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Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany – Sources, Transport, Deposition and potential Hazards

Summary

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Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany – Sources, Transport, Deposition and potential Hazards

Summary

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Summary

1 Background

Substances emitted from natural or technical sources into the atmosphere are deposited at Earth's surface in some distance to the sources, depending from their chemical and physical characteristics as well as from the meteorological conditions. This atmospheric deposition occurs as

- ▶ wet deposition (precipitation: rain out, wash out),
- ▶ dry deposition (sedimentation, gas diffusion) or
- ▶ occult deposition (interception of fog, clouds).

Substances deposited on the ground might impact ecosystems. By this, structures and functions of ecosystems can be modified if specific critical effect values or critical loads are exceeded. The assessment of ecotoxicological hazards of emissions includes the determination of effect values and loads as well as measurements of atmospheric deposition. The quantification of atmospheric deposition through – in best case complementarily by technical devices as for instance by bulk deposition or wet deposition samplers, by biomonitors such as mosses, leaves or needles or by numeric modelling – is difficult and, as holds true for other methods, associated with inherent uncertainties. This uncertainty is also significant for the assessment of ecological risks in terms of structural and functional ecosystem impacts. Long-term ecosystem change is to be expected in cases with exceedance of critical effect values and loads, the opposite may be assumed, if not. This also prevails for low exceedances of critical loads by atmospheric deposition of heavy metals since they are persistent and accumulate.

Minimising risks for mankind and his environment is the aim of national and international environmental law and politics.¹ Since 1979 the United Nations Economic Commission for Europe (UN-ECE) Convention on Long-range Transboundary Air Pollution (CLRTAP) has been seeking to limit, reduce and prevent air pollution including long-range transboundary air pollution. Under CLRTAP, the Aarhus Protocol, last amended in 2012, aims at reducing emission of cadmium (Cd), lead (Pb) and mercury (Hg). In this context the European Monitoring and Evaluation Programme (EMEP) collects emission data and measurements of air and precipitation quality from European countries to model atmospheric transport and deposition of air pollutants. The model results are validated against standardised wet deposition measurements at, depending from the respective element, around 70 sites across Europe. The EMEP model has so far produced data at a spatial resolution of 50 km by 50 km (Tørseth et al. 2012). LE (Bultjes et al. 2014; Schaap et al. 2008) calculates deposition values on a 25 km by 25 km grid covering Europe and on a 7 km by 7 km grid for Germany.

The measurements and modelling of atmospheric deposition by EMEP is added by the Working Group on Effects (WGE) encompassing several subsidiary bodies, among them: International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests), ICP Integrated Monitoring, ICP Waters, ICP Modelling and Mapping and The International Co-operative Programme on the Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation). In 2000, the ICP Vegetation extended its remit by taking over the coordination of the European Moss Survey (EMS) from the Nordic Council of Ministers. Since

¹ In Germany, the regulatory framework for atmospheric deposition comprises among others: the *Bundesimmissionsschutzgesetz* and the *Bundesimmissionsschutzverordnungen*, the *Technische Anleitung Luft*, the *Gesetz zum Schutz vor schädlichen Bodenveränderungen und zur Sanierung von Altlasten (Bundes-Bodenschutzgesetz)* as well as the *Bundes-Bodenschutz- und Altlastenverordnung*.

1990, EMS every 5 years has been providing data on concentrations of up to 40 metallic elements in moss, concentrations of nitrogen since 2005 and persistent organic pollutants since 2010. In Germany, during 1990-2005 moss was sampled at roughly 700-1000 sites. All over Europe, up to 7300 sites were sampled (Harmens et al. 2015). This monitoring data was used for evaluating the EMEP model and for mapping atmospheric deposition of heavy metals (HM) (Cd, Hg, Pb) and N at a spatial resolution of 5 km by 5 km (Schröder et al. 2011, 2012) which were included in this investigation together with the above mentioned data of HM accumulation in needles and leaves collected by ICP Forests and ESB.

Besides EMS, other biomonitoring programmes provide data on HM concentrations potentially correlated with atmospheric deposition of HM. The German Environmental Specimen Bank (ESB) is an archive for samples documenting environmental quality. The specimens are collected in 13 areas representing specific ecosystem types at regular time intervals. They allow monitoring changes in the concentration of various substances in specimens across time (Rüdel et al. 2009). In this investigation HM concentrations in leaves and needles collected at ESB sites were included. Respective data from 103 German Level 2 plots from the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) were considered. An overview of the ICP Forests monitoring design is given by Ferretti and Fischer (2013). Data on foliar chemistry collected at roughly 1900 sites of the nation-wide soil monitoring (Hilbrig et al. 2014) could not be included, yet, but are intended to be.

As in Europe, German, clean air policy is based on monitoring with bioindicators and technical deposition measurements as well as on modelling and mapping: Six sites are equipped with technical measurement devices, integrated into the EMEP and run by the German Environment Agency, are complemented by deposition networks of the 16 federal states of Germany. The data collected by these stations all together are used to validate deposition modelling for the territory of Germany and to enhance the spatial resolution of deposition maps (1 km by 1 km) compared to the EMEP deposition raster maps (50 km x 50 km). By this, a more specific characterisation of stress impacted by deposition (critical loads exceedances) should be enabled (Bultjes et al. 2011; Nagel et al. 2008, 2011). Thus, deposition monitoring and modelling in Germany serve the spatial specification of corresponding activities on the European scale and support precautionary national clean air policy.

2 Objectives

Main objectives of this research project are: spatial differentiation, ecosystem specific quantification and mapping of current atmospheric deposition of heavy metals in terrestrial ecosystems across Germany. To this end, a system enabling continuous up-dating should be established based on literature research, data analyses (exploration of data bases, GIS, modelling). This system should contain valid information on heavy metals deposition for modelling element budgets of ecosystems, effect assessments and the calculation of exceedances of critical loads of ecosystems. The research focus on three three groups of heavy metals, prioritised by intensity of investigation as follows:

- ▶ Group A: Cd, Hg, Pb.
- ▶ Group B: As, Cr, Cu, Ni, Zn.
- ▶ Group C: V, Mn, Sb, Ti Th, Co, Mo, Pt. Two of them are to be used for the impact assessment (Chapter 3, Part 2).

