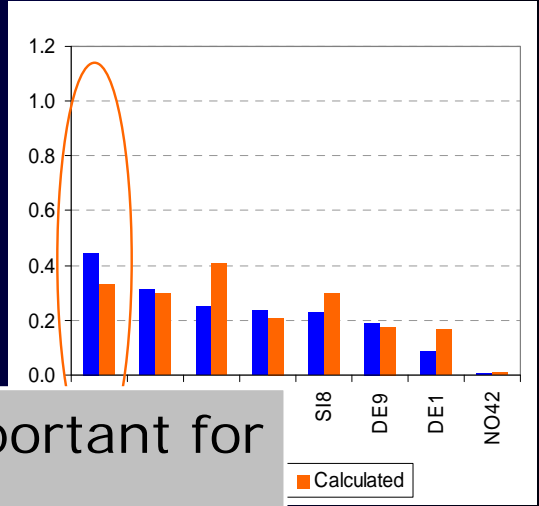


Emissions and measurement sites

3 times lower than at PL5

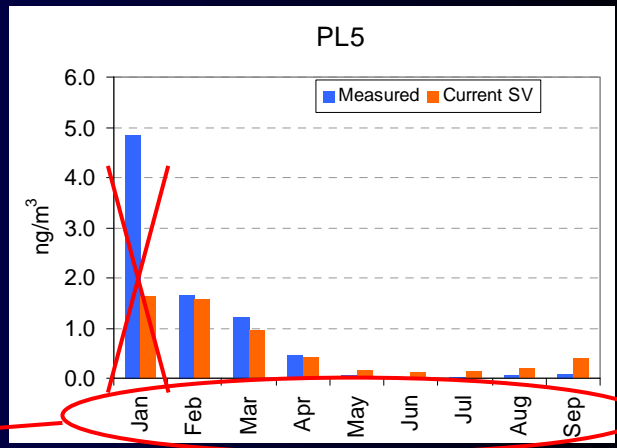
Non-complete year

Annual averages



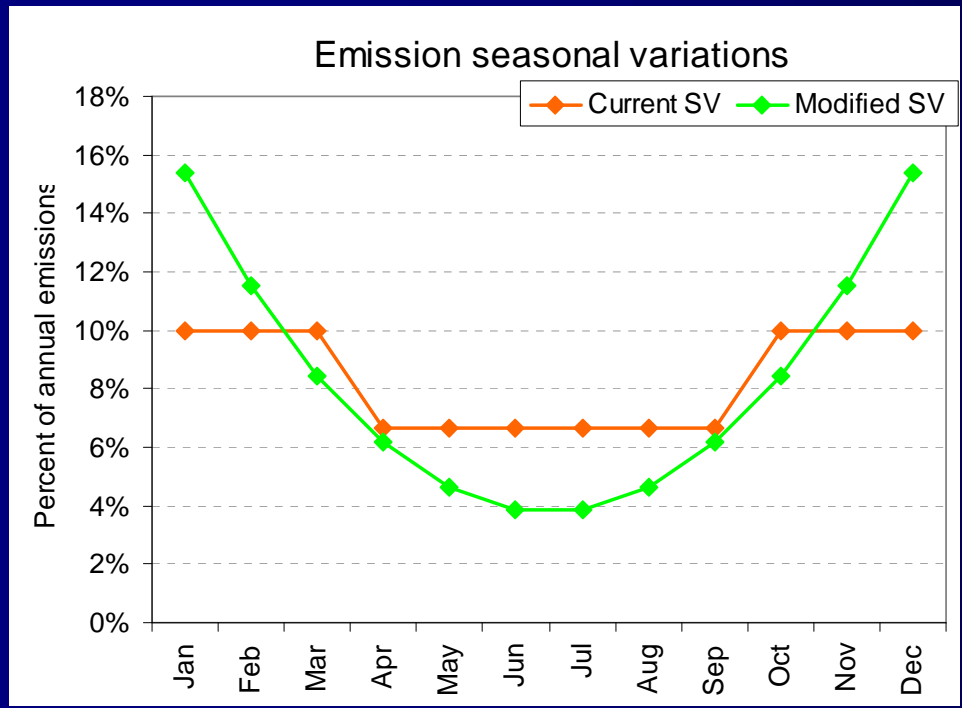
Seasonal variations are important for PAH assessment

Monthly averages





# Modification of emission seasonal variations for B[a]P

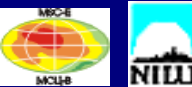


Current seasonal variations (SV) – Baart et al., 1995

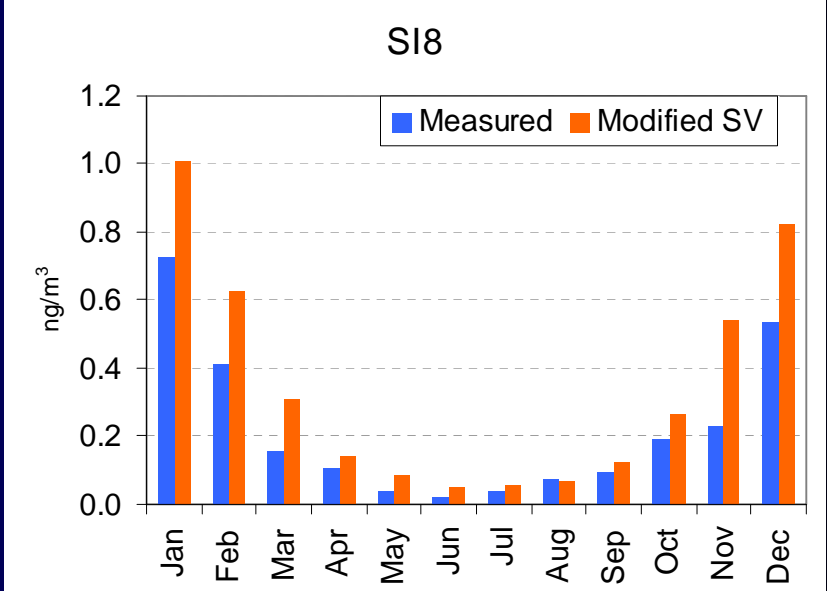
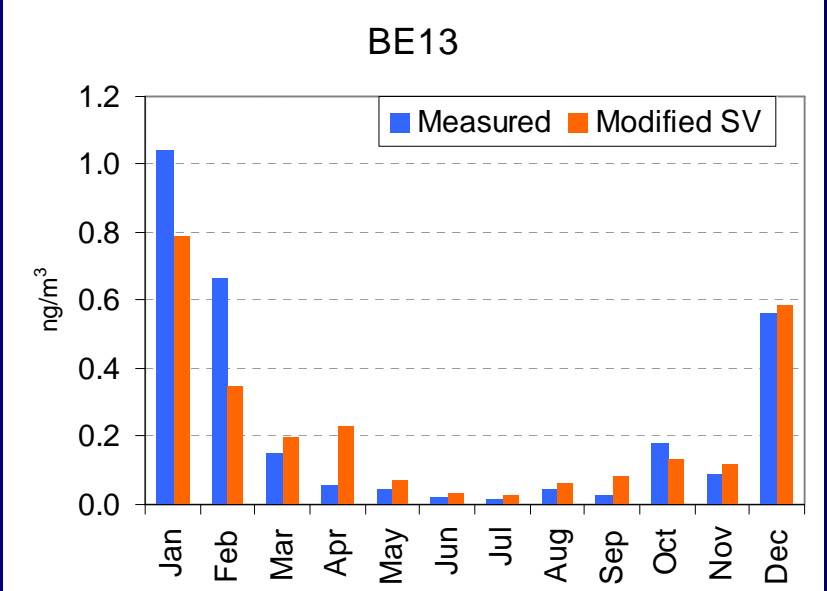
Morville et al., 2011:

