Annex A

EVALUATION OF MODELLING RESULTS VS. OBSERVATIONS

Calculated mean annual concentrations in air and annual sums of wet deposition of Pb, Cd and Hg were evaluated via comparison with the corresponding values measured at the EMEP monitoring network. The agreement between modelled and observed values is influenced by uncertainties of model parameterizations, emissions and monitoring data.

Since description of various environmental processes considered in the model is based on a number of assumptions, any model is capable of describing pollution levels only approximately. Analysis of the model uncertainties undertaken some time ago [*Travnikov and Ilyin*, 2005] demonstrated that intrinsic model uncertainty (i.e. uncertainty of the model as such, without effect of emission data) of modelled deposition of heavy metals was amounted to ±30-40% for Europe as a whole. Intrinsic uncertainty for air concentrations of particulate metals (Pb, Cd) is around ±40%, and Hg - around ±20%.

Uncertainty estimates of the heavy metal emission data are available for several EMEP countries. Table A.1 contains results of the uncertainty analysis carried out by national emission experts. The presented uncertainty values are related to total emission values in the countries. As seen, in some counties the uncertainties of Pb emissions reach almost 500%, of Cd – almost 450% and Hg – around 180%. Even median values of the uncertainties are significant: 100% for Pb, about 80% for Cd and around 70% for Hg. These high uncertainties may affect the modelling results and interpretation of evaluation of calculated concentrations and deposition against measurement data.

Table A.1. *Uncertainties (%) of the national total values of heavy emission data used in calculations for 2016*

2015	Pb	Cd	Hg	Reference
Belarus	192	266	111	*IIR Belarus* [2016]
Belgium	106	81	32	*IIR Belgium* [2017]
Croatia	140	291	78	*Poljanac et al.* [2017]
Cyprus	95	81	13	*Papadopoulos and Charalambous* [2016]
Denmark	488	449	103	*Nielsen et al.* [2017]
Estonia	184	134	182	*Kohv et al*. [2017]
Finland	29	29	19	*IIR Finland* [2017]
France	163	39	34	*Ringuet* [2017]
Latvia	60	70	68	*Skrebele at al*. [2017]
Poland	67	69	68	*Dębski et al*. [2017]
Sweden	23	37	70	*IIR Sweden* [2017]
United Kingdom	29	-30 to >50	-30 to 50	*Wakeling et al*. [2017]

Quality of Pb and Cd monitoring data is regularly evaluated via laboratory intercomparison tests. According to the most recent results, related to measurements in 2016, almost all laboratories managed to predict theoretical values of Cd and Pb concentrations in precipitation with satisfactory accuracy (within ±25%) [*CCC,* 2018]. However, these tests characterize only uncertainty of analytical methods applied in country's laboratories. Uncertainties arisen at other steps of monitoring (e.g.,

sampling, transportation, storing etc.) are not taken into account. Therefore, full uncertainty is most likely higher than the uncertainty estimated via considered tests.

This fact is indirectly confirmed when real measurement data are analyzed. Almost at every station there are some samples which values are flagged as 'invalid'. These samples are not included in the process of comparison of modelled and measured values. If more than half of samples have flag 'invalid', annual mean values are not considered in the comparison procedure. For example, measurements of heavy metals in precipitation at Portugal stations, and Cd in precipitation at French stations in 2016 are not used because of this reason. Besides, concentrations of Pb and Cd in air measured at Estonian station EE9 are ignored because their annual mean values are several times higher than the values in the previous year.

Modelled air concentrations and wet deposition of Pb in 2016 were somewhat higher than the corresponding observed levels. For concentrations in air mean relative bias is 23%, and for wet deposition – almost 8% (Table. A.2). At most of the stations the bias between modelled and observed annual mean concentrations in air is within ±30% (Fig. A1a). Good agreement is noted for wet deposition fluxes in the United Kingdom, most of stations in Germany, the Czech Republic, France (Fig. A1b). At some of the stations (DK12, SE5, NO90, ES17) the overestimation of the observed air concentrations by the model may be linked with overestimated contribution of wind re-suspension. Overestimation of wet deposition fluxes due to the same reason is noted for some stations in Germany, Slovenia, and Poland. Nevertheless, at most of the stations, e.g. in Germany, the United Kingdom, France, the Czech Republic, the usage of re-suspension favoured improvement of agreement between modelled and observed values. Therefore, further work on improvement of parameterization of this process can facilitate better modelling results for the EMEP countries. At some stations (e.g., DE3 for concentrations in air, PL5, SK4 and SK7 for wet deposition) even the anthropogenic component of the modelled value considerably exceeds the observed value. It can be explained by the uncertainties of the emissions in the vicinity of these stations. Hence, further work on the emission data is needed. There are countries (e.g., Slovakia, the Netherlands) where good agreement for wet deposition for some stations is accompanied by large discrepancies for other stations. This situation results in relatively low correlation between annual wet deposition fluxes (0.47) compared to that for concentrations in air (0.88).