Additionally, following research should be conducted:

1. Identifying the share of long-range transport in current deposition (Chapter 2, Part 1).
2. Estimation of mercury deposition and sources for a hydrological catchment (case study) (Chapter 2, Part 1).
3. Comparing the heavy metals deposition with data derived by bioindication and other information (Chapter 2, Part 2).
4. Impact assessment, evaluation of applied critical (guidance, recommended, target, threshold) values, their topicality and comparison of respective risk assessments (Chapter 3, Part 2).

3 Quantifying atmospheric deposition of heavy metals

This study aims to establish the atmospheric deposition of heavy metals to terrestrial ecosystems in Germany. The metals cadmium, lead, mercury, arsenic, chromium, copper, nickel, zinc, vanadium, manganese, tin, titanium, thorium, cobalt, molybdenum and platinum were in focus. To quantify the atmospheric heavy metal input to ecosystems two methodologies have been used. For all metals a first order assessment will be made based on experimental data of air concentration and wet deposition. Four different station types (urban, rural, traffic and industrial) were considered. Through combination of air concentrations with effective dry deposition velocities, typical ranges for dry deposition fluxes were estimated for each land use class. These dry deposition estimates were combined with wet deposition data will to arrive at estimates for the total deposition. In the second methodology the chemical transport model LE was used to calculate deposition distributions across Germany for the metals vanadium, copper, nickel, zinc, arsenic, cadmium and lead. The modelling was based on either existing emission databases or the modeling of PM in combination with metal contents.

For the observations-based approach, first the availability of measurements was assessed. Dry deposition observations are not available, so to estimate the dry deposition estimate the air concentration observations were used. For air concentrations of As, Pb, Cd, and Ni over 100 measurement stations across Germany were available. However, for the other metals, recent measurements in Germany were scarce. Therefore, for some metals older data or measurements from countries near Germany were included in the assessment of air concentrations. Especially in formation on the size fractionation (i.e. which part of the metal particles are smaller than 2.5 μm) was scarce. After selecting the most appropriate data sources and averaging strategy, an estimate of the 'representative' air concentration of the 17 metals over Germany was made considering industrial, rural, urban and traffic locations separately. These concentrations were then multiplied by the land use dependent effective dry deposition velocity for fine and coarse particles from LE.

For wet deposition, measurements are available, although the quantity and geographical coverage over Germany was not in all cases sufficient to come to reliable results for the whole country. For, e.g., As, Cd and Pb measured in some federal states, the number of observations was skewed strongly. The observations of the Länder show a much higher range than those from UBA and are higher in general. The fluxes reported for stations in the federal states networks was about a factor of 10, whereas the fluxes at the UBA stations are typically within a factor 3 of each other. This can partly be due to the fact that the UBA stations are real background locations, whereas some Länder stations are located close to sources. There are large differences between the observation ranges at stations of different Länder, which indicates there might be inconsistencies between networks.

Adding the estimated dry and wet deposition based on observations gives the estimated total deposition. The lowest deposition is estimated for Cd with $40 \mu\text{g}/\text{m}^2/\text{year}$ on average. Deposition of As, V, Sb and Mo is estimated to be in the range of $100\text{-}250 \mu\text{g}/\text{m}^2/\text{year}$ for each metal. For Pb, Cr, Cu and Mn, the deposition estimates arrive at 1160, 350, 2300, 560 and $2190 \mu\text{g}/\text{m}^2/\text{year}$, respectively, while the highest deposition is estimated for Zn with $62000 \mu\text{g}/\text{m}^2/\text{year}$.

The results found in this work were compared to those of Knappe (2008), who used a comparable approach but different data sources. For all metals and land use classes, Knappe (2008) arrives at much higher deposition values. This is due to the much higher dry deposition estimate; for wet deposition, the numbers found by Knappe (2008) and this study agree quite well. The difference in dry deposition estimate is caused by large differences in both the air concentration estimates and the dry deposition velocity used, both of which are markedly higher in the work by Knappe (2008). This comparison highlights the large uncertainties associated with generalizing a limited amount of observation data to a whole country.

The second methodology to estimate deposition of heavy metals relies on the LE chemistry transport model. Since emission data are scarce and often uncertain, the results obtained via this approach are also associated with large uncertainty. For Pb and Cd, the most recent emission data and the largest amount of observations was available. Model validation for these metals shows that at rural and urban background stations, the modelled data are in general agreement with the observations outside the direct source areas. In the Ruhr area the modelled concentrations are higher than the observations and in Sachsen there is an indication that modelled concentrations underestimate the observed values.

The model exercise shows that wet deposition for all metals is largest in the Ruhr area, with some local hot spots in other areas as well. A comparison with wet deposition observation data shows that LE generally underestimates the observed concentrations by a large amount, and also underestimates the spatial variability. This is in large part due to uncertainties in the emission databases for the several heavy metals. Given the uncertainties in emissions as well as the scale at which the LE model operates, comparing model outcomes with observations at background locations is the most relevant approach; emission data and model resolution are not sufficiently detailed to model concentration and deposition accurately near local sources.

The quality of the modelled deposition fluxes highly relies on the available emission information. For all components the uncertainties in the emission values is estimated to be 100-200%. For some metals the model ready emission data have the reference year 2000. Hence, to significantly improve our understanding of heavy metal deposition an improvement of the emission information is highly needed.

4 Case Study: Mercury

Mercury is an element and is naturally occurring. Trace amounts of mercury are found in most plants, animals and soils. Almost all mercury compounds are toxic and can be dangerous at very low levels in both aquatic and terrestrial ecosystems. The atmosphere is the foremost transport pathway of Hg, whereas land and ocean processes play an important role in the redistribution of Hg in ecosystems. Once deposited to land or oceans, mercury can be converted by microorganisms to the extremely toxic methylmercury, and begins its rise in the food chain. This process of bioaccumulation, in living organisms, inflicting increasing levels of harm on higher order species such as predatory fish, birds and mammals is known as "biomagnification".

The temporal and spatial scales of Hg transport in the atmosphere and its transfer to aquatic and terrestrial ecosystems depend primarily on its chemical and physical forms. Following emission,

gaseous elemental mercury (GEM) can be transported long distances before oxidation and removal by particle and gas-phase dry deposition or scavenging by precipitation. The atmospheric residence time of GEM is several months to a year. Mercury can therefore be transported and deposited to remote locations such as the Arctic and Antarctic. Gaseous oxidized mercury (GOM) and particulate bound mercury (PBM) have a shorter atmospheric residence time than GEM ranging from hours to days, and as a result are generally deposited locally or regionally.