For air concentrations  
Max/Min = up to 9 times

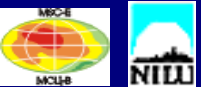
Current and modified emission seasonal variations (SV) for B[a]P



# Improvements resulting from emission modification (B[a]P)



Comparison of calculation results with measurements



## **Assessment of PCDD/Fs**

The work is performed in collaboration with national experts  
(IVL, Stockholm University and Umeå University)

Evaluation of EMEP contamination by PCDD/F mixture in 2009

Examination of congener composition of PCDD/F mixture

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### Measurements used:

- congener-specific daily averages of air concentrations (SE12 and FI96)  
with wind direction specification
- congener-specific monthly means of deposition fluxes (SE35)

Period: 2006 – 2007

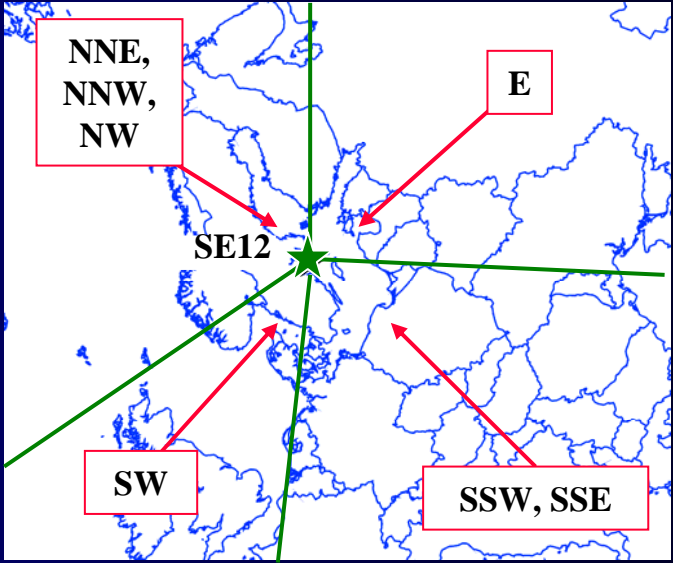
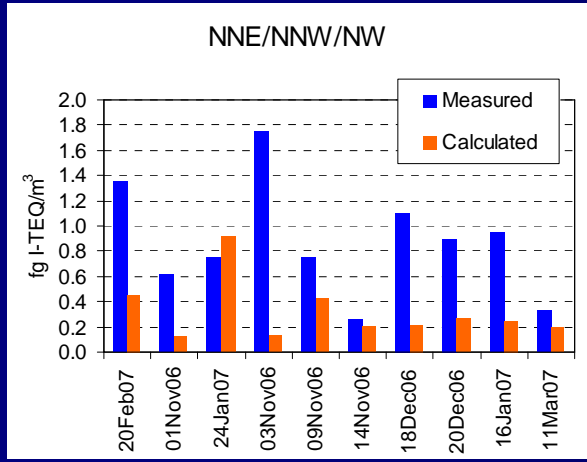
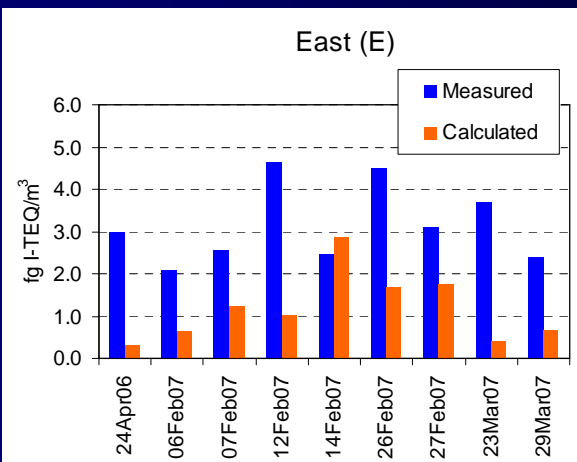
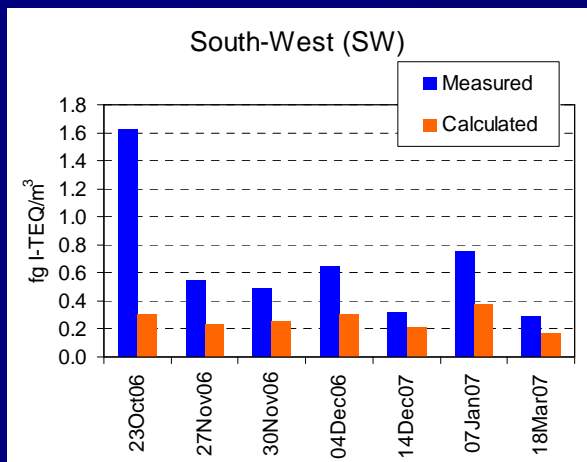
Data on emission congener  
composition: POPCYCLING-BALTIC  
project

Congeners considered:

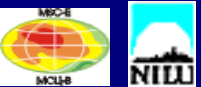
- 2,3,4,7,8-PeCDF (congener fraction: 30 – 40% of total toxicity)
- 1,2,3,7,8,9-HxCDD
- OCDD
- OCDF



