Atmospheric deposition of Copper on the Baltic Sea

HELCOM Baltic Sea Environment Fact Sheet (BSEFS), 2021

Authors: Ilia Ilyin, Olga Rozovskaya, Victor Shatalov, Alexey Gusev, EMEP MSC-E

Key message

Levels of annual total atmospheric deposition of copper to the Baltic Sea have decreased in period from 1990 to 2019 by 42%, although the decrease was higher in the earlier part (1990-1996) of the assessment period.

Results and Assessment

Relevance of the BSEFS for describing developments in the environment

This BSEFS shows the levels and trends in copper atmospheric deposition to the Baltic Sea. The deposition of copper represents the pressure of the emission sources on the Baltic Sea aquatic environment as described in the BSEFS "Atmospheric emissions of copper in the Baltic Sea region".

Policy relevance and policy reference

The updated Baltic Sea Action Plan states the ecological objectives that concentrations of hazardous substances in the environment are to be close to background values for naturally occurring substances. HELCOM Recommendation 31E/1 identifies the list of regional priority substances for the Baltic Sea.

Copper is essential trace element for biological systems. However, excess of copper can cause harmful effects for humans [*Gautam et al.*, 2014]. Copper is also toxic for aquatic organisms even at low concentrations and for soil microorganisms [*Gautam et al.*, 2014, *Flemming and Trevor*, 1989]. European Chemical Agency classified copper as toxic to aquatic life with long lasting effects. Therefore, although this substance is not presented in the HELCOM list of priority hazardous substances, copper satisfies, at least, some of the criteria for selection and priority setting of substances.

Protocol on Heavy Metals of CLRTAP does not include copper as priority metal. Nevertheless, parties to the CLRTAP regularly report cooper emission data. Besides, copper concentrations in air and in precipitation are regularly measured at the EMEP stations. Finally, EC directive on industrial emissions 2010/75/EU sets limits on emission of copper and its compounds to air and water from industrial installations.

Assessment

Model assessment of copper long-range transport and deposition within the Baltic Sea region in period 1990-2019 was carried out taking into account anthropogenic emissions officially reported by HELCOM and other EMEP countries. In addition, natural and secondary emissions due to wind re-suspension of particle-bound copper from terrestrial and seawater compartments were considered. Though the uncertainties of officially reported copper emissions are still high, model estimates of regional scale copper pollution levels show, in general, reasonable agreement with observed concentrations and deposition fluxes. Better results in terms of the consistency with available measurements were obtained for the last decade of considered period, while for the earlier years more significant discrepancies are noted.

Model simulations indicate that atmospheric input of copper to the Baltic Sea declined by 42% in the period from 1990 to 2019 (Figure 1, Table 1). The most substantial decline of copper deposition took place in the Bothnian Bay sub-basin (-74%) followed by the Archipelago Sea (-68%) and the Bothnian Sea (-53%) sub-basins (Figure 2). The lowest decline is noted for the Western Baltic (-18%) and the Sound (-24%) sub-basins. The decline of Cu deposition to the Baltic Sea over considered period was non-uniform. The period was split in two parts, and deposition trend in each part was analysed using Mann-Kendall test [*Gilbert*, 1987; *Connor et al*, 2012]. In the period from 1990 to 1996, strong decline took place. Mean annual rate of deposition decline during this period was about 6.8 tonnes per year with confidence factor equal to 99.9%. The subsequent period from 1997 to 2019 is characterised by smaller mean annual decline rate of about 0.7 tonnes with confidence factor 99.7%. The values of the confidence factors indicates that the trends for the both parts of the assessment period are significant. Similar dynamics can be seen for most of the sub-basins. The exceptions are the Kattegat, Sound, and Western Baltic sub-basins, where the rate of deposition decline slightly increased after 2005.

Changes of total copper deposition to the Baltic Sea in the period 1990-2019 does not follow the changes of anthropogenic emissions of HELCOM countries. Temporal variations of total copper depositions are affected by changes of anthropogenic emissions of countries as well as changes of secondary emissions. It should be noted also that only fraction of copper, emitted by the sources of particular country, deposits to the Baltic Sea. This fraction depends on the location of the country and prevailing atmospheric transport pathways. In particular, the largest fraction of total national emissions, deposited to the Baltic Sea, is estimated for Denmark (about 30%) while the lowest one for Russia (about 0.5%). Model simulations indicate that deposition from anthropogenic sources to the Baltic Sea declined from 1990 to 2019 approximately by 25%. The most significant contribution to these changes were made by the decline of copper emissions of Finland (by 74%). More significant decrease of deposition is estimated for secondary emission sources (about 75s%). Thus, overall decline of copper depositions from both anthropogenic and secondary sources is amounted to 42%.

Spatial distributions of annual total deposition fluxes of copper in 1990 and 2019 within the Baltic Sea region are shown in Figure 3. Total deposition fluxes of copper vary significantly among the sub-basins. The highest spatially mean total deposition flux in 2019 among the Baltic Sea sub-basins is noted for the Sound sub-basin. This sub-basin has the lowest area and is characterized by significant land-based emission sources located nearby. The lowest flux is estimated for the Bothnian Bay sub-basin which is explained by its relatively large area and low levels of emissions in the surrounding areas.