Sources of Hg to the atmosphere can be from either primary natural and anthropogenic sources or can be due to reemission of deposited Hg (secondary emission). Overall, total global Hg emissions to the atmosphere range from 6500 to 8200 Mg yr⁻¹, of which 4600 to 5300 Mg yr⁻¹ are from natural processes and sources (primary geogenic plus secondary emissions). Primary anthropogenic sources release 1400–2900 Mg yr⁻¹ compared with primary natural (geogenic) inputs of 80–600 Mg yr⁻¹. Hence, roughly one-third of the mercury emissions to the atmosphere are of primary anthropogenic nature. Globally, energy production is the largest source for mercury, followed by gold mining activities, non-ferrous metal production and cement production. Other sources include combustion of waste and cremations. With an emission of 10 Mg Hg per year the German contribution to the global emission is about 0.5 % (relative to a central global estimate of 2000 Mg/yr). In the stack about 60 % of the Hg is present as elemental mercury and 40 % as reactive mercury (GOM+PBM). Hence, a large part of the emission occurs as a global pollutant. For the behaviour of reactive mercury a parallel with oxidized nitrogen, of which it is estimated that 30% of the German emission is deposited within the country, can be drawn. Applying this share to the reactive mercury emissions indicates that only about 15 % of the German emissions deposit on Germany territory.

There is considerable uncertainty regarding the atmospheric redox chemistry of mercury. Common understanding is that halogen atoms, most importantly bromine but also chlorine and iodine, are important oxidants for Hg(0) in the atmosphere. Hence, modelling the oxidation of mercury requires modelling the halogen cycles and sea salt. Many regional model systems for mercury, however, do not incorporate these processes, but rather prescribe the halogen concentrations. The aqueous oxidation of mercury by halogen compounds in the atmosphere is less well understood, as are the reactions that reduce oxidized mercury compounds. Slow reduction reactions of Hg(II) to Hg(0) are incorporated in current chemistry schemes. However, there is appearing evidence for rapid Hg(II) reduction taking place in power plant plumes. Atmospheric observations in plumes and in polluted regions show much lower reactive to elemental concentration ratios than inferred from emission inventories, which could be explained by a fast reduction of reactive to elemental mercury. In case in-plume reduction is important, the nature of mercury pollution would be increasingly global, with much lower gradients between source regions and natural areas than previously assumed.

The removal from the atmosphere is mostly governed by the solubility of the different mercury forms. Wet deposition by rain provides an efficient sink for GOM as the components are very soluble in water. In addition, rain out is the primary loss process for particle bound mercury. Elemental mercury is not soluble and therefore does not rain out. For dry deposition it is often assumed that GOM and PBM act as nitric acid and fine aerosol, respectively. For Germany typical dry deposition velocities are about 1.6 cm/s and 0.16 cm/s for forest, respectively. Estimated annual v_d for GEM mostly range between 0.05–0.08 cm s⁻¹ over vegetated surfaces and below 0.05 cm s⁻¹ over urban areas, which is generally 20–30 times smaller than those of GOM, and 2–6 times smaller than PBM.

Background atmospheric concentrations of elemental mercury typically range from 1.3 to 1.7 ng m⁻³ in the Northern Hemisphere, whereas concentration levels are about 30% less in the

southern hemisphere. Measured GEM concentrations in Germany are at the higher end of the northern hemispheric range. GOM+PBM concentrations are typically a factor 100-200 lower than GEM. For background conditions we provide a dry deposition estimate based on measurement at Waldhof of almost $1 \mu\text{g}/\text{m}^2/\text{a}$ combined with a typical wet deposition flux for Germany of $10 \mu\text{g}/\text{m}^2/\text{a}$ resulting in an estimate of nearly $11 \mu\text{g}/\text{m}^2/\text{a}$. Assuming that reactive mercury in source areas may be 10 times higher than observed in Waldhof we arrive at typical values of 14 and $18 \mu\text{g}/\text{m}^2/\text{a}$ for grass and forests across Germany. Hence, only near sources the dry deposition process becomes important. Deposition of elemental mercury may be in the same order, but is assumed to partly be re-emitted.

Atmospheric deposition is a significant source of mercury in a catchment area. As a case study the regional deposition of two power plants in Bavaria was discussed with indicative calculations using the LE model and a local dispersion model. The dispersion model indicates that within the first ten kilometers from a large power plant an annual mean concentration can be up to $90 \text{pg}/\text{m}^3$, up to 10 times higher than the background measured at Waldhof. Atmospheric surface concentrations of reactive Mercury induced by the plants are on average 1.1 and $0.35 \text{pg}/\text{m}^3$ in the Isar and Salzach catchment areas. These are in the order of 10% and 2% of the surface concentration on average, which hints at similar contributions to the dry and wet deposition. Modelled total deposition from the two plants arrives at about $1.1 \text{ug}/\text{m}^2/\text{yr}$ and $0.5 \text{ug}/\text{m}^2/\text{yr}$ for Isar and Salzach, respectively. These estimates are in the order of 7 and 3 % above the background values, respectively.

These results were compared to the MoRE model input which is derived from the EMEP model. The EMEP model provides an input of $174 \text{kg}/\text{a}$ for the catchment of the Isar and $130 \text{kg}/\text{a}$ for the Salzach catchment. The central estimation for background conditions as derived based on data at Waldhof fits very well to the depositions used within the MoRE modelling. The central value of $16 \text{ug}/\text{m}^2/\text{yr}$ or $0.16 \text{g}/\text{ha}/\text{yr}$ is surprisingly the central value in the mapped range used in MoRE. The spatial disaggregation of the EMEP model results on $50 \text{km} \times 50 \text{km}$ resolution occurred via topology. Inspecting the resulting deposition distribution within the catchments shows that the variability is rather low. Given the importance of the wet deposition we would expect that signal of the precipitation amounts should be clearly visible in the distributions. Hence, we would advise to update the spatial disaggregation by using high resolution rain fall data in contrast to topology.