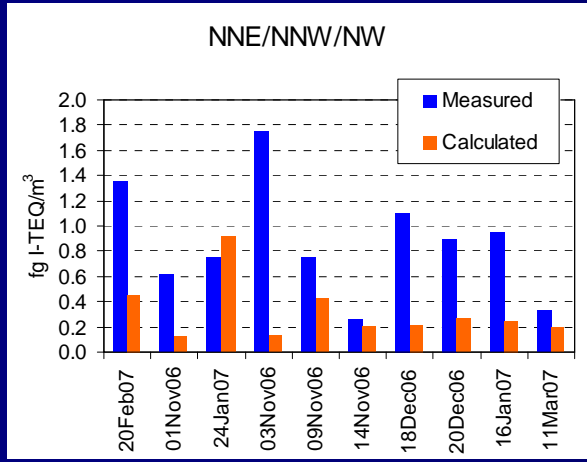
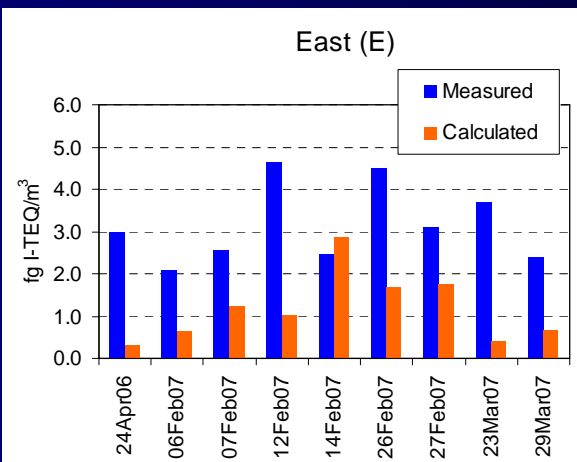
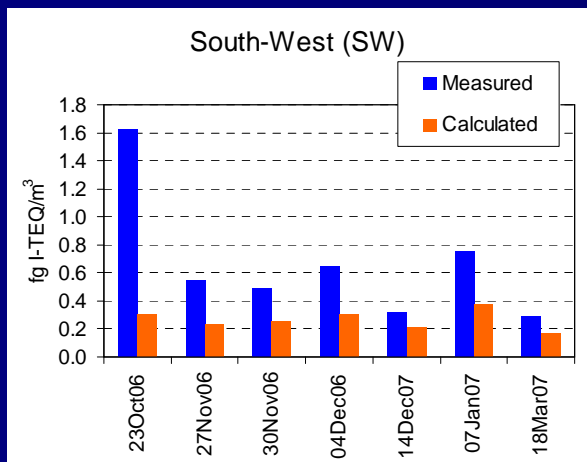
# Step 2: comparison with measurements (2,3,4,7,8-PeCDF)



Air concentrations (site SE12)

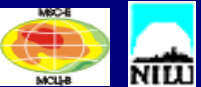


# Step 2: comparison with measurements (2,3,4,7,8-PeCDF)

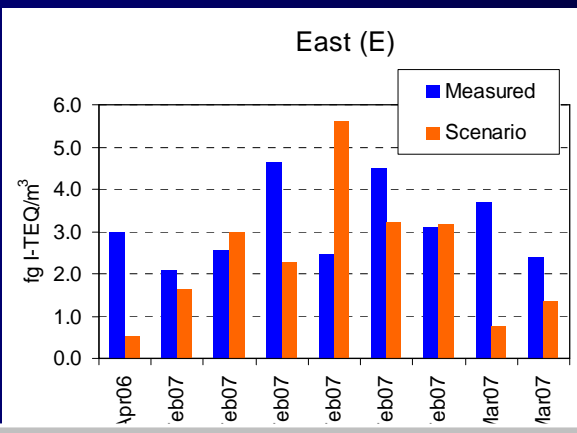
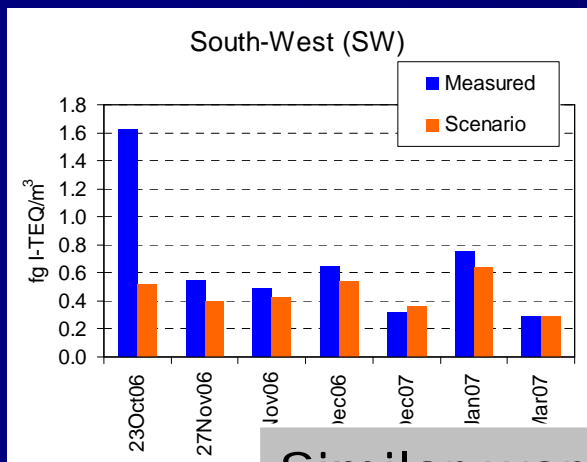


Indicator	Base	Threshold
Fac 2	54%	> 50%
Corr.	0.58	> 0.6
Regr.	1.89	1 ± 0.3
NMB	0.63	< 0.2
SR	4.77	< 2.1

Air concentrations (site SE12)



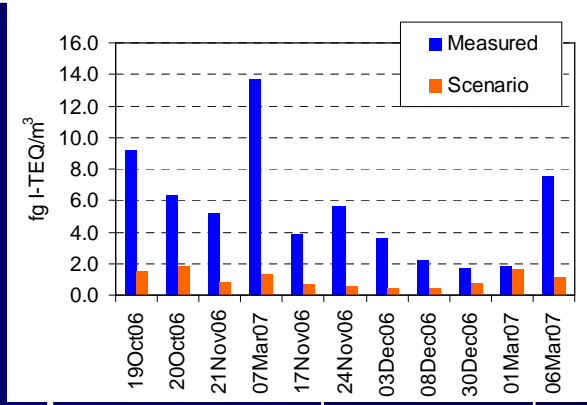
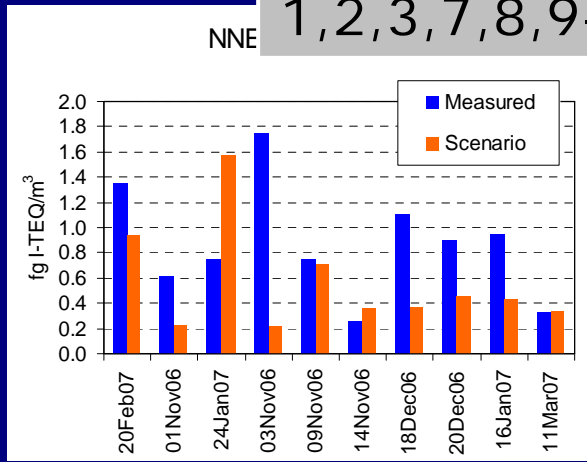
# Scenario calculations (2,3,4,7,8-PeCDF)



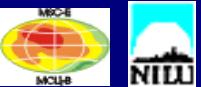
Correction factors:

- emission totals:
  - Poland 1.5
  - Russian West 3
- congener fraction: 1.7

Similar work was carried out for 1,2,3,7,8,9-HpCDD, OCDF and OCDD



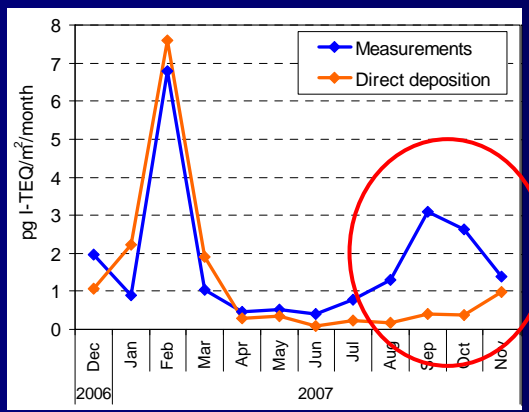
Measured	Threshold
62%	> 50%
0.60	> 0.6
0.96	1 ± 0.3
0.28	< 0.2
1.94	< 2.1



# Scenario calculations (PCDD/Fs)

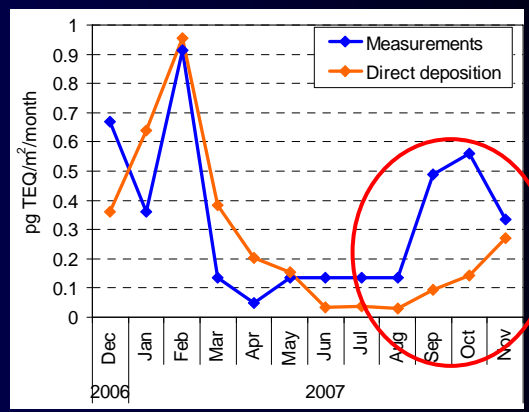
Variations of congener composition with constant toxicity