The HELCOM Contracting Parties contributed 77% to total deposition of copper to the Baltic Sea in 2019 (Table 2). The largest contribution is made by Germany (23%) followed by Denmark (15%) and Poland (14%) (Figure 4). It is important to note that contributions of the Contracting Parties to deposition to particular sub-regions differ significantly. Reduction of atmospheric input of copper from anthropogenic sources to the Baltic Sea is a result of various activities including abatement measures, economic contraction, and industrial restructuring, which took place in the HELCOM countries as well as other EMEP countries.

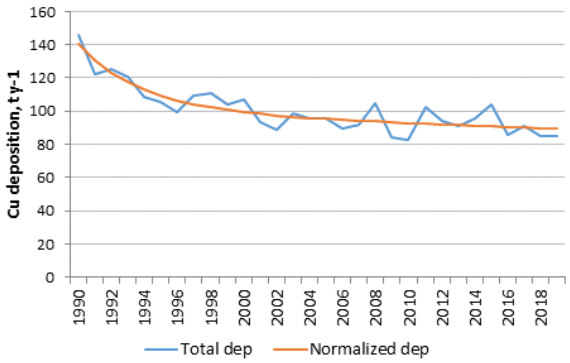


Figure 1. Changes of modelled (blue line) and normalized (red line) total annual atmospheric deposition of copper to the Baltic Sea for the period 1990-2019, (t y^{-1}). Normalized depositions were obtained using the methodology described below in the metadata section 5.

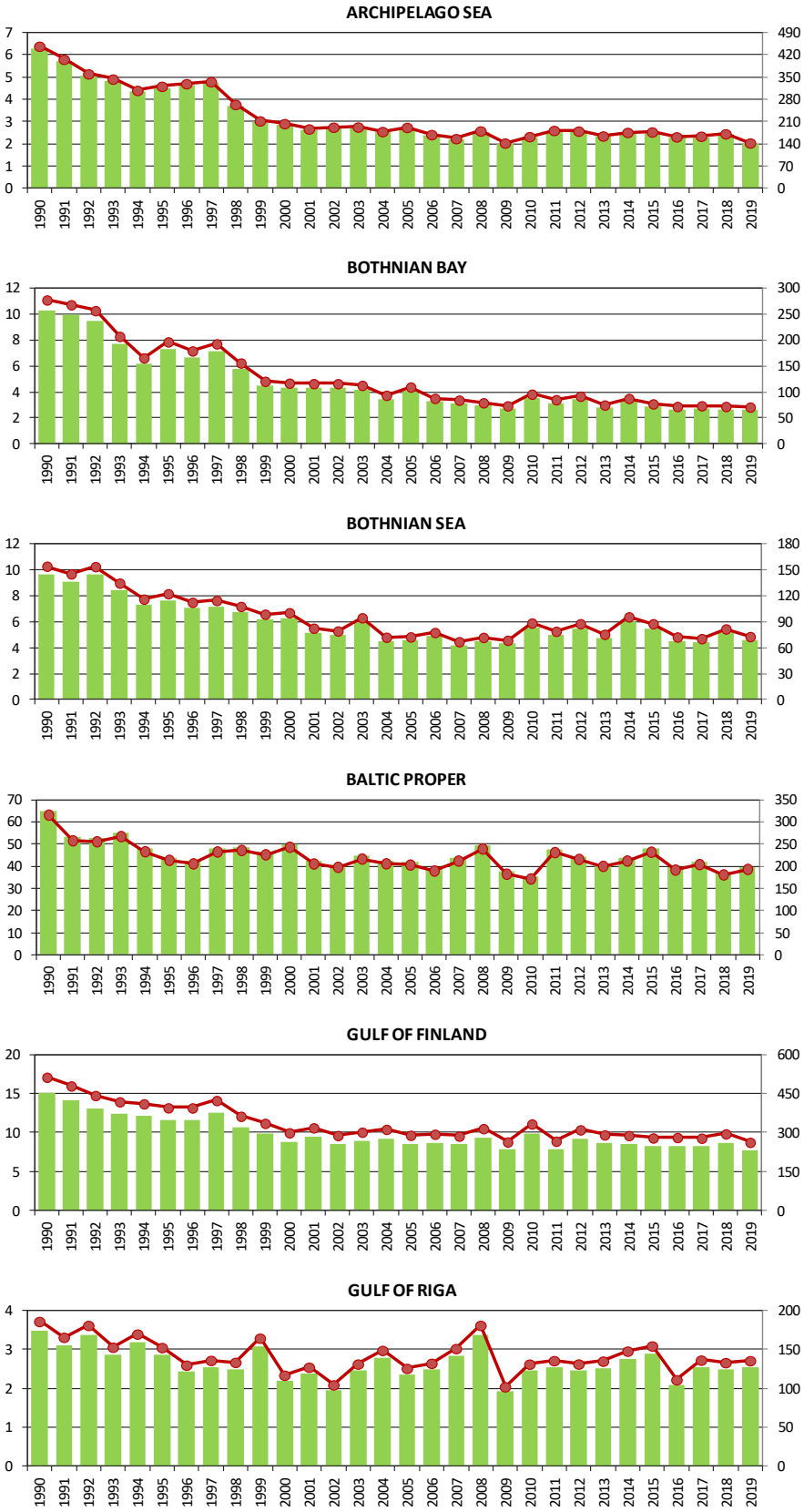


Figure 2. Time-series of computed total annual atmospheric deposition of copper to nine sub-basins of the Baltic Sea for the period 1990-2019 in t y^{-1} as green bars (left axis) and total deposition fluxes in g km^{-2} y^{-1} as red lines (right axis).