5 Integrative data analysis

Background and aim. The exposure of ecosystems to atmospheric deposition can be accomplished by technical samplers, biomonitoring or modelling. Hence, as a general rule, complex phenomena such as deposition cannot be captured in total by use of only one method. However, using several methods complementarily enables to derive ranges and uncertainty of deposition values. Therefore, in this investigation scientific basics for an optimised complementary method should be developed. To this end, exposure data from different biomonitoring networks and results from two deposition models were compiled and evaluated. Based on this, eligible combinations of methods for collecting data on deposition of eight heavy metals are recommended.

Materials and methods. The integrative data analysis compares deposition data derived by two chemical transport models (CTM), i.e. the model of the European Monitoring and Evaluation Programme (EMEP) and the LE, as well as with concentrations in biological matrices derived from suitable biomonitoring programmes. The latter data comprise those collected from the European Moss Survey (EMS, Harmens et al. 2006), surface estimations derived from the EMS

data (Pesch et al. 2007), heavy metals concentrations in leaves and needles sampled for the German Environmental Specimens Bank (ESB) (UBA 2008) and in leaves, needles and organic surface soils collected within the ICP Forests Level II programme (ICP Forests 2010).

The integrative evaluation of the above mentioned data regards spatial patterns and temporal trends of heavy metals deposition and concentration, respectively. The comparison was based on statistical values calculated by descriptive statistics, inference statistics, correlation and regression analysis, and trend analysis. Thereby, the focus was on Cd and Pb (heavy metals group A) since only for these two metals deposition values from both CTM were available. Additionally, according to data availability, data on six further heavy metals were examined: As, Cr, Cu, Ni, V, and Zn. Special focus was laid on comparing spatial patterns and temporal trends of LE and EMEP modelling results on the strength of correlation between results of deposition modelling and whether their differences are specific for elements, specimens, age classes, ecosystem types or soil layers and implications for the quality of the CTMs and their amendment, respectively. Available data from biomonitoring programmes were evaluated with regard to the comparison of spatial patterns and temporal trends of heavy metals deposition and concentration, respectively. For enhancing of the complementary method, options for combined use of both CTMs and biomonitoring data were implemented and evaluated by use of Regression Kriging (Hengl et al. 2004; Odeh et al. 1995; Schröder et al. 2011).

Results. Correlation of LE and EMEP modelled HM deposition values differ considerably. The LE median of total Cd deposition (2007-2011: 25.70 $\mu\text{g}/\text{m}^2\text{a}$) is by 72 % lower than the median calculated for Germany using the EMEP model (2007-2011: 35.59 $\mu\text{g}/\text{m}^2\text{a}$). For Pb, LE median amounts to 604.62 $\mu\text{g}/\text{m}^2\text{a}$ (= 49 % of the EMEP median, 1245.08 $\mu\text{g}/\text{m}^2\text{a}$). The results of EMEP and LE differ significantly (Wilcoxon test, $\alpha = 0.05$). EMEP and LE results are significantly correlated with $r_s = 0.47$ (2007-2011, $p < 0.01$) and $r_s = 0.39$ (2005, $p < 0.01$) for Cd and with $r_s = 0.56$ (2007-2011, $p < 0.01$) and $r_s = 0.35$ (2005, $p < 0.01$) for Pb. Correlating the ratios spatial distributions of total atmospheric Cd and Pb deposition modelled by use of EMEP and LE indicates that the differences between the results are strongly correlated with the amount of EMEP values reveal a very strong statistical relation ($r_s > 0.9$). Differences between both EMEP and LE were primarily found in highly impacted regions as for instance in North Rhine-Westfalia. In the South of Bavaria LE deposition values exceed those modelled by EMEP (Cd: 45 % higher; Pb: 12 % higher), mainly due to relative high wet deposition rates compared to EMEP. LE deposition values (Cd, Pb, 2007-2011) which were based on emission data from 2005 and EMEP deposition values for these years do not show any significant temporal trends (Mann-Kendall-Test). This is in contrast to time spans of more than 10 years as proved for EMEP values (Cd: 1998-2011, $r_\tau = -0.54$, $p < 0.01$; Pb: 1998-2011, $r_\tau = -0.60$, $p < 0.01$). Such long-term data does only exist for EMEP but not for LE modelling.

With regard to land use-specific modelling, the most distinct differences between EMEP and LE results were calculated for coniferous forests, followed by those for deciduous forests and grassland. The differences between EMEP and LE are much more pronounced for Pb than for Cd. Regions with higher EMEP deposition values for grassland are located in Northwestern Germany. LE values exceeding EMEP values for grassland were identified in Southern Germany. For forests EMEP calculated values are much higher than those derived by LE, especially in Northern Germany. For Cd, the coefficients quantifying the correlation between EMEP and LE values are for coniferous forests $r_s = 0.7$, for deciduous forests $r_s = 0.44$ and for grassland $r_s = 0.22$. For Pb, correlations between EMEP and LE amount for coniferous forests by $r_s = 0.54$, for deciduous forests by $r_s = 0.37$ and grassland by $r_s = 0.26$. All correlations were significant at a level of $p < 0.01$. Thus, the spatial Cd and Pb deposition patterns mapped from the EMEP and LE data are most similar for coniferous forests. The median value of Cd deposition modelled for forests exceeds that for grassland by factor 3.2 (EMEP) and 1.4 (LE), respectively. The median Pb

deposition for forests as calculated by LE exceeds the LE grassland deposition value by factor 1.4 which is clearly lower than that derived from EMEP modelling (2.9). The latter value corresponds to empirical measurements of Cd and Pb concentrations in moss sampled beneath canopies and beyond forests conducted during 2012 and 2013 (Meyer 2016; Meyer et al. 2015).