Correction factor = 1.7  
 (fraction of total toxicity becomes  $30\% \cdot 1.7 = 51\%$ )



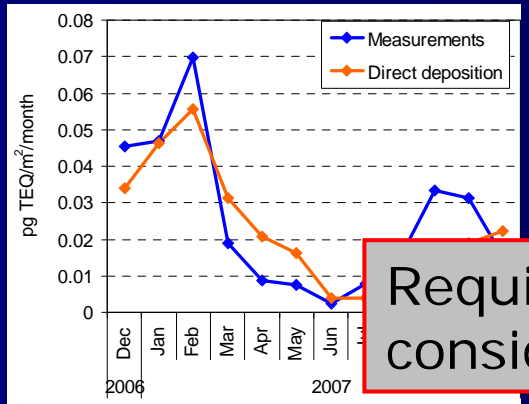
Correction factor = 3

2,3,4,7,8-PeCDF



1,2,3,7,8,9-HxCDD

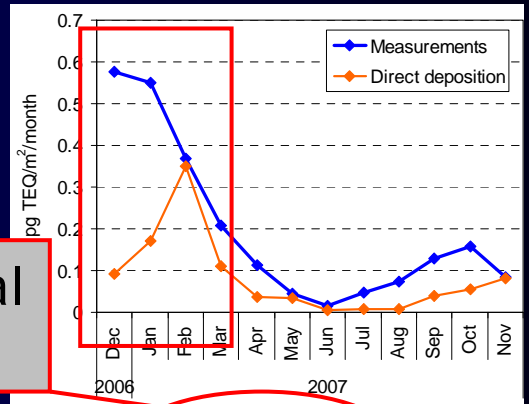
Correction factor = 6



Correction factor = 6

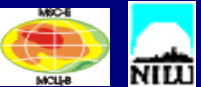
Requires additional consideration

OCDF



OCDD

Deposition flux (site SE35)



## **Peculiarities of OCDD**

OCDD can be generated in air by atmospheric reactions involving other contaminants (PCP)  
[*Baker and Hites, 2000*]

Contributions of OCDD to D&F toxicity in PCP preparations ranges from 60% to 90%.  
[*SEPA report, 2009*]

Simultaneous modelling of OCDD and PCP can refine the assessment

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! Data on congener composition in emissions in countries are one of key points for evaluation of pollution levels

A paper "Modelling the Atmospheric Transport and Deposition to the Baltic Sea" in co-authorship with Swedish experts is in preparation

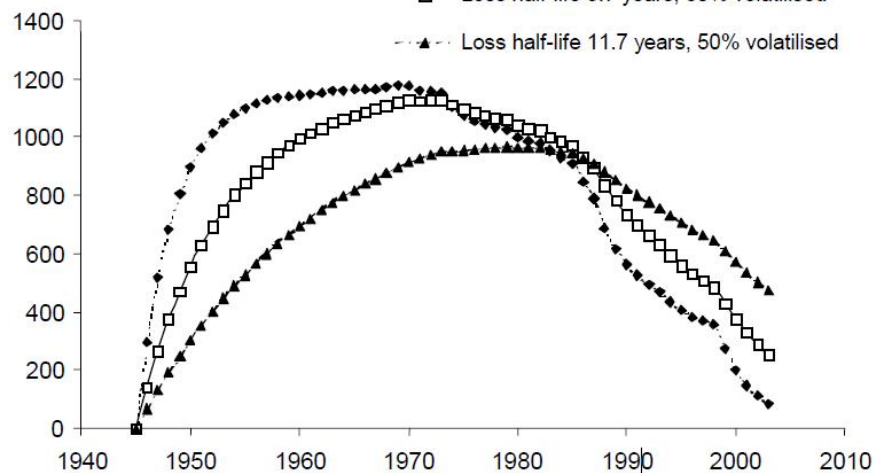


# Assessment of HCB contamination in EMEP

Re-volatilization from soil is one of the most important sources of HCB contamination

[Barber et al., 2005] (EuroClor Science Dossier)

Mass of HCB volatilised from soil (in tonnes)



Mass of HCB volatilized from soil on global level: 200 - 400 t/y

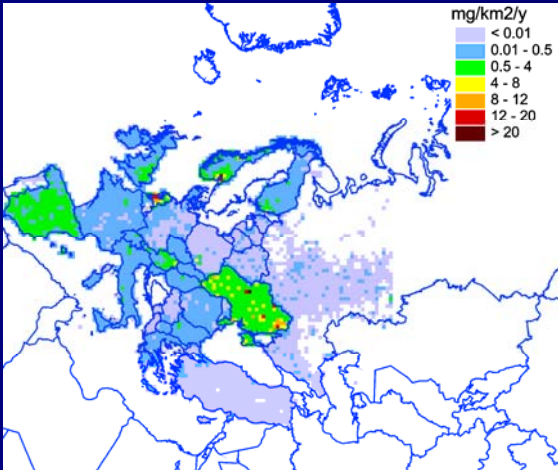
Global anthropogenic emissions in 2004 – 27 t/y

EMEP emission in 2009 – 9 t/y

Franke et al., 1996: anthropogenic emissions in Germany – 200 kg/y;  
re-volatilization from soil in Germany – 10 – 50 t/y

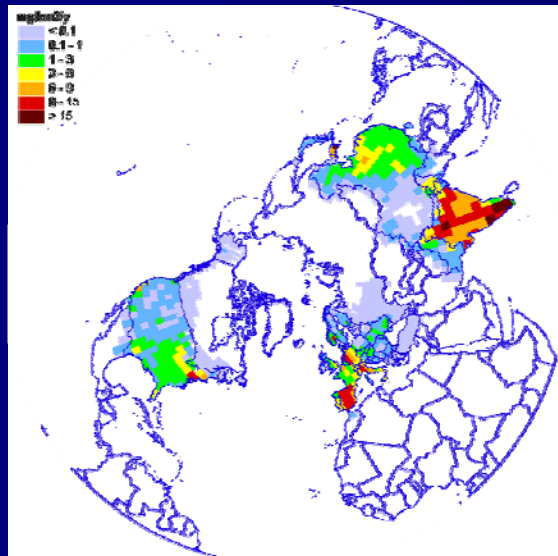
# Step 1: Preliminary assessment

## HCB emissions



### EMEP domain:

Official data and TNO estimates for 2009

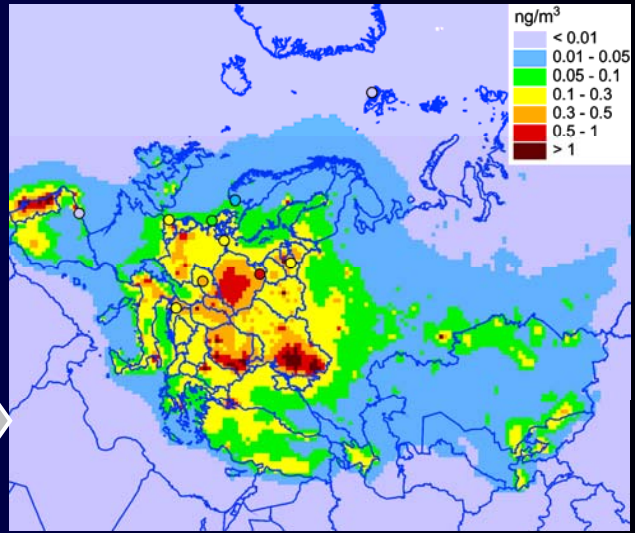


### Northern Hemisphere:

Official data and TNO estimates for 2009

Historical emissions from 1990 to 2009 at hemispheric level  
Bailey [2001]