Figure 2 (continued). Time-series of computed total annual atmospheric deposition of copper to nine sub-basins of the Baltic Sea for the period 1990-2019 in t y^{-1} as green bars (left axis) and total deposition fluxes in g km^{-2} y^{-1} as red lines (right axis).

a) b)

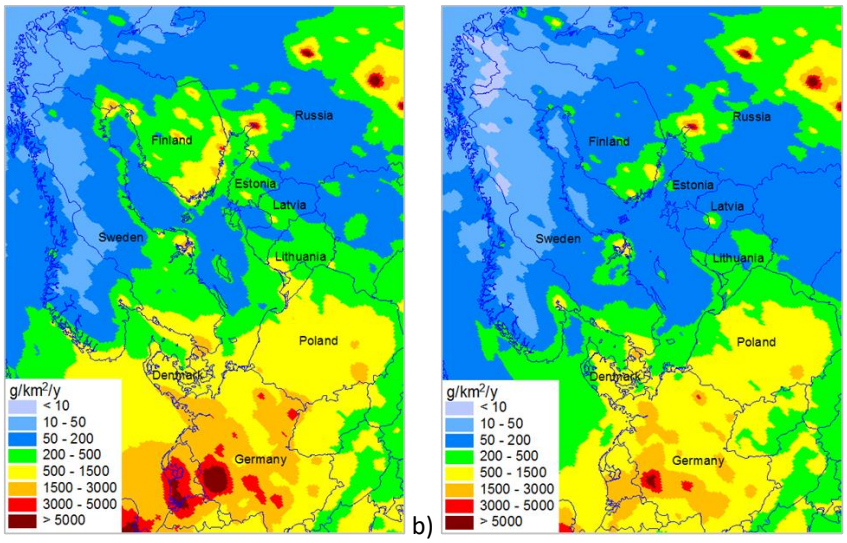


Figure 3. Spatial distribution of modelled annual total copper deposition fluxes in the Baltic Sea region for 1990 (a) and 2019 (b), g km^{-2} y^{-1}.

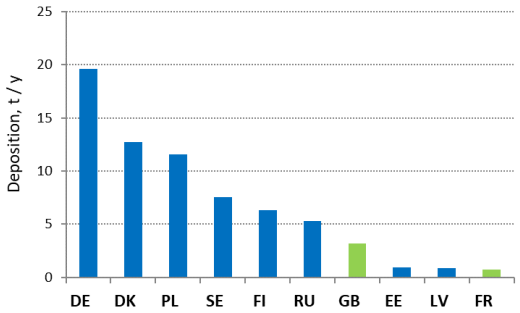


Figure 4. Ten countries with the highest contribution to annual total deposition of Cu to the Baltic Sea estimated for 2019, t y^{-1}. Green bars indicate non-HELCOM countries.

Data

Numerical data on computed copper depositions to the Baltic Sea are given in the following tables.

Table 1. Computed total annual deposition of copper to nine Baltic Sea sub-basins, the whole Baltic Sea (BAS) and normalized deposition* to the Baltic Sea (Norm) for the period 1990-2019. Units: t y^{-1}.