Correlation of EMEP and LE modelled HM deposition values and respective HM concentrations measured in moss 2005 and spatially estimated for unsampled locations. The integrative analysis of LE deposition values (2005, 2007-2011) with geostatistical surface estimations of heavy metals concentrations in moss (EMS 2005, Germany) (see report 2, chapter 2.5) revealed higher statistical correlations as with heavy metals concentrations measured in moss (see report 2, chapter 2.4). Moderate correlations between LE modelling results and geostatistical estimates of moss concentrations were found for As ($r_s = 0.48$) and Pb ($r_s = 0.49$), weak correlations for Ni ($r_s = 0.34$), Cd ($r_s = 0.37$), Cu ($r_s = 0.26$) and V ($r_s = 0.31$) (significant with $p < 0.01$). In case of Pb the correlations of geostatistically estimated heavy metals concentrations in moss with LE values were higher than with those calculated by EMEP, for Cd lower with LE than with EMEP results. Highest correlations were computed for correlations of geostatistically estimated moss concentrations with the arithmetic mean of LE and EMEP values. The strength of correlations was found to depend from the amount of deposition: In regions with heavy metals concentrations in moss below the median, the correlations between geostatistically estimated and modelled values were stronger with LE. Where heavy metals concentrations in moss above the median, the correlations between geostatistically estimated and modelled values were stronger with EMEP. The correlations also proved to be specific for different deposition processes: In case of As, Cd, Cu, Pb, V and Zn they were higher for dry deposition (LE) than for wet deposition (LE). The comparison of the LE deposition normalised for 2005 with the geostatistically estimated heavy metals values in moss reveals that the core areas of highest values are spatially disparate and located in the Middle West (deposition) and the Middle East (As concentrations in moss) indicating a lack of emission data for deposition modelling. Such distinct spatial differences of patterns were also detected for biomonitoring estimations (hot spot in the Northwest) and deposition data (hot spots in the Middle West) for Cr and V (North Sea and Baltic Sea coast). The high Cr concentrations in moss detected in Northeastern Germany could not be verified by data from the European Pollutant Emission Register. Whether these patterns only hold true for 2005 or not should be investigated in the moss survey 2015. Testing of the temporal trend for Cd and Pb concentrations in moss proved the development of Pb concentrations as statistically significant (1991-2005, $n = 4$, $r_\tau = -1.00$, $p < 0.1$). The modelled atmospheric deposition (EMEP, 1998-2011) decreased accordingly.

Correlation of EMEP and LE modelled HM deposition values and respective HM concentrations in tree foliage (ICP Forests, ESB) and surface soil specimens (ICP Forests). The correlation of LE and EMEP modelling results with the heavy concentrations in leaves and needles collected for the German ESB revealed following significant coefficients for Cd and Pb (Germany, 2007-2011): Beech (Cd: $r_\tau = 0.29$; $p < 0.05$; Pb: $r_\tau = 0.44$; $p < 0.01$), poplar (Cd: $r_\tau = 0.36$; $p < 0.05$; Pb: $r_\tau = 0.63$; $p < 0.01$), spruce (Cd in nature near and forested ecosystems: $r_\tau = 0.49-0.64$; $p < 0.05$; Pb: $r_\tau = 0.29$; $p < 0.05$). For two out of five heavy metals belonging to group B significant correlations could be found: Cr in leaves of poplar ($r_\tau = 0.61$) and Zn in needles of spruce ($r_\tau = 0.44$) are correlated with respective LE deposition values ($p < 0.05$). Cd and Pb were found to correlate stronger with LE than with EMEP deposition values. The differences between these correlation coefficients could not be proved to be significant. Analysing the temporal trends of heavy metals concentrations in leaves and needles revealed clear and, according to Mann-Kendall-Test, significant trends for one year old needles of spruce (Cd: $r_\tau = -0.51$; Pb: $r_\tau = -0.87$; $p < 0.01$) and pine (Pb: $r_\tau = -0.80$; $p < 0.01$). For the respective specimens the correlations with EMEP deposition values and spruce amounted for Cd to $r_\tau = 0.42$ ($p < 0.05$) and Pb to $r_\tau = 0.67$ ($p < 0.01$) and pine for Pb to $r_\tau = 0.67$ ($p < 0.01$).

Regarding the heavy metals concentrations between land use specific LE deposition values and in leaves and needles sampled within ICP Forests (Cd, Cu, Pb, Zn) highest and most significant correlations were calculated for pine needles (Cd: $r_{\tau} = 0.38$; Cu: $r_{\tau} = 0.34$; Pb: $r_{\tau} = 0.44$; Zn: $r_{\tau} = 0.33$; alle $p < 0.01$). Correlations between land use specific EMEP deposition values and spruce needles (Cd: $r_{\tau} = 0.28$; Pb: $r_{\tau} = 0.34$; both $p < 0.01$) and leaves of beech (Cd: $r_{\tau} = 0.21$, $p < 0.05$; Pb: $r_{\tau} = 0.40$, $p < 0.01$) were somewhat lower. Quite different results were computed for pine and not land use specific deposition where the highest correlations were found for EMEP compared to LE. The age specific analysis corroborated, with the exception of Cd, in most cases higher correlations with LE and the two years old pine needles (Cu: $r_{\tau} = 0.49$; Pb: $r_{\tau} = 0.56$; Zn: $r_{\tau} = 0.35$; alle $p < 0.05$) and den two years old spruce needles (Pb: $r_{\tau} = 0.58$, $p < 0.01$). In case of Cd this year's concentrations in pine needles show highest correlations with deposition modelling results (z.B. LE: $r_{\tau} = 0.43$; $p < 0.01$). Differing from the results for specimens collected for the German ESB, the heavy metals concentrations collected in ICP Forests (Cd, Pb) show for all significant correlations higher correlations with EMEP values compared to those computed with LE. A comparison of temporal trends in EMEP and Level II (Cd, Pb) data was omitted since the latter do not show hardly any trends.

The correlations between heavy metals concentrations in four organic surface soil layers sampled within ICP Forests Level II (Cd, Cu, Cr, Ni, Pb, Zn; OL, OF, OFH, OH) and respective LE deposition values were found to be significant in 58 % of the investigated 24 cases (Cd: $r_{\tau} = 0.31$; Cr: $r_{\tau} = 0.26-0.29$; Cu: $r_{\tau} = 0.32-0.44$; Pb: $r_{\tau} = 0.21-0.38$; Zn: $r_{\tau} = 0.28-0.39$; alle $p < 0.01$). Correlations of Cd and Pb concentrations in organic soil layers were stronger with EMEP than with LE deposition values and statistclally significant. Whether these differences between the correlation coefficients with EMEP and LE were statistically significant could not be testet due the small sample size. Preferences for one oft the organic soil layers as indicator for atmospheric deposition could not be concluded.