Model calculations

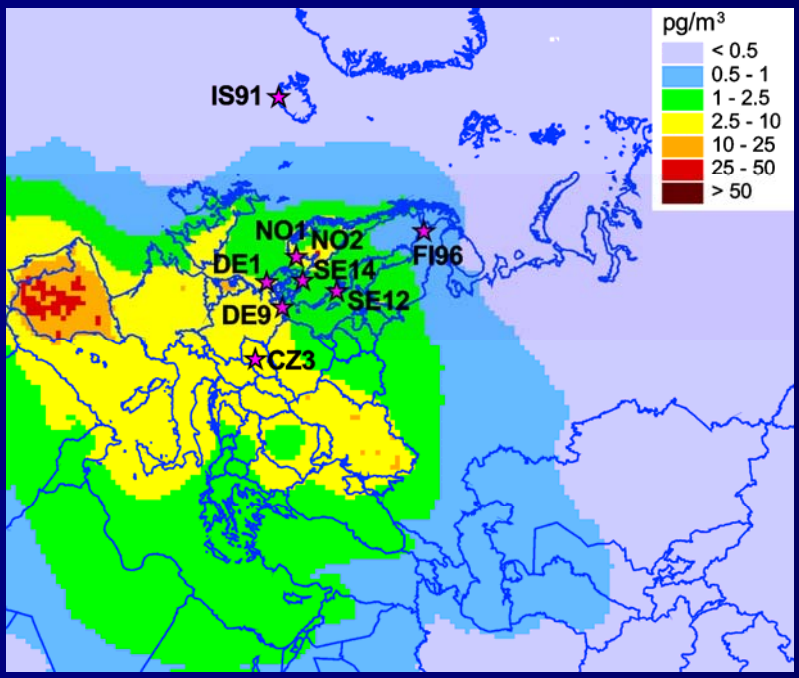


Calculated HCB air concentrations in 2009 taking into account transport and accumulation from 1990 to 2009 at hemispheric level

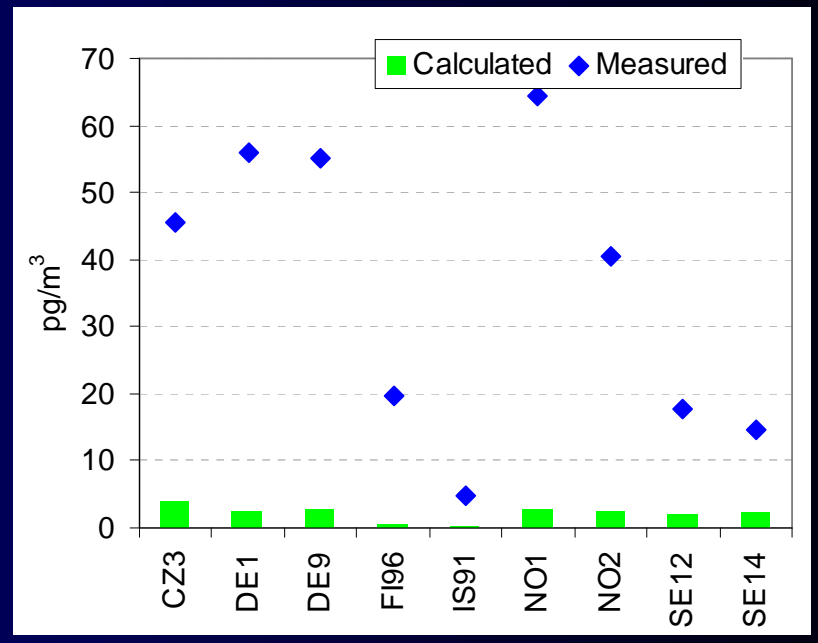
# Step 2: Evaluation of agreement

MSC-E calculations made in 2011

Air concentrations



Comparison with measurements



Underestimation is about a factor of 17 (7 – 30)

## **Step 3: Possible reasons of discrepancies**

Underestimation is about a factor of 17 (7 – 30)

### Measurement data.

EMEP measurements: 5 – 70 pg/m<sup>3</sup>,  
other measurements: 10 – 80 pg/m<sup>3</sup> (Barber et al., 2005)

### Model uncertainties.

Model parameterization: sensitivity study, model  
intercomparison → uncertainty may be up to a factor of 2;

### Emission uncertainties.

Historical and contemporary emissions → ???

## **Step 3: Possible reasons of discrepancies**

Historical emissions -> soil concentrations -> re-emission flux

MSC-E calculations made in 2011

### Uncertainties in description of re-emission flux:

uncertainties in historical emissions [Bailey, 2001] used in calculations for 2009 lead to the fact that soil concentrations calculated by the model are essentially lower than measured [Barber et al., 2005].

As a result – model underestimation of air concentrations 7 – 30 times.

Main reason – underestimation of re-emission flux.