	ARC	BOB	BOS	BAP	GUF	GUR	KAT	SOU	WEB	BAS	Norm
1990	6.3	10.3	9.7	65.0	15.1	3.5	16.3	4.6	15.0	145.7	140.2
1991	5.7	9.9	9.1	53.1	14.1	3.1	11.7	4.1	11.7	122.5	130.7
1992	5.1	9.5	9.6	52.6	13.0	3.4	14.8	4.4	13.1	125.5	123.3
1993	4.8	7.7	8.4	55.0	12.3	2.9	13.0	4.0	12.6	120.7	117.5
1994	4.3	6.1	7.3	48.0	12.1	3.2	11.6	3.5	12.4	108.5	112.9
1995	4.5	7.3	7.7	44.0	11.6	2.9	11.4	3.7	12.4	105.4	109.3
1996	4.6	6.6	7.0	42.3	11.6	2.4	9.5	3.4	12.1	99.7	106.4
1997	4.7	7.1	7.2	47.9	12.5	2.5	11.8	4.1	11.7	109.4	104.1
1998	3.7	5.8	6.7	48.6	10.7	2.5	12.9	4.4	15.5	110.8	102.2
1999	3.0	4.5	6.2	46.6	9.9	3.1	13.5	4.2	13.3	104.2	100.6
2000	2.9	4.3	6.3	50.1	8.8	2.2	13.5	4.4	14.5	107.0	99.4
2001	2.6	4.3	5.2	42.3	9.4	2.4	10.9	4.2	12.2	93.4	98.3
2002	2.7	4.3	5.0	40.7	8.5	2.0	10.1	3.4	12.0	88.6	97.4
2003	2.7	4.2	5.9	44.6	8.9	2.5	13.0	4.0	12.8	98.6	96.6
2004	2.5	3.5	4.5	42.4	9.2	2.8	12.7	4.7	13.2	95.5	95.9
2005	2.7	4.1	4.5	41.8	8.5	2.4	12.9	4.4	14.3	95.6	95.3
2006	2.4	3.2	4.9	39.0	8.7	2.5	11.5	4.1	13.0	89.2	94.8
2007	2.2	3.1	4.2	43.6	8.4	2.8	10.3	4.2	12.5	91.5	94.2
2008	2.5	2.9	4.5	49.2	9.3	3.4	13.7	4.7	14.6	104.9	93.8
2009	2.0	2.7	4.3	37.5	7.8	1.9	11.9	3.9	12.4	84.4	93.3
2010	2.3	3.5	5.5	35.3	9.8	2.5	8.9	3.5	11.5	82.9	92.9
2011	2.6	3.2	4.9	47.6	7.9	2.5	13.6	4.4	16.1	102.7	92.5
2012	2.5	3.4	5.5	44.4	9.2	2.5	11.2	3.7	11.5	93.9	92.1
2013	2.3	2.8	4.7	41.2	8.6	2.5	11.8	4.0	12.9	90.8	91.7
2014	2.5	3.2	6.0	43.7	8.5	2.8	12.1	3.6	13.3	95.6	91.3
2015	2.5	2.9	5.5	47.8	8.2	2.9	15.1	4.2	15.0	104.1	90.9
2016	2.3	2.7	4.5	39.5	8.3	2.1	10.3	3.9	12.5	85.9	90.6
2017	2.3	2.7	4.4	42.0	8.2	2.5	11.9	4.0	13.0	91.1	90.2
2018	2.4	2.7	5.1	37.2	8.7	2.5	10.9	3.2	11.9	84.6	89.9
2019	2.0	2.6	4.6	39.8	7.7	2.5	10.1	3.5	12.3	85.1	89.5

* - normalized depositions were obtained using the methodology described below in the metadata section 5.

Table 2. Computed contributions by country to annual total deposition of copper to nine Baltic Sea sub-basins for the year 2019. Units: t y^{-1}. HELCOM: contribution of anthropogenic sources of HELCOM countries; EMEP: contribution of anthropogenic sources in other EMEP countries; Other: contributions of sources other than primary anthropogenic emissions (natural, secondary (re-suspension), and non-EMEP sources).