Regression analysis of the strongest statistical relations between LE deposition values LE (Cd, Pb, 2005 and As, Ni, arithmetic mean of years 2009-2011) and respective concentrations in moss (2005) resulted in models with rather week explanatory power of $0.17 \leq R^2 \leq 0.30$. For statistical modelling the geostistical surface estimations proved to be as eligible. The residuals of the respective models exhibited significant spatial autocorrelation with nugget / sill-ratios for As of 1 %, for Cd of 15 %, for Ni of 1 %, and for Pb of 10 %). The integration of the respective four regression maps on heavy metals in moss, derived by application of the regression functions on the geostatistical surface estimations of heavy metals in moss, with the residual maps estimated by Kriging interpolation yielded the calculation of deposition maps with high spatial resolution (3 km x 3 km).

Discussion and conclusions. From the investigations on heavy metals emissions and deposition can be concluded that the emissions of Cd, Hg and Pb decrease since 1990 (Pacyna et al. 2009) and that the same holds true for their accumulation in moss (Harmens et al. 2010). However, emission data need being complemented by a spatial and ecosystem type specific ecological monitoring combining depostion measurements with technical samplers in high temporal resolution and biomonitoring in high spatial resolution.

Compared with deposition analyses based on technical samplers, bioindication with moss is rather cheap enabling spatial dense monitoring of atmospheric deposition. Therefore, moss surveys are particularly convenient to validate and differentiate modelled deposition patterns and to localise uncertainties due to missing or wrong emission data used for modelling. This is especially true for geostatistical surface estimations of heavy metal concentrations in moss calculated from moss survey data. Thus, the network design of moss surveys should comply with geostatistical criteria for spatial estimation of sample point data. For validating temporal trends in modelled deposition and in biomonitoring data the timely high resolved data collected for ESB are eligible, especially the annual needles of pine (Pb) and spruce (Cd, Pb). This data could, as

shown by example of LE modelling results, complement the moss data to investigate uncertainties in modelled trends. To this end, long-term data (at least 10 years) are needed. For validation of temporal trends, data from ICP Level II are of second order priority. Due to spatial scarce networks, ESB und ICP Forest Level II are of limited suitability for spatial validation of modelling results. This especially holds true if the specimens are differentiated according to matrix, ecosystem type, age class and soil layer since this reduces the sample size. Thus, to ensure valid statistical analyses, the minimum sample size needed should be calculated in addition to the geostatistical measures indicating spatial representativity.

Further investigations in particular risk analysis based on the critical load approach should complement the collection of heavy metals concentrations in moss by information on those characteristics of the sample sites and their surroundings that could influence the heavy metals concentration accumulated in moss. This is currently done in the research and development project "Impacts of Heavy Metal Emission on Air Quality and Ecosystems across Germany - Sources, Transport, Deposition and potential Hazards" (UBA FKZ 3715 63 212 0). These statistical relationships between HM concentrations in biomonitors and further potential predictors such as distance from emission sources, density of different land-use classes, population density, elevation or precipitation should be further explored by multivariate statistics such as e.g. Principal component analysis, Classification and Regression Trees (Breiman et al. 1984) or Random Forests (Breiman 2001). As an alternative to geostatistical surface estimation of heavy metals concentrations, Random Forest could enable the mapping of moss concentrations based on available surface data data on predictors. Similar computations should be applied to exposure data from ESB and ICP Forests Level II.

The most severe drawback of the presented comparison of modelling and monitoring data indicating atmospheric deposition was the missing moss data for 2010. This is especially true since the surface estimations of HM concentrations in moss derived from moss sampled in 2005 could be corroborated as peculiarly appropriate for comparison with results from deposition modelling and for improving respective models. Thus, future moss survey designs should ensure spatial validity of measurements. This could be supported by integrating environmental monitoring programmes such as the European Moss Survey, ICP Forests, the Environmental Specimen Bank, and the second nation-wide soil survey (BZE II). Additionally, exposure data based on technical deposition samplers derived from ICP Integrated Monitoring, ICP Forests Level II, and deposition networks of UBA and the German federal states should be included, since they are rumoured to be more precise than exposure data from biomonitoring and should therefore be used for comparison and validation. This needs harmonising experimental designs of deposition monitoring networks mentioned above.

Cd and Pb deposition modelled with LE (2005, 2007-2011) show lower median values (factor > - 2 for Cd, factor > -3 for Pb) and maximum values compared with EMEP results, suggesting that both models used different emission data. This could be explained by the fact that EMEP partly modifies emission data based on expert judgements (Berdowski et al. 1997). This indicates that a closer cooperation between experts for modelling, deposition and biomonitoring is indispensable. One issue should be the timely and spatial resolution of modelling. Another one should be to run EMEP and LE modelling with identical input data on emission and meteorology and validate the respective results for identical time periods with bioindication and deposition monitoring data (EMS, ESB, ICP Forests Level II, ICP Integrated Monitoring).

6 Environmental impact assessment

Background and objectives. The task and objective of work package 3 was to assess the risks associated with the current heavy metal inputs quantified in part 1 of this project. The study should focus on the possible effects on terrestrial ecosystems.

The critical values for heavy metal fluxes available in Germany should be analyzed, assessed with regard to the possibilities and applicability of the risk assessment, and be prepared for evaluation in comparison to the inputs (Part 1).

For 2 metals, for which up to now very little was known about the effects on humans and ecosystems, analysis and assessments of current or future levels of concern should be derived from data contained in international literature about the effects on humans and the ecotoxicological effects.

As far as possible the various assessments for the priority heavy metals, should be subjected to a comprehensive evaluation. In addition data and maps of the sensitivity of different receptors with regard to the heavy metal inputs should be created. Critical loads and other available critical values should be compared to the heavy metals inputs (particularly those from Part 1 of this report) in order to determine compliance with and / or exceedance of the calculated critical limits. The assessment of the heavy metals inputs should also evaluate the extent to which current targets of the National Strategy for Biodiversity (NBS 2007) and the objectives of the EU Air Pollution Strategy for heavy metals have already been met or could be met through further development.

Comparison of the critical values. For the protection of terrestrial ecosystems and human health, critical values of air pollutants from the following regulations, directives and recommendations are used:

The thirty-ninth regulation for the implementation of the Federal Immission Protection Act (Regulation on air quality standards and maximum emission levels of 2 August 2010 BGBl. I p. 1065) is legally binding. Crops, wild plants and particularly sensitive ecosystems are explicitly named as protected natural resources (§1 sentence 17). An "immission limit" for the protection of human health is given for lead. In addition "target values" for arsenic, cadmium and nickel are predefined for the protection of man and the environment. These target values are based solely on human toxicological data and are therefore only partly suitable as a criterion for the sensitivity of different environments.