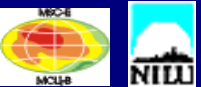
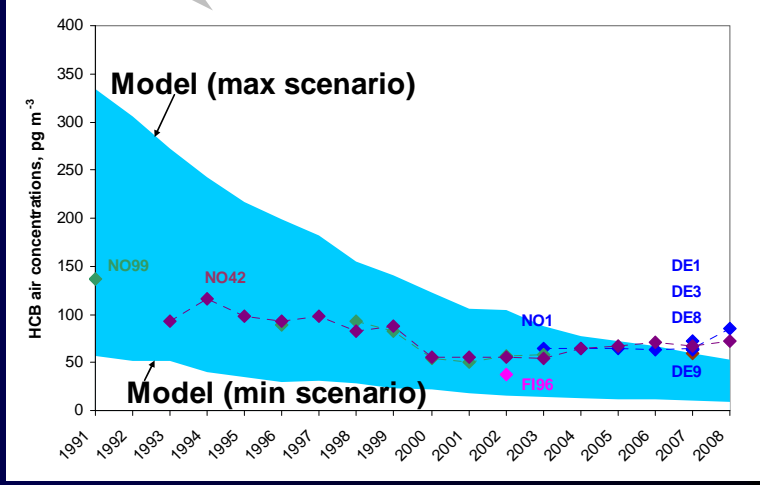
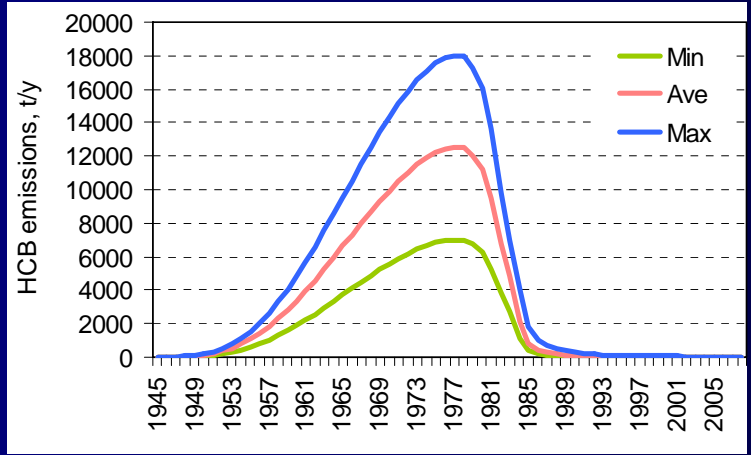
# Step 3: Possible reasons of discrepancies: re-emission fluxes

MSC-E calculations made in 2010

Measurements at EMEP monitoring network are in between calculation results obtained with maximum and minimum scenarios. Agreement with average scenario – factor 2 – 4

Test simulations from 1945 to 2008 for evaluation of accumulation in soil

Emission scenarios based on FAO data (taking into account agricultural use)

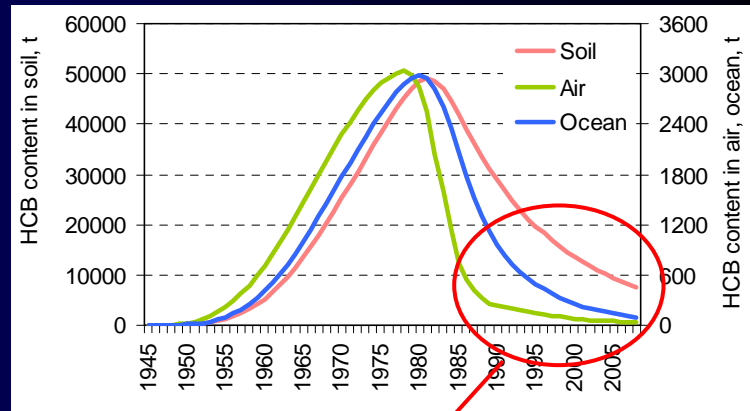
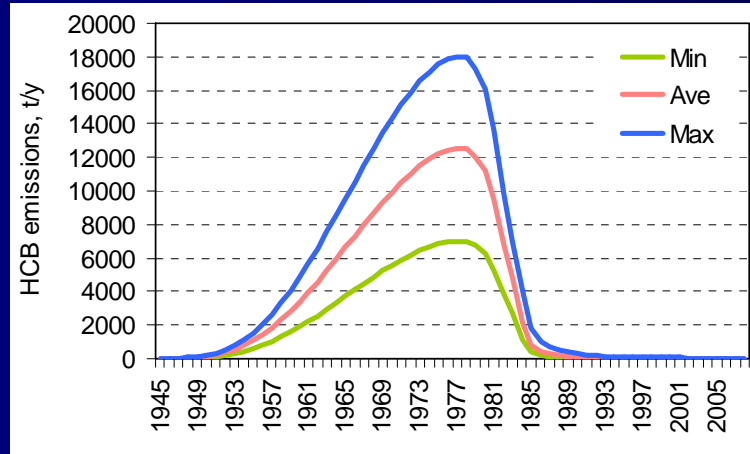


# Step 3: Possible reasons of discrepancies: re-emission fluxes

MSC-E calculations made in 2010

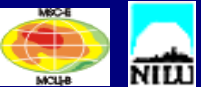
Test simulations from 1945 to 2008 for evaluation of accumulation in soil

Emission scenarios based on FAO data (taking into account agricultural use)



HCB content in media

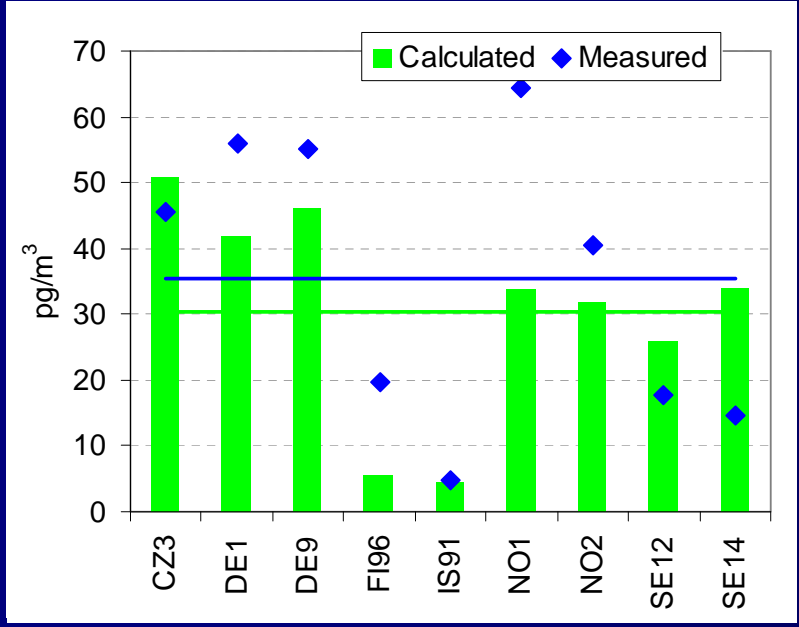
Different rates of decay of soil and air concentrations lead to enlargement of re-emission flux



# Step 3: usage of emission scenarios

MSC-E calculations made in 2011 based on official EMEP data, TNO and Bailey, 2005 (global scale)

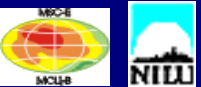
Scenario 1	Anthrop. emissions × 3, re-emissions × 7
Scenario 2	...