Country	ARC	BOB	BOS	BAP	GUF	GUR	KAT	SOU	WEB	BAS
DK	3.38E-02	1.04E-02	6.11E-02	2.68E+00	2.35E-02	5.52E-02	4.04E+00	2.23E+00	3.58E+00	1.27E+01
EE	2.38E-02	8.44E-03	2.64E-02	1.28E-01	5.78E-01	1.54E-01	1.26E-03	2.18E-04	1.43E-03	9.21E-01
FI	7.93E-01	1.45E+00	9.37E-01	3.80E-01	2.65E+00	9.05E-02	6.64E-03	1.53E-03	5.71E-03	6.32E+00
DE	1.81E-01	4.34E-02	2.70E-01	1.05E+01	2.42E-01	3.94E-01	1.88E+00	3.57E-01	5.77E+00	1.96E+01
LV	2.17E-02	5.59E-03	2.71E-02	1.90E-01	3.32E-02	5.59E-01	1.37E-03	2.50E-04	1.68E-03	8.40E-01
LT	1.20E-02	6.42E-03	2.17E-02	3.49E-01	1.74E-02	6.49E-02	3.86E-03	5.09E-04	2.35E-03	4.78E-01
PL	1.33E-01	6.76E-02	2.27E-01	9.59E+00	1.68E-01	3.99E-01	4.70E-01	6.60E-02	4.47E-01	1.16E+01
RU	8.18E-02	1.34E-01	4.58E-01	1.26E+00	3.22E+00	9.38E-02	3.20E-02	3.79E-03	2.40E-02	5.31E+00
SE	3.24E-01	5.63E-01	1.38E+00	4.16E+00	1.14E-01	1.13E-01	6.66E-01	1.70E-01	6.38E-02	7.56E+00
AL	8.72E-06	7.96E-06	3.29E-05	9.56E-05	1.22E-05	1.11E-05	1.37E-05	2.37E-06	1.99E-05	2.05E-04
AM	9.55E-05	3.03E-04	4.77E-04	1.31E-03	4.19E-04	1.91E-04	3.92E-05	3.60E-06	6.00E-05	2.90E-03
AT	4.67E-03	7.76E-03	1.44E-02	3.22E-01	1.47E-02	2.63E-02	3.86E-02	5.25E-03	4.39E-02	4.77E-01
AZ	6.67E-07	1.10E-06	1.50E-06	5.68E-06	2.30E-06	6.78E-07	8.84E-08	9.08E-09	1.32E-07	1.22E-05
BA	1.82E-03	1.65E-03	7.83E-03	3.40E-02	2.11E-03	2.92E-03	3.34E-03	4.63E-04	4.07E-03	5.82E-02
BE	9.73E-03	1.63E-03	1.69E-02	1.99E-01	1.12E-02	1.49E-02	8.02E-02	1.08E-02	7.65E-02	4.21E-01
BG	7.42E-04	9.62E-04	2.28E-03	1.43E-02	2.13E-03	1.51E-03	3.82E-03	1.54E-04	2.40E-03	2.83E-02
BY	2.48E-03	2.13E-03	7.25E-03	4.37E-02	6.79E-03	6.91E-03	1.58E-03	1.67E-04	7.32E-04	7.18E-02
CH	1.69E-03	1.71E-03	4.12E-03	9.21E-02	6.93E-03	4.49E-03	1.72E-02	2.21E-03	2.09E-02	1.51E-01
CY	6.75E-07	1.27E-06	1.71E-06	2.46E-05	5.37E-06	1.45E-06	2.00E-06	1.91E-07	4.79E-06	4.20E-05
CZ	6.25E-03	4.78E-03	1.03E-02	4.64E-01	1.05E-02	2.16E-02	5.12E-02	6.21E-03	5.51E-02	6.30E-01
ES	2.90E-03	4.10E-03	5.27E-03	5.56E-02	6.40E-03	5.06E-03	1.15E-02	1.12E-03	7.02E-03	9.89E-02
FR	1.31E-02	9.56E-03	2.82E-02	3.81E-01	2.21E-02	1.85E-02	1.32E-01	1.54E-02	1.27E-01	7.47E-01
GB	6.36E-02	2.26E-02	2.06E-01	1.29E+00	8.51E-02	7.21E-02	9.42E-01	7.19E-02	4.48E-01	3.20E+00
GE	1.94E-06	5.40E-06	9.55E-06	2.77E-05	1.35E-05	5.74E-06	6.34E-07	6.34E-08	8.73E-07	6.54E-05
GR	3.77E-04	3.53E-04	1.21E-03	4.47E-03	5.84E-04	8.73E-04	2.16E-03	4.26E-05	1.46E-03	1.15E-02
HR	8.25E-04	8.88E-04	2.33E-03	2.62E-02	1.26E-03	2.63E-03	2.83E-03	3.68E-04	2.39E-03	3.97E-02
HU	2.38E-03	2.51E-03	8.34E-03	9.84E-02	4.10E-03	8.65E-03	9.60E-03	1.06E-03	1.14E-02	1.46E-01
IE	1.20E-03	2.88E-04	3.77E-03	9.53E-03	1.58E-03	8.28E-04	8.16E-03	4.78E-04	2.55E-03	2.84E-02
IS	2.11E-06	4.71E-06	7.11E-06	3.17E-05	2.16E-06	2.03E-06	2.91E-05	2.98E-06	1.43E-05	9.62E-05
IT	4.77E-03	5.38E-03	1.19E-02	2.09E-01	1.64E-02	1.65E-02	2.53E-02	2.78E-03	1.89E-02	3.11E-01
KY	4.87E-08	1.75E-06	9.48E-08	2.68E-07	3.00E-07	3.45E-08	4.44E-09	5.13E-10	3.28E-09	2.50E-06
KZ	2.04E-05	9.04E-05	4.36E-05	5.52E-04	6.62E-05	4.04E-05	2.06E-05	2.00E-06	2.75E-05	8.63E-04
LU	1.76E-04	6.90E-05	3.89E-04	7.20E-03	2.94E-04	4.41E-04	1.97E-03	3.32E-04	2.99E-03	1.39E-02
MC	1.96E-06	1.70E-06	3.48E-06	6.07E-05	5.60E-06	4.65E-06	8.52E-06	9.14E-07	6.16E-06	9.36E-05
MD	9.59E-05	6.86E-05	4.49E-04	1.66E-03	3.99E-04	3.27E-04	1.86E-04	1.67E-05	1.35E-04	3.33E-03
ME	7.90E-06	3.93E-06	3.32E-05	1.03E-04	8.93E-06	1.19E-05	1.07E-05	1.42E-06	1.11E-05	1.93E-04
MK	5.51E-05	3.33E-05	1.78E-04	6.40E-04	8.45E-05	9.57E-05	8.39E-05	8.46E-06	6.85E-05	1.25E-03
MT	5.80E-06	6.69E-06	1.96E-05	9.41E-05	3.80E-06	4.26E-06	4.25E-05	5.41E-06	3.01E-05	2.12E-04
NL	1.07E-02	1.97E-03	2.06E-02	2.90E-01	1.19E-02	1.43E-02	1.17E-01	1.64E-02	1.29E-01	6.13E-01
NO	1.66E-02	1.89E-02	5.22E-02	1.62E-01	9.82E-03	1.12E-02	6.62E-02	3.70E-03	1.54E-02	3.56E-01
PT	2.36E-04	1.57E-04	2.59E-04	4.72E-03	4.75E-04	4.07E-04	7.86E-04	1.00E-04	5.91E-04	7.73E-03
RO	2.88E-03	2.11E-03	1.10E-02	5.60E-02	9.24E-03	7.81E-03	7.29E-03	4.87E-04	6.48E-03	1.03E-01
RS	3.09E-03	2.49E-03	1.11E-02	4.96E-02	4.45E-03	5.04E-03	5.38E-03	6.07E-04	6.28E-03	8.81E-02
SI	4.27E-04	5.75E-04	1.21E-03	1.90E-02	9.54E-04	1.86E-03	2.32E-03	3.41E-04	1.86E-03	2.85E-02
SK	1.59E-03	2.32E-03	5.90E-03	9.01E-02	3.13E-03	6.69E-03	8.74E-03	1.18E-03	8.86E-03	1.29E-01
TJ	3.84E-08	3.46E-07	6.74E-08	2.14E-07	2.55E-07	3.00E-08	3.59E-09	4.30E-10	2.73E-09	9.57E-07
TM	1.39E-07	5.42E-07	2.93E-07	1.06E-06	5.80E-07	1.28E-07	2.23E-08	2.05E-09	3.54E-08	2.81E-06
TR	5.07E-04	1.01E-03	1.42E-03	1.45E-02	3.44E-03	1.55E-03	1.23E-03	8.44E-05	8.90E-04	2.46E-02
UA	9.09E-03	5.70E-03	3.03E-02	1.23E-01	2.90E-02	1.76E-02	7.59E-03	8.95E-04	7.01E-03	2.30E-01
UZ	8.75E-07	8.84E-06	1.50E-06	5.65E-06	4.69E-06	6.72E-07	1.02E-07	9.67E-09	1.37E-07	2.25E-05
Other	0.2	0.2	0.7	6.5	0.4	0.3	1.4	0.5	1.45	11.86
EMEP	0.16	0.10	0.47	4.07	0.27	0.27	1.55	0.14	1.00	8.03
HELCOM	1.60	2.29	3.41	29.21	7.05	1.92	7.11	2.83	9.89	65.32
Total	2.01	2.63	4.57	39.81	7.75	2.53	10.06	3.50	12.35	85.21