The EU Position Paper "Ambient air pollution by As, Cd and Ni compounds" (European Commission 2000) contains recommended ambient air quality targets (concentrations in the fine dust fraction PM₁₀) for arsenic, cadmium and nickel. For cadmium, a limit value for the deposition is proposed. These are proposals on the basis of expert estimates, which were derived solely from human toxicological data, but at the same time should also protect the environment.

The TA Luft 2002 (The first general administrative regulation on the Federal Immission Control Act - Technical Instructions on Air Quality Control - TA Luft of 24 July 2002) contains binding immission values for arsenic, lead, cadmium, nickel, mercury and thallium and their inorganic compounds which have been attributed to human toxicological data. Although the TA Luft in accordance with No. 1 para. 1 is to serve both as security and precautionary measure against the dangers of immisions, the defined pollution values, which concern the environmental resources, merely serve as protection against damage. It is therefore not considered to be precautionary. An amendment is currently being prepared.

The effect based critical load based on the implementation **of the Convention on Long-Range Transboundary Air Pollution (CLRTAP)** indicate the overall input rate (deposition and from

management measures), below which negative impacts on ecosystems and human health can be ruled out in the long term. As a result this can be seen as very precautionary-orientated critical value, because when the critical loads are not exceeded a minimization of risks is achieved. The determination of critical loads for heavy metal inputs for the protection of ecosystems $CL(M)_{eco}$ is based exclusively on eco-toxicological threshold values. Critical Loads are not legally binding, but serve as a recommendation or as a guideline.

The Federal Soil Protection and Contaminated Sites Ordinance 2015 (BBodSchV) (GBBl.I. 1554 of 12 July 1999, last amended through Art. 102 of the Ordinance of 31 August 2015) (GBL. I S. 1474), the implementation of the law is used for the protection against harmful soil changes and the remediation of contaminated sites (Federal Soil Protection Act - BBodSchG) (BGBl. I 1998, last amended in 2015) and contains legally binding precautionary measures for the metals Cadmium, Chromium, Copper, Nickel, Mercury and Zinc (critical concentrations in the soil). The precautionary values are in principle derived from eco-toxicological aspects, but are compared to background values (HGW) for unevenly widely contaminated soils, as well as acceptable additional loads in the form of annual loads when the precautionary values have already been reached. The acceptable additional loads therefore have only a limited precautionary character in terms of a sustainable avoidance of risks of adverse effects caused by the accumulation of pollutants.

The German Working Group on Water Issues of the Federal States and the Federal Government (LAWA), with the approval of the Conference of Environmental Ministers, published the report "Derivation of threshold values for groundwater" (see LAWA 2004). In 2016 an update was published. The concentration is determined as a minimum threshold, that meet the requirements of the relevant drinking water regulations or where the corresponding derived values are not exceeded, at which no relevant eco-toxicological effects can occur despite an increase in the substance contents compared to regional background values.

The Implementation Guide (LUA Brandenburg 2008) serves as a guideline for the FFH-compatibility study according to Article 6 (3) of the Fauna-Flora Habitat Directive and is not legally binding. The implementation guide specifies industrial-related or project-related irrelevance limits for the additional loads (to be applied in the FFH preliminary-examination) and significance limits for the FFH impact assessment. The irrelevance limits correspond to a percentage of the effects-based critical values (eco-toxicologically effects-based critical concentration in the soil, groundwater or surface water). If the critical concentration is already exceeded by the pre-existing environmental burdens or exceeded after the realization of the project examined by the total load, an additional project-related substance input is negligible if it is irrelevant, even if the critical concentration is exceeded. This means that the irrelevance limit becomes the limit of significance. The conversion of the predicted loads caused by a plant's contribution to the concentration of the substance in the soil should be calculated according to a predefined formula taking into account the exposure time (usually the normal economic life time of the plant) to the substance inputs.

Due to the methodological differences of their derivation, the critical values of the individual regulations are only conditionally comparable to one another and to the critical loads. The sometimes major differences exist due to different levels of protection, various protective goods and the effect relationship.

Concerns regarding unregulated metals. Critical loads for **thallium** for the protection of ecosystems cannot yet be determined because no valid database for the derivation of effects-based ecosystem-related critical limits exists. A preliminary rough estimate of the risk of thallium inputs in the receptor ecosystems of Germany provides a calculated balance in the form of margins for in- and acceptable outputs. The rough estimate gives an acceptable input rate of

0.046-0.446 g ha⁻¹ a⁻¹ for forests, of 0.145-0.894 g ha⁻¹ a⁻¹ for arable land and 0.03-0.46 g ha⁻¹ a⁻¹ for grasslands. Since there are no country wide deposition studies of Germany for Thallium, it is not possible to do an assessment of the existing pollution levels. A measurement station in Dortmund did however record an annual average concentration in 2013, which results in a deposition rate of 0.15 g ha⁻¹ a⁻¹ (LANUV NRW 2015). When using the established ecotoxicological minimum threshold for inputs into the groundwater (Zeddel et al., 2016) for the calculation of the critical leaching in the assessment, it is not possible to rule out the risk, at least not in the Ruhr valley.

Modeled deposition for **vanadium** is available for the whole of Germany. A risk assessment by means of an input and output balance based on a human-toxicological minimum limit (Zeddel et al., 2016), which is lower than the determined ecotoxicological limit, results in an acceptable input rate of 0.735-6.697 g ha⁻¹ a⁻¹ for forests, 2.24-13.66 g ha⁻¹ a⁻¹ for arable land and 0.57-7.62 g ha⁻¹ a⁻¹ for grasslands. A health risk due to the inputs of 2010 exists in the worst case scenario. Thus, the maximum deposition of 2010 for forests and grasslands is slightly above the minimum acceptable output. In the worst case scenario (maximum deposition occurs in areas with minimal outputs), also it is not possible to exclude the risk of damage to the ecosystem in the long run.