Comparison with measurements (Scenario 1)

## Results

Indicator	Initial calc.	Scen1	Thresh. level
FAC 2	11%	78%	> 50%
Corr	0.74	0.73	> 0.6
Regr.	3.75	0.96	1 ± 0.3
NMB	0.78	0.14	< 0.2
SR	2.53	0.99	< 2.3





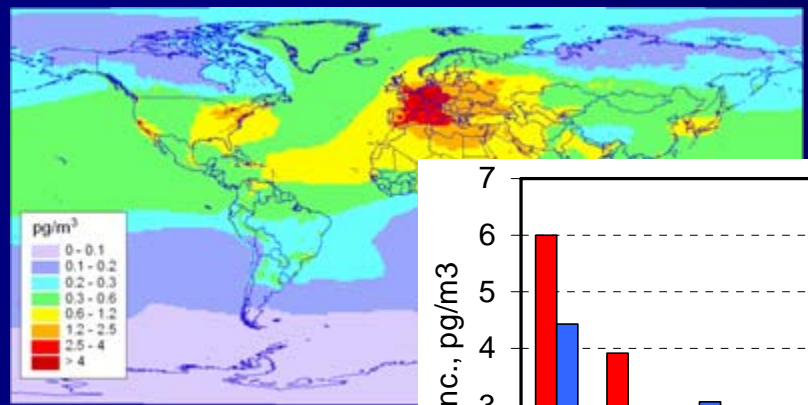
## **Influence of global transport on POP pollution within EMEP**

According to HTAP assessment 2010 and MSC-E estimates:

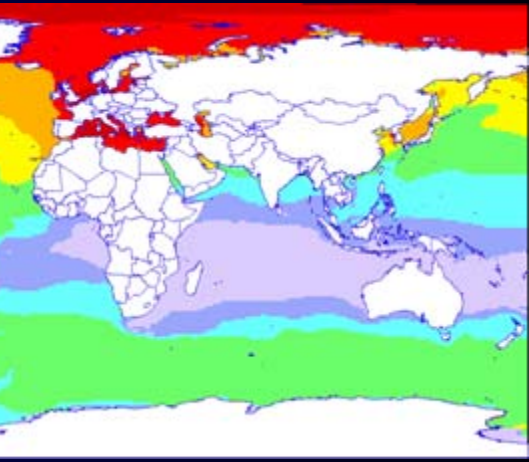
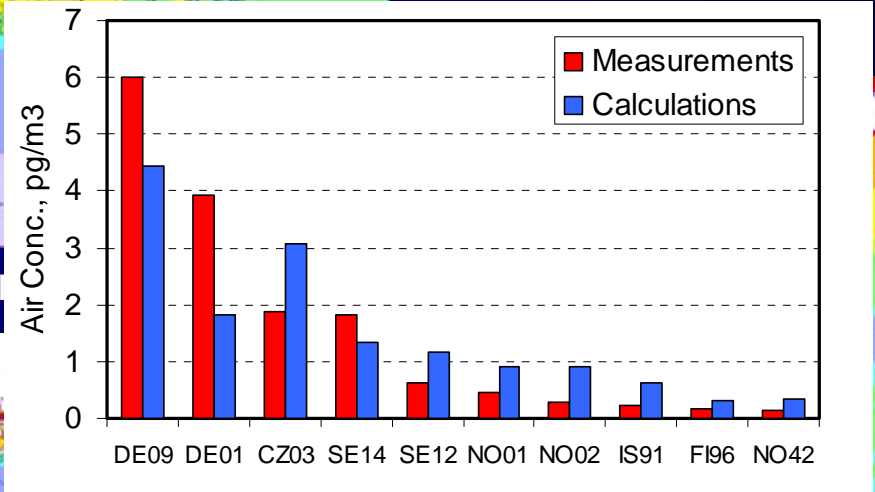
Contributions of non-EMEP sources to depositions to particular European countries for POPs reaches up to 50%.

# Simulations of PCB-153 global transport in 2009

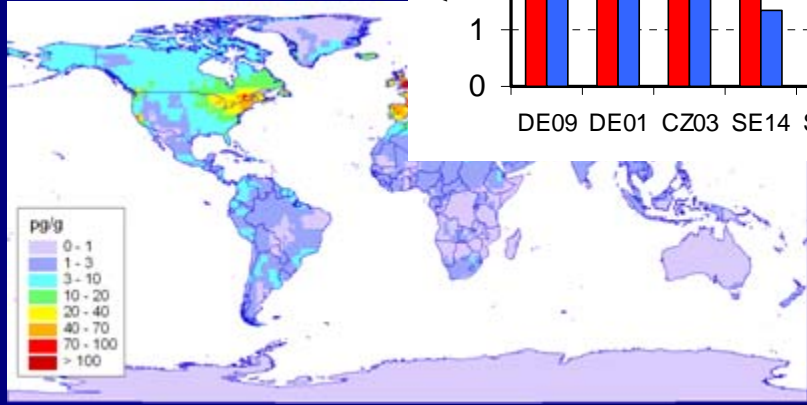
## PCB-153 annual mean concentrations in 2009



surface air



surface seawater, pg/L

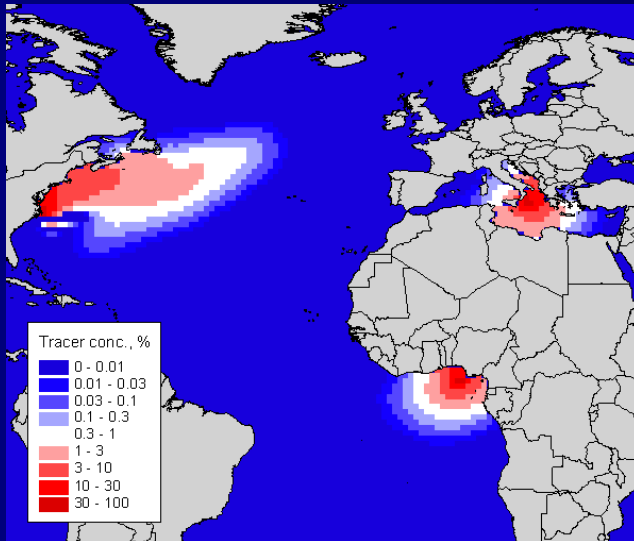


soil (top 5 cm), pg/g

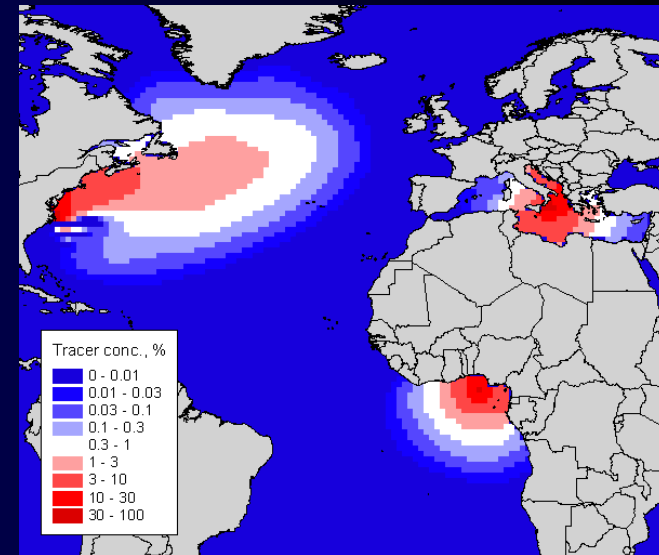
## Testing the ocean model in GLEMOS

Tracer test for POP-like substance (advection, vertical and horizontal diffusion, partitioning, degradation, and sedimentation; no exchange).