Metadata

Technical information

1. Source:

Meteorological Synthesizing Centre East (MSC-E) of EMEP.

2. Description of data:

Levels of atmospheric deposition of copper over the Baltic Sea for the period from 1990 to 2019 were obtained using the latest version of GLEMOS model developed at EMEP/MSC-E (http://en.msceast.org/index.php/j-stuff/glemos). The latest available official emission data for the HELCOM countries have been used in the model computations. Emissions of copper for each year of this period were officially reported by most of the HELCOM countries. These data are available from the EMEP Centre on Emission Inventories and Projections (CEIP) (http://www.ceip.at/). The information on copper emission data used for modelling is presented in the indicator report on the copper emission to the air.

3. Geographical coverage:

Atmospheric depositions of copper were estimated for the European region and surrounding areas covered by the EMEP modelling domain.

4. Temporal coverage:

Time-series of annual atmospheric deposition are available for the period 1990 – 2019.

5. Methodology and frequency of data collection:

Atmospheric input and source allocation budget of copper deposition to the Baltic Sea and its catchment area were computed using the latest version of GLEMOS model over the new EMEP domain (https://www.ceip.at/ms/ceip_home1/ceip_home/new_emep-grid/). Model estimates describe regional scale distribution of pollution levels and source-receptor relationships.

Global modelling framework GLEMOS is a multi-scale multi-pollutant simulation platform developed for operational and research applications within the EMEP programme [*Tarrason and Gusev, 2008; Travnikov et al.,* 2009*; Jonson and Travnikov*, 2010; *Travnikov and Jonson,* 2011]. The framework allows simulations of dispersion and cycling of different classes of pollutants (e.g. heavy metals and persistent organic pollutants) in the environment with a flexible choice of the simulation domain (from global to local scale) and spatial resolution. In the vertical the model domain covers the height up to 10 hPa (ca. 30 km). The current vertical structure consists of 20 irregular terrain-following sigma layers. Among them 10 layers cover the lowest 5 km of the troposphere and height of the lowest layer is about 75 m.

Anthropogenic national total emission data of copper have been derived from CEIP data bases. Gridding of Cu emission data was carried out by MSC-E assuming similarity of spatial distribution of Cu and PM2.5 sectoral emissions. Gridded data on PM2.5 emissions with spatial resolution 0.1x0.1

degree is provided by CEIP. Meteorological data used in the calculations for 1990-2019 were obtained using WRF meteorological data pre-processor [*Skamarock et al*., 2008] on the basis of meteorological re-analyses data (ERA-Interim) of European Centre for Medium-Range Weather Forecasts (ECMWF). Normalized deposition values for the period 1990-2019 were obtained on the basis of results of model simulations using bi-exponential approximation [*Colette et al.,* 2016].