Table A2. *Main statistical indicators of agreement between annual modelled and measured levels of air concentrations and wet deposition fluxes in 2016*

	Pb		Cd		Hg	
	C_{air}	Wet Dep	C_{air}	Wet Dep	C_{air}	Wet Dep
Mean relative bias, %	23.1	7.8	31	-45	6	68.2
Correlation coefficient	0.88	0.47	0.79	0.55	-0.74	0.73
NRMSE	0.44	0.64	0.73	0.48	0.10	0.95
F2, %	78	70	78	64	100	76
F3, %	90	91	88	81	100	94
N	40	43	40	36	8	17

C_{air} – concentration in air
Wet Dep – wet deposition flux
NRMSE – Normalized Root Mean Square Error
F2 – fraction of values fitting to factor of 2 difference
F3 – fraction of values fitting to factor of 3 difference
N – number of model-observation pairs

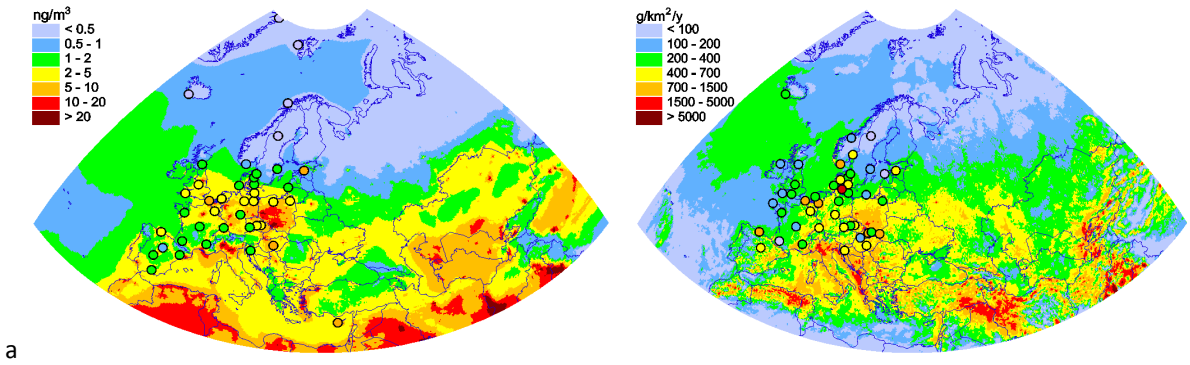


Fig. A1. *Spatial distribution of modelled and observed Pb concentrations in air (a) and wet deposition fluxes (b) in 2016*

Model performance for Cd in air is similar to that of Pb. There are some overestimation (about 30%) of mean observed values by the model and significant (0.79) spatial correlation between modelled and measured air concentrations (Table A.2). At most of stations the difference between modelled and observed concentrations in air is within a factor of two (Fig. A.2a). At some stations (e.g., BE14, NL8, GB17) high contribution of wind re-suspension produces the overestimation of the observed Cd concentrations in air. Similar to Pb, anthropogenic component of Cd concentrations in air at station DK12 and DE3 is higher than the observed concentration. Most likely it can be connected with uncertainties of anthropogenic emissions in the vicinity of these stations. Modelled wet deposition fluxes of Cd are lower than the observed ones by 45% on average. Large (2-fold and more) deviations of modelled values from observed ones can be explained by uncertainties of national emission data or monitoring issues. Understanding of the reasons requires further investigation. Satisfactory agreement between modelled and observed annual wet deposition fluxes is noted for stations in the United Kingdom, most of stations in Germany, some stations in Poland, Sweden, Slovakia and the Netherlands (Fig. A.2b).