After 7 months



After 12 months



Tracer ocean concentrations in the upper model layer (percent of the maximum value) from three point sources calculated by the GLEMOS ocean module

## **Climate change and POP interlinkages**

- ❖ Evaluate **sensitivity** of POP pollution levels to variation of **meteorological** and **environmental factors**.
- ❖ Investigation of **climate change** influence on meteo/env. parameters
- ❖ Perform **modelling experiments** of future changes in POP pollution using the **GLEMOS** and available **climate change scenarios** data

# **Sensitivity of model results to meteorological and environmental parameters**

## Target parameters:

Transport distance  
(considered earlier)

Mean air concentrations  
in a country

Total deposition flux  
to a country

## Factors:

Temperature

Precipitation intensity

Wind speed

Wind direction

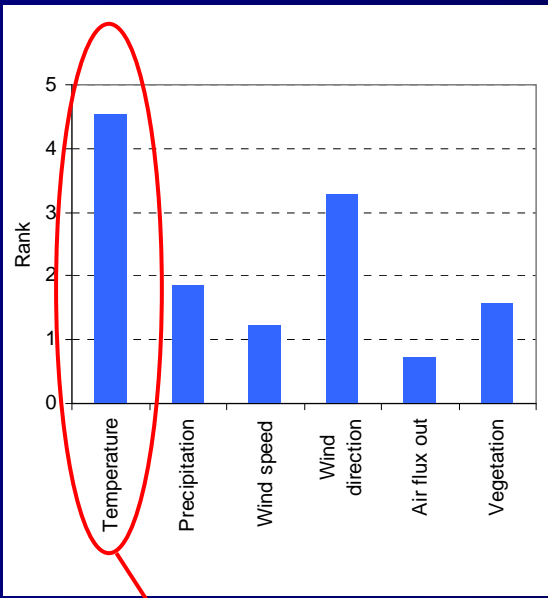
Outflow through boundaries

Coverage by vegetation

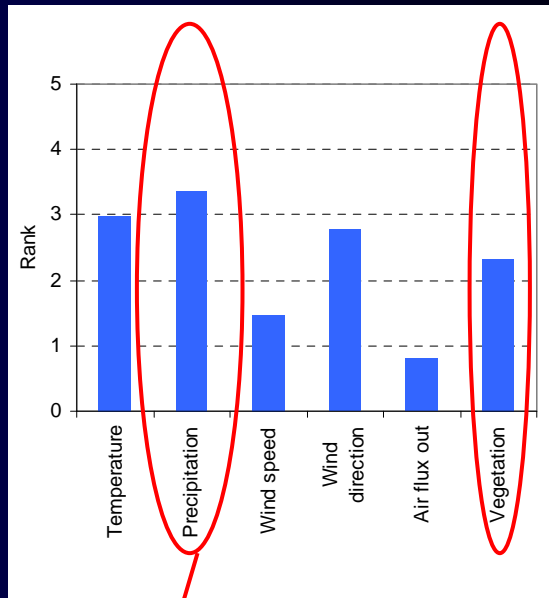
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# Ranking of factors: air concentrations over Europe

particulate, degradable (B[a]P)



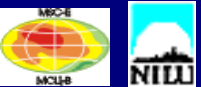
gaseous/particulate (PCB-153)



Most important – temperature, precipitation and wind direction

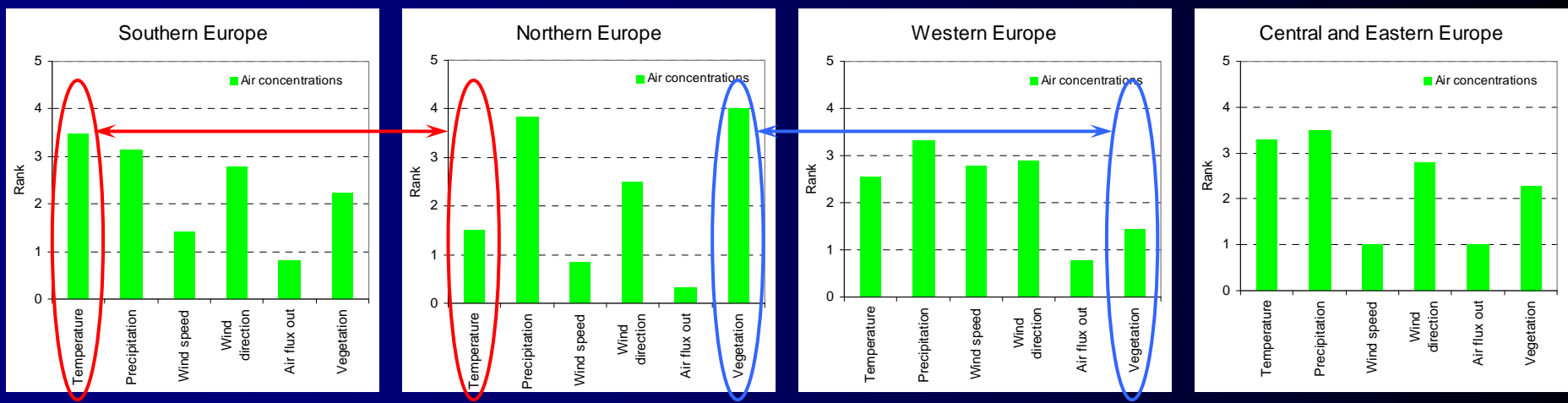
Highest priority – temperature

Highest priority – precipitation intensity



# Ranking of factors: different locations

PCB-153



Regions	Priority parameters
Northern Europe	Vegetation cover, precipitation
Western Europe	Precipitation, wind speed and direction
Central and Eastern Europe	Temperature, precipitation
Southern Europe	



## **Modelling of POP fate using climate change scenarios data**

Climate change leads to the change of meteorological and environmental parameters

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### *Selection of climate change scenarios data :*

GCM model output for a number of scenarios is used to prepare meteorological input for GLEMOS (2010-2100)

### *Planning of modelling experiments :*

Explore effect of changes of climate and emissions on POP long-range transport, source-receptor relationships, and distribution of POPs in media and re-emissions (PAHs, PCDD/Fs, ...)



# Future activities

CCC

Review, store and make available EMEP monitoring data for the modelling centres and Parties.

Evaluate new measurements data of POPs from Eastern Europe, the Caucasus and Central Asia.

Maintain close interaction with relevant organizations and bodies in relation to integration of observations.

...

# Future activities

## MSC-E

Model assessment of **transboundary pollution** on regional and global scale.

Model parameterization of **air/vegetation exchange**.

Implementation of the integrated approach for POPs, including **adjoint modelling**.

**Model investigation of climate change effects** on POP transport and fate.

Pilot calculations of POP pollution on a **local scale**.

...

**Thank you for your  
attention!**

# Step 3: Possible reasons of discrepancies: re-emission fluxes

Historical emissions -> re-emission flux

Uncertainties in description of re-emission flux:

Measurements at EMEP monitoring network are in between calculation results obtained with maximum and minimum scenarios. Agreement with average scenario – factor 2 – 4

2001) lead to the fact model are essentially

media and re-behavior (PCB-153);

Test simulations from 1945 to 2008 for evaluation of accumulation in soil

Emission scenarios based on FAO data and MSC-E estimates (taking into account agricultural use)