Updating and mapping of Critical Loads for heavy metals for Germany. For a comparison of the critical values, the critical loads for cadmium, lead and mercury inputs, for which Critical Loads were published in 2008 (Nagel et al., 2008), were updated based on the new input data. Critical Loads were calculated for additional heavy metals (arsenic, copper, zinc, chromium and nickel). The critical loads refer to the protection of human health (quality of drinking water, Cd in food) and the protection of the structure and function of ecosystems (effects on plants, invertebrates and soil microorganisms). The results show that the sensitivity of the various protective goods in relation to the same heavy metal can differ from one another in magnitude. For example in the case of copper, zinc and mercury, the sensitivity of the ecosystems is higher than the requirements for the protection of drinking water; in the case of arsenic, chromium and cadmium the situation is reversed. For lead, the CL range for protection of drinking water is within the CL range for ecosystem protection. $CL(Cd)_{\text{food}}$ for wheat products is significantly lower than the $CL(Cd)_{\text{drink}}$ for drinking water or ecosystem protection.

The random sensitivity calculations have been designed in such a way that the possible range of the deviations of the input data used in this project for the CL calculation is mapped from values from the literature. The highest deviations occurred in the metal contents in plants used to calculate the output through the harvesting of the biomass. The critical load calculation has the highest sensitivity to changes in the pH value.

Risk assessment of heavy metal inputs. Critical Loads ($CL(M)_{\text{drink}}$, $CL(M)_{\text{eco}}$) for arsenic, nickel, zinc and chromium were not exceeded in Germany for 2009-2011.

From the **comparison of the human-toxicological critical values** with the atmospheric inputs in 2013 (mercury) or 2010 (all other metals), it can be shown that in the long term a risk to human health could be associated with the consumption of drinking water since the critical loads for protection of drinking water for lead and mercury were not met in some regions of Germany. While the statutory and non-legally binding critical values were adhered to, the critical loads for protection of drinking water ($CL(M)_{\text{drink}}$) are not always below the limits. Especially the low rainfall regions of Germany (especially Brandenburg, lowlands of Saxony-Anhalt, Leipzig Bay, Ruhr valley) with wood vegetation are affected of the Hg and Pb inputs. The affected area could be even bigger, since the German CL data set 2016 might not be able to display areas at a scale, where maximum deposition rates intersect a very low critical load (worst case scenario). The Critical Loads for cadmium for the protection of drinking water $CL(Cd)_{\text{drink}}$ and for the

protection of human food from wheat products $CL(Cd)_{\text{food}}$ are not exceeded in the receptor surfaces of the German data set 2016 due to atmospheric depositions in 2010, but in the worst case scenario the maximum atmospheric deposition in 2010 exceeded the $CL(Cd)_{\text{drink}}$ and $CL(Cd)_{\text{food}}$. Although no Critical Loads for the protection of drinking water could be calculated for nickel as the BTrinkwV does not impose a concentration limit on nickel, the comparison of the inputs in 2010 with the assessment concentrations for nickel, which are recalculated in annual input rates in the EU policy paper, shows an exceedance for arable land and pasture and meadows in the worst case scenario.

Comparing the heavy metals entry 2013 (mercury) or 2010 (all other metals) with the **ecotoxicologically based critical loads**, the same picture emerges: The critical loads for the ecosystem protection $CL(M)_{\text{eco}}$ are exceeded due to the mercury and lead inputs in some regions of Germany with wood vegetation (especially Brandenburg, Leipzig Bay, Saxony-Anhalt, Ruhr valley); in addition $CL(Cu)_{\text{eco}}$ is exceeded by copper entries 2010 in the area surrounding Berlin and in the Ruhr valley. The forests of the subcontinental climatic regions are particularly vulnerable to atmospheric inputs of heavy metals (e.g. low rainfall, high evaporation rate), as well as habitat types in accordance with Annex I of the Habitats Directive with restricted or prohibited use (moist forests, dry and wet heaths, moors, tall forb communities on riverbanks and similar habitats). In the worst case scenario, $CL(Cd)_{\text{eco}}$ could be exceeded by the maximum cadmium inputs of 2010.

However, this rough risk assessment must be discussed with regard to the **context of the uncertainties and assumptions**:

The deposition calculations in Part 1 of this project do not depict direct loads of individual pollutants limited to a small area. This is also demonstrated by empirically determined deposition values, which are partly well above the modelled deposition values. This explains the character of the modeled values as a background deposition and why the plant-related critical values of TA Luft and the BBodSchV are not exceeded by these deposition rates.

The deposition from the atmosphere represents only a fraction of the inputs compared to the inputs from the use of fertilizers. With the inclusion of all input pathways, the critical loads and the acceptable additional loads of the BBodSchV could be more widespread and significantly higher particularly on arable land.

As with the critical loads for the Protection of Human Health, the ecosystem's critical loads can also lead to a harmless accumulation in the ecosystem as long as the critical limits have not yet been reached. Once the critical limits have been reached, an adverse effect to the protected product is to be expected, even if only after the appropriate reaction time of the ecosystem. Especially in the case of heavy metal deposits, it can take centuries for a visible negative change in the protective goods to occur when the critical loads are permanently exceeded. With regard to mercury inputs for example, soils have a very high buffering capacity. Other metals such as cadmium and nickel are more mobile and accumulate in the biomass in proportion to the content in the soil so that the assumptions on the discharge rates from the biomass are very conservative for the critical load calculations, because this calculation is generally carried out using very low concentrations in the biomass (values taken from literature).

The objectives of the EU Air Pollution Strategy, which aim to eliminate unacceptable impacts on people and the environment by 2020, have not yet been met with the 2010 deposition rates.

With regard to **the objectives of the National Biodiversity Strategy**, ecosystem-related impact thresholds for pollutants that describe the impact on biodiversity should be established by 2015. The Critical Loads provide a very precautionary scientific basis for discussion for the protection of ecosystems.

Further measures to reduce emissions are necessary:

Since cadmium, lead and mercury are transported over long distances in the atmosphere, both national and international measures are necessary to reduce these emissions, in addition to industrial and project-related emission limitations.

For the other metals, the focus is on industrial-related reduction within Germany. A first step towards this could be the mandatory obligation to measure and report on the actual emission levels (especially for mercury emissions) in the operation of the large-scale emitters.

However, a special focus is also to be laid on agricultural related inputs, in particular to protect agricultural areas from harmful substances.

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