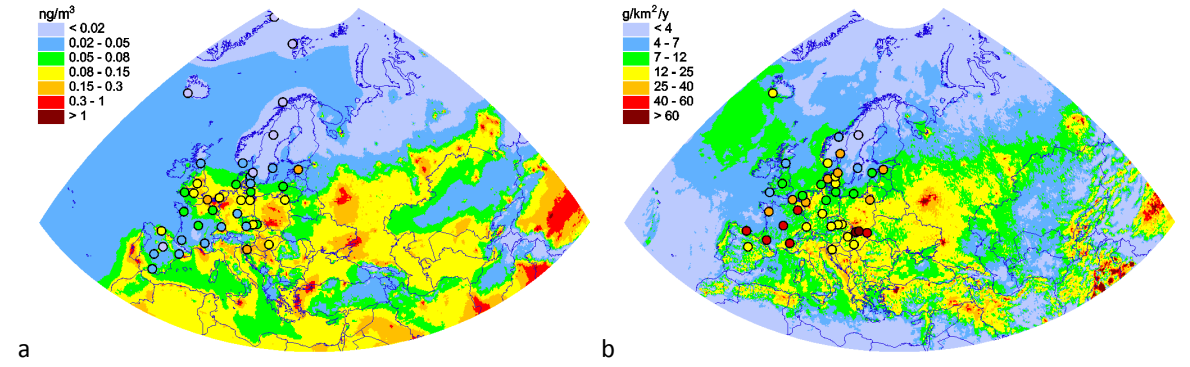
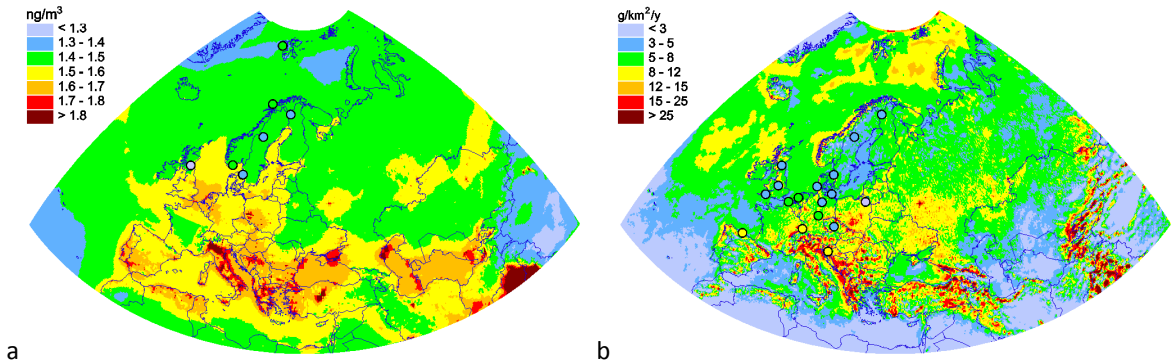


Fig. A.2. *Spatial distribution of modelled and observed Cd concentrations in air (a) and wet deposition fluxes (b) in 2016*

Mercury concentrations in air are distributed relatively smoothly over the EMEP region. Therefore, both modelled and measured values are within the range 1.3-1.6 ng/m^3 (Fig. A.3a). The difference between calculated and observed concentrations does not exceed ±15%. Taken into account low variability of Hg concentrations and low number of stations, negative spatial correlation between

modelled and observed values is not representative for characterizing the model performance. The model overestimates wet deposition fluxes of Hg by 68% on average. Significant uncertainties affecting modelling of Hg concentrations and deposition are connected with poor information about Hg speciation of anthropogenic emissions. Mercury is emitted as relatively inert and long-lived elemental form as well as in short-lived gaseous reactive and particulate Hg forms. Information about fractions of these three forms is not available in the official emission data. This information is derived from the expert estimates. Another source of uncertainties is atmospheric chemistry of Hg. Elemental form of Hg is oxidized and converted to reactive gaseous or particulate form, but rates and products of this process are not well established yet. In spite of general overestimation of the observed levels, at many stations (e.g. BE14, DE2, DE9, ES8, NL91, GB17, GB48) the agreement between modelled and observed values is within ±50% (Fig. A.3b).



a b

Fig. A.3. *Spatial distribution of modelled and observed Hg concentrations in air (a) and wet deposition fluxes (b) in 2016*

Discrepancies between modelled and observed concentrations can be explained by various reasons including intrinsic uncertainties of model parameterizations, emission data and sometimes quality of measurements. Transition to the finer spatial resolution resulted to higher detalization of pollution level patterns in the EMEP countries. At the same time, it is in line with the outcome of country-specific studies stating that improvement of the model performance due to refinement of the grid can be achieved if quality of input data is also improved. The performed comparison demonstrated that further work is needed on anthropogenic and secondary emissions in the EMEP region.