Copper presents in the atmosphere being bound to aerosol particles. Therefore, atmospheric properties of Cu, such as wet scavenging, dry deposition velocity or potential to travel over long distances is governed by properties of the particles-carriers. Unlike Pb and Cd, background atmospheric levels of copper are characterized by bi-modal or even three-modal particle size distribution [*Allen et al*, 2001]. The first mode corresponds to particle size around 0.5 – 1 µm, and the second – abound 3 – 10 µm. Similar results were obtained by [*Đorđević et al*, 2014; *Birmili et al*, 2006; *Sulejmanović et al.*, 2014; *Samara and Voutsa*, 2005; *Lough et al*, 2005; *Wåhlin et al.*, 2006; *Pant and Harrison*, 2013 and references therein] for urban and traffic sites. Most likely, this size distribution is explained by contribution of different emission sources to Cu concentrations in air. From 40% to 60% of anthropogenic emissions in the HELCOM Contracting Parties is made by emission sector 'Road Transport'. The major part of this sector is presented by tyre and brake ware.

Atmospheric processes governing dispersion and deposition of Cu to the Baltic Sea are similar to that used in the GLEMOS modelling system for other particulate species such as Pb and Cd. Comparison of observed concentrations in air and precipitation of Cu reveals that washout ratio for Cu is much higher than that for Pb and Cd. Values of in-cloud and below-cloud coefficients used in the modelling are 9.0×10^{-3} s^{-1} and 3.0×10^{-3} s^{-1}, respectively. These values are significantly higher than those used for Cd and Pb modelling.

Unlike Pb and Cd, contribution of intercontinental transport of Cu was not taken into account. On one hand, global-scale gridded emission data for Cu are not available. On the other hand, analysis of modelling results for Cd demonstrated that the contribution of non-EMEP sources to deposition to the Baltic Sea is minor. Taking into account higher wet scavenging of Cu compared to Cd, it was supposed that the effect of intercontinental transport on Cu deposition to the Baltic Sea is minor.

Copper is naturally occurring element with mean content in the Earth's crust 60 ppm [*CRC*, 2008]. Therefore, some Cu can enter the atmosphere due to suspension of wind-blown dust. Parameterization of wind re-suspension of Cu from soil and seawater is similar to that applied for Pb and Cd [*Gusev et al.*, 2006*; Ilyin et al*., 2007]. Information on spatial distribution of background Cu concentrations in topsoil is based on the results of FOREGS project [*Salminen*, 2005]. Besides, enrichment of soil by anthropogenic inputs was assumed in order to take into account long-term accumulation of Cu from anthropogenic sources and to reach a better fit of the modelled concentrations and wet deposition with the EMEP measurement data.

In the current work secondary emissions of Cu from the territories of the HELCOM countries (except for Russia) and the Baltic Sea area were estimated at level of about 385 t in 1990 and about 90 t in 2019. The major part of the secondary emissions is assumed to be due to the re-suspension of urban street dust containing Cu. The decline of secondary emissions for the considered period is higher than the reduction of anthropogenic emissions in the Baltic region and is partly explained by the

reduction of anthropogenic emissions of Cu. This higher decline was assumed in order to reach better fit of modelled concentrations and deposition with observations of Cu in the considered period.

Modelling of atmospheric transport and deposition of Cu over the EMEP region over long period of time was performed by MSC-E first time. Previous experience of modelling of Cu pollution levels includes generation of boundary concentrations for regional-scale applications with the focus on area surrounding Italy [*Ilyin et al*, 2017].

Quality information

6. Strength and weakness:

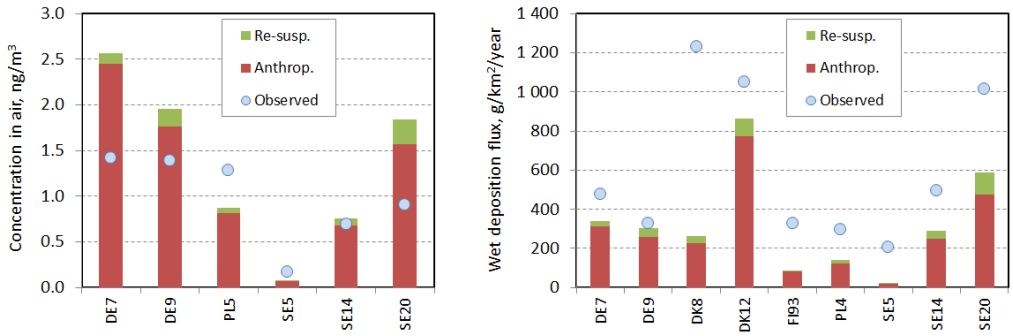
Strength: annually reported data on copper emissions to the atmosphere.

Weakness: uncertainties in the officially submitted copper emission data and estimates of secondary emissions.

7. Uncertainty:

Modelled copper concentrations in air and wet deposition fluxes simulated for the period from 1990 to 2019 were compared with the values observed at the HELCOM monitoring stations. In general, the model tends to somewhat underestimate (by 30% on average) the observed concentrations in air in the beginning of the considered period (1990 - 1999), and somewhat overestimate (by 30% on average) in the end of the period (2010-2019). At most of the stations the ratio of modelled and observed concentrations lies within a factor of 2.

For example, mean bias between modelled and observed concentrations in air for the HELCOM stations in 2019 makes up 37%, and for wet depositing flux it is about -50% (Figure 3).



a b

Figure 3. Modelled and measured concentrations in air (a) and wet deposition fluxes (b) at the HELCOM stations in 2019. Red bar depicts contribution of anthropogenic sources, and green bar – wind re-suspension.

The model performance for wet deposition differs for particular stations and years. In general, the agreement between the modelled and observed deposition fluxes in the end of the considered period is much better than that in the beginning of the period. For example, wet deposition fluxes observed at station DE9 (Zingst, Germany) from 1995 to 2008 exceed the modelled ones by a factor of 2 – 7, while in 2017 – 2019 the bias is less than 30% (Figure 4a). Other examples of reasonable agreement between modelled and observed deposition fluxes at the end of the considered period

are stations DK12 and SE11. For most of model-measurement pairs of annual fluxes the bias does not exceed ±30% (Figures 4b,c).

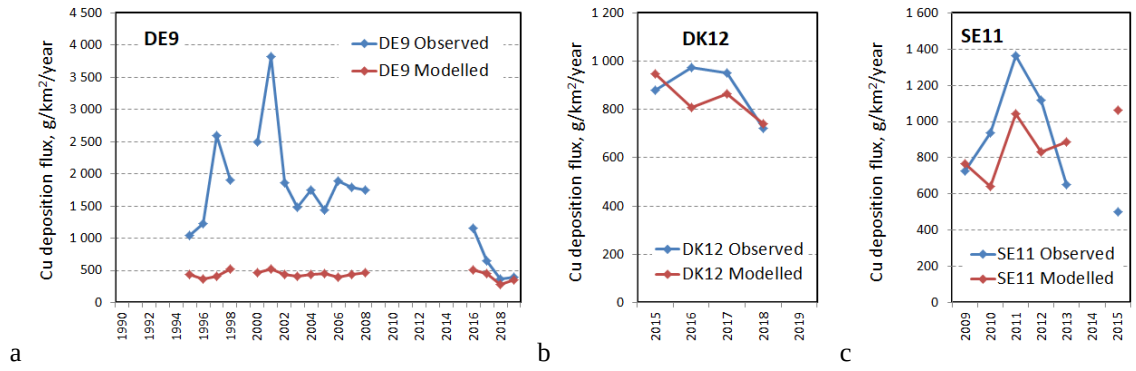


Figure 4. Time series of Cu wet deposition fluxes at stations DE9 (Zingst, Germany) (a), DK12 (Risoe, Denmark) (b) and SE11 (Vavihill, Sweden) (c).

Discrepancies between the modelled and observed values can be caused by a number of reasons. One of them is uncertainties of officially reported emission data. In addition to this, uncertainties of spatial distribution as well as distribution along the vertical also contributes to the emission-related uncertainties.

Another source of the discrepancies is uncertainties of the model parameterizations and input data. Most of parameterizations of physical processes used in GLEMOS were transferred from previous model MSCE-HM used in operational modelling under EMEP [*Travnikov and Ilyin*, 2005]. The MSCE-HM model has been verified in a number of intercomparison campaigns with other regional HM transport models [*Gusev et al.*, 2000; *Ryaboshapko et al.,* 2001, 2005] and has been qualified by means of sensitivity and uncertainty studies [*Travnikov*, 2000]. It was concluded that the results of heavy metal airborne transport modelling were in satisfactory agreement with the available measurements and the discrepancies did not exceed on average a factor of two [*UNEP*, 2010a,b]. The model was thoroughly reviewed at the workshop held in October, 2005 under supervision of the EMEP Task Force of Measurements and Modelling (TFMM). It was concluded that "MSC-E model is suitable for the evaluation of long-range transboundary transport and deposition of HMs in Europe" [*ECE/EB.AIR/GE.1/2006/4*].

Finally, the discrepancies can be contributed by the uncertainties of measurements. Regular laboratory intercomparisons are carried out annually by the supervision of CCC. In the majority of laboratories analyses of Cu satisfy data quality objectives [*CCC*, 2021]. However, it is important to mention that laboratory intercomparison provides only analytical component of the uncertainties of measurement data. Other sources of the uncertainties (sampling, storing, shipping etc.) remain unaccounted.

Presented modelling results demonstrate the first attempt to assess Cu pollution levels in the Baltic Sea region. Research of Cu atmospheric pollution has gained less attention comparing to the first priority heavy metals listed in the Århus Protocol on Heavy Metals (Pb, Cd, Hg). Nevertheless, analysis of model simulations results for copper shows comparable level of agreement with measurements as that obtained for some of the metals of first priority.

8. Further work required:

Further work is required to reduce uncertainties in HM modelling approaches applied in the GLEMOS model. It can be reached through joint efforts of measurement, emission and modelling communities.